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ABSTRACT: 1,1-Diphenylethylene (DPE) and functional derivatives of DPE have been used to prepare a variety of novel copolymers by living anionic polymerization. This research focuses on exploiting reactivity ratios to prepare copolymers with a variety of structures including alternating, tapered, statistical and telechelic copolymers. The copolymers were analysed by a variety of techniques including 1D and 2D NMR spectroscopy, MALDI-ToF mass spectrometry, differential scanning calorimetry and transmission electron microscopy.

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List of Abbreviations

ATRP	Atom Transfer Radical Polymerization
Bd	Butadiene
BHT	2,6-Di-*tert*-butyl-4-methyl phenol
BuLi	Butyllithium
COSY	Correlation Spectroscopy
DCDMS	Dichlorodimethylsilane
DCTB	*trans*-2-[3-(4-*tert*-butylphenyl)-2methyl-2-propenylidene] -malonitrile
DMA	Dynamic Mechanical Analysis
dn/dc	Refractive Index Increment
DNA	Deoxyribonucleic Acid
DPE	1,1-Diphenylethylene
DPE-CN	4-Cyanodiphenylethylene
DPE-OSi	*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene
DPMK	Diphenylmethylpotassium
DSC	Differential Scanning Calorimetry
DVB	Divinylbenzene
f_A	Volume Fraction of Monomer A
HF	Heat Flow
HSQCAD	Heteronuclear Single Quantum Coherence Adiabatic
MALDI-ToF	Matrix Assisted Laser Desorption/Ionisation – Time of Flight
MeOSt	Methoxystyrene
MMA	Methyl Methacrylate
M_n	Number Average Molecular Weight
MS	Mass Spectrometry
MSMS	Tandem Mass Spectrometry
M_w	Weight Average Molecular Weight
N	Number Average Degree of Polymerization
NMP	Nitroxide Mediated Radical Polymerization
NMR	Nuclear Magnetic Resonance
P(Bd-*co*-D)	Poly(Butadiene-*co*-1,1-Diphenylethylene)
PI-*b*-PS	Polyisoprene-*block*-Polystyrene
PMMA	Poly(Methyl Methacrylate)
P(S-*co*-D)	Poly(Styrene-*co*-1,1-Diphenylethylene)
P(S-*co*-D)-*b*-PBd	Poly(Styrene-*co*-1,1-Diphenylethylene)-*block* Polybutadiene
PS-PBd-PS	Polystyrene-Polybutadiene-Polystyrene
RAFT	Reversible Addition-Fragmentation Chain Transfer

RI	Refractive Index
RNA	Ribonucleic Acid
RT	Room Temperature
ROMP	Ring Opening Metathesis
SEC	Size Exclusion Chromatography
SET	Single Electron Transfer
Stilbene	1,2-Diphenylethylene
Sty	Styrene
TEM	Transmission Electron Microscopy
T_g	Glass Transition Temperature
T_g^{∞}	Glass Transition Temperature of a Theoretical Polymer at Infinite Molar Mass
TGIC	Temperature Gradient Interaction Chromatography
THF	Tetrahydrofuran
T_M	Melting Point
TMEDA	Tetramethylethylenediamine
$W_{0.5}$	Peak Width at Half Height
w/w	Mass Fraction
wt.	Weight
Đ	Dispersity
χ	Flory-Huggins Interaction Parameter

Statement of Copyright

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CHAPTER 1

Introduction

1. Introduction

Although it was not until 1920 that Staudinger discovered that polymers were long chains held together by covalent bonds,[1] as all life is formed from polymers, natural polymers have been around for billions of years. In 1839 Charles Goodyear discovered the process of cross-linking natural rubber to create a strong and durable material, and the first entirely manmade synthesized plastic was created in 1907 by Leo Bakeland. This material, called Bakelite, was a thermoset with a high heat resistivity and was used as an electrical insulator. Since then due to the wide range and versatile properties of polymers, they have become used for numerous applications. Polymers are more widely used than any other material; notable applications include tyres, packaging (which is of particular importance to the food industry), as additives in paints, ink and fuel, as a building material and more recently have been used for medical applications and as smart materials that respond to an external stimulus. One of the main advantages of polymers over other types of material is the ability to tailor the properties which can be done in a variety of different ways. The properties can be tuned by modifying the chemical structure (i.e. the monomer or monomers), the skeletal architecture of the polymer, the molecular weight, the dispersity of the molecular weight (previously called polydispersity) or even by blending different polymers together. Polymers are still finding new and exciting areas of applications and as there are countless ways to modify these materials they are likely to continue being used for more and more applications. In recent years extensive research has been performed on how the properties can be controlled by the polymer architecture. In nature, the polymer sequence, for example the sequence of amino acids in a protein or nucleotides in DNA is often responsible for the structure which allows natural polymers such as enzymes to perform complex tasks. For this reason ways of controlling/influencing the monomer sequences in synthetic polymerizations will be investigated herein.

1.1. Polymer Classification

As there are countless possible structures and properties of polymers, it is possible and desirable to classify polymers in a number of ways. One example is according to the polymer architecture as this strongly impacts the polymer behaviour. Alternatively the polymer can be classified according to the polymer composition, i.e. the monomer/co-monomer sequence. The other commonly used method of classification is according to the properties of the polymer.

1.1.1. Classification according to Polymer Architecture

Polymer properties are strongly dependent on their architecture. The simplest type of polymer architecture is a linear chain; however, the introduction of branch points leads to a wide variety of potential architectures. Broadly speaking there are three main categories of polymer architecture: linear; branched and network. Branched polymers can be subdivided into many different types, including stars, comb, randomly branched, etc. and networks can have either a low or high density of cross-links. These general classifications are discussed in introductory textbooks.[2]

1.1.2. Classification according to Polymer Composition

If the polymer contains only a single monomer, then it is termed a homopolymer; however, often polymers contain two or more monomers and such polymers are termed copolymers. Copolymers can have a wide variety of compositions which will also affect the overall properties. Given the wide range of available monomers, copolymerization can result in an almost infinite variety of possible structures; the main types of copolymer are as follows (Figure 1.1):

- *Block copolymers* which can be di-block, tri-block or multi-block and contain long sequences of a particular monomer – called a block – followed by one or more blocks of other monomers
- *Statistical copolymers* are copolymers where the monomers are copolymerized together, the resulting sequence depends on the relative reactivity preferences of the co-monomers – alternating, random and tapered copolymers are all specific examples of statistical copolymers
- *Alternating copolymers* contain alternating sequences of the different monomers and are formed when both monomers exclusively react with the other co-monomer
- *Random copolymers* are formed when the monomers react without preference to monomer type

- *Tapered copolymers* are block copolymers with a statistical region between each block
- *Telechelic* copolymers have a block comprised of a single monomer, but the beginning and end of the chain contains one different monomer unit
- *Graft copolymers* are branched block copolymers, they have a comb like architecture but the arms consist of a different repeating monomer

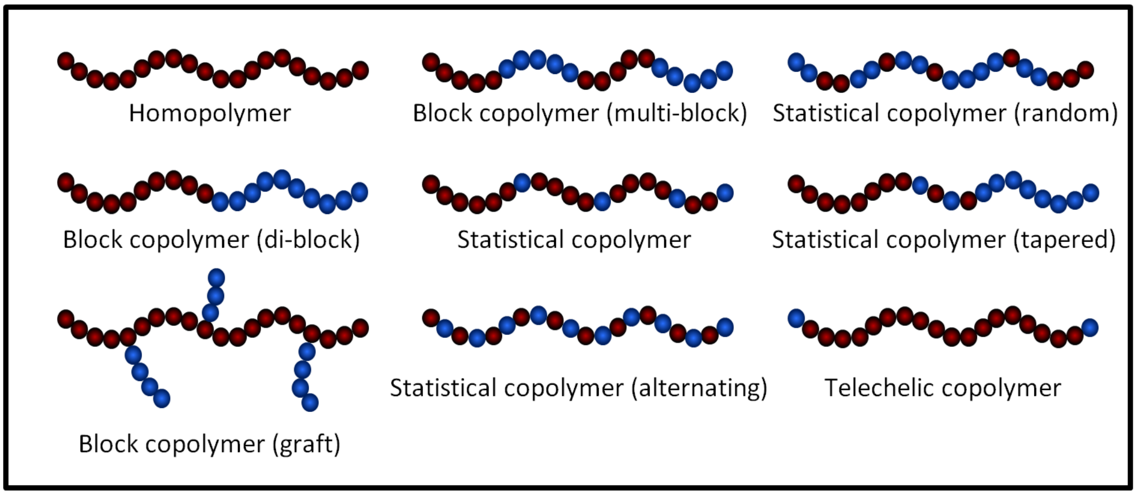

Figure 1.1: Types of (co)polymer compositions

1.1.3. Classification by Properties

The most common way of classifying polymers is according to their properties, in which they are separated into three main groups: *thermoplastics*; *elastomers* and *thermosets*. Thermoplastics can be subdivided into semi-crystalline and amorphous polymers. An additional group is *thermoplastic elastomers* which combine the properties of thermoplastics and elastomers.

Thermoplastics (often termed plastics) are linear or branched polymers which are usually solid at room temperature. Amorphous polymers are made up of disordered, entangled chains whereas semi-crystalline polymers contain both regions of highly ordered crystalline domains and disordered amorphous domains. Below the glass transition temperature, T_g, the amorphous domains become frozen and the resulting glassy polymer is hard and brittle although the frozen amorphous domains contain the molecular disorder of a liquid. Above the T_g the chains in purely amorphous polymers are able to flow past each other and the polymer becomes rubbery, however, semi-crystalline polymers remain solid above the T_g of the amorphous domains, held together by crystalline domains. If the polymer is heated above the melting point, T_M, then both the amorphous and crystalline domains are now able to flow and the polymer becomes a viscous liquid. Upon cooling thermoplastic polymers resolidify and amorphous or crystalline regions reform. Thermoplastics may be reheated and reprocessed making them ready candidates for recycling.

Elastomers are rubbery networks with low cross-link densities. Since they are above their T_g at room temperature they are able to be stretched to high extensions (up to 10x their original dimensions). However, once they are cross-linked they cannot be reprocessed.

Thermosets consist of rigid networks which contain a high cross-link density. Due to the restriction on the movement of chains caused by the cross-links they are unable to be stretched, and like elastomers they cannot be reprocessed once the cross-links have been formed. Thermosets will eventually degrade instead of melting upon the application of heat.

Thermoplastic elastomers contain non-permanent and reversible cross-links which allow the polymer to stretch and recover but can still be reprocessed upon heating above the T_g.

1.2. Polymer Synthesis

Since Bakelite, the first synthetic polymer, was created in 1907 there has been extensive research on new methods of polymerization. Polymer synthesis can be classified as either step-growth or chain-growth polymerizations. Step-growth polymerizations involve successive reactions between functional groups present on the monomer whereas chain-growth polymerizations proceed by the reaction of activated chains with the monomer.

1.2.1. Step Growth Polymerization

Step growth polymerizations occur by the reaction of bi-functional or multifunctional monomers. Initially the monomers react to form dimers, but as the concentration of the monomer decreases, reactions involving dimers and oligomers dominate and eventually long chains are formed. Such polymerizations proceed via intermolecular stepwise addition (polyaddition) reactions or condensation (polycondensation) reactions. Polyaddition reactions involve two monomers reacting without the elimination of other molecules, such as the reaction of diisocyanate with diols to form polyurethanes. Conversely, in polycondensation reactions small molecules are eliminated, such as water in the case of dicarboxylic acids reacting with diols to form polyesters.

In the simplest case where the monomers are bi-functional, the molar mass is predicted by Carothers theory. This states that the number-average degree of polymerization, $\bar{x}_n$, is calculated from the equation:

$$\bar{x}_n = \frac{N_0}{N} \qquad [1.1]$$

where N_0 is the initial number of molecules and N is the number of molecules remaining after time t of the polymerization. This can then be related to the extent of the reaction, p, at time t by the equation:

$$\bar{x}_n = \frac{1}{1-p} \qquad [1.2]$$

This equation (1.2) demonstrates the importance of high conversion, as very high extents of reaction are required in order to obtain polymers with useful physical properties, i.e. for a degree of polymerization in the order of 100 or above, a value of $p \geq 0.99$ is required. An additional consequence of Carothers theory is that the dispersity, Đ, tends to 2 as the reaction goes to completion. Hence it is not possible to obtain polymers with a narrow dispersity using step growth polymerizations.

Step growth polymerizations can involve either the homopolymerization of one monomer containing two different functional groups:

$$nAB \rightarrow A-(B-A)_{n-1}-B \tag{1.3}$$

or, conversely, the copolymerization of more than one monomer, which contain only one distinct type of functional group:

$$n(A-A)+n(B-B) \rightarrow AA-(BB-AA)_{n-1}-BB \tag{1.4}$$

In the latter case involving two monomers, stoichiometry is extremely important as an excess of one monomer will result in incomplete reactions and lower molecular weight polymers. It is similarly important that these reactions are performed in the absence of impurities as these can also prohibit the reaction from reaching high conversion.

If a multifunctional monomer is included in the polymerization, initially a branched polymer would form but ultimately this could lead to the formation of a network.

1.2.2. Chain Growth Polymerization

Chain growth polymerization proceeds via the propagation of monomers (usually substituted alkenes) with an activated chain, which can involve reactions with radicals, cations, anions or transition metal complexes.

1.2.2.1. Free-Radical Polymerization

Free-radical polymerizations comprise of three main steps: initiation, propagation and termination. The initiation step begins with the formation of one or two radicals created from the initiator species which subsequently react with the monomer:

$$\mathrm{I} \rightarrow 2\mathrm{R}^{\bullet} \tag{1.5}$$

$$\mathrm{R}^{\bullet}+\mathrm{M} \rightarrow \mathrm{R\text{-}M}^{\bullet} \tag{1.6}$$

where I represents an initiator, $R^{\bullet}$ a radical and M a monomer unit. Once all the initiator has reacted with the monomer, conversely to step-growth polymerizations, reactions can only occur between an activated chain and a monomer (termed propagation):

$$\text{R-M}^\bullet + n\text{M} \rightarrow \text{R-(M)}_n - \text{M}^\bullet \qquad [1.7]$$

Propagation then continues until all the monomer has been consumed or until all the activated chains are terminated. Termination competes with propagation and involves the deactivation of activated chains. Termination can occur by two methods: recombination (Figure 1.2a) or disproportionation (Figure 1.2b). Another competing process is chain transfer which involves the termination of one chain whilst simultaneously activating another chain (Figure 1.2c). As the chain can be reactivated at any point in the chain, this process leads to chain branching.

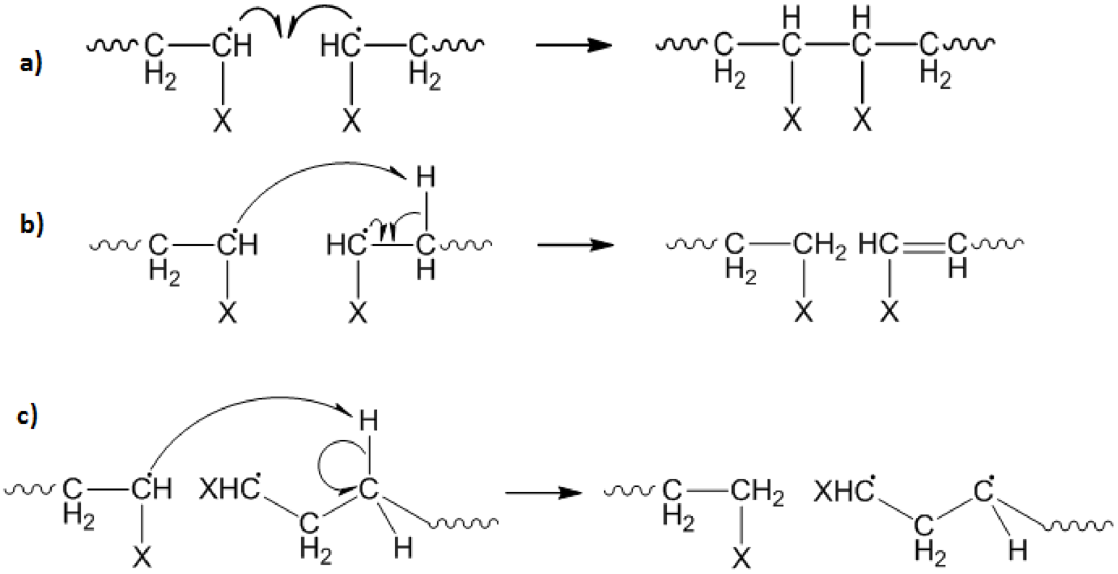

Figure 1.2: Mechanism for termination by (a) recombination (b) disproportionation and (c) chain transfer for a polymerization of a generic vinyl monomer, CH_2=CHX.

1.2.2.2. Ionic Polymerization

Ionic polymerizations occur in a similar manner to free-radical polymerizations except that the propagating species is an ion rather than a radical. The chain end may carry either a positively charged (cationic polymerization) or negatively charged (anionic polymerization) active centre. Ionic polymerizations are more sensitive to the type of monomer, and typically require an alkene with an electron donating group (for cationic polymerization) or an electron withdrawing group (for anionic polymerization). As in free-radical polymerizations these polymerizations proceed via initiation, propagation and termination steps. In cationic polymerizations, the initiator can be either a strong protic acid, or more commonly a lewis acid, such as $AlCl_3$ or BF_3. Typically a co-catalyst

a) $BF_3 + H_2O \rightleftharpoons H^+[BF_3OH]^-$

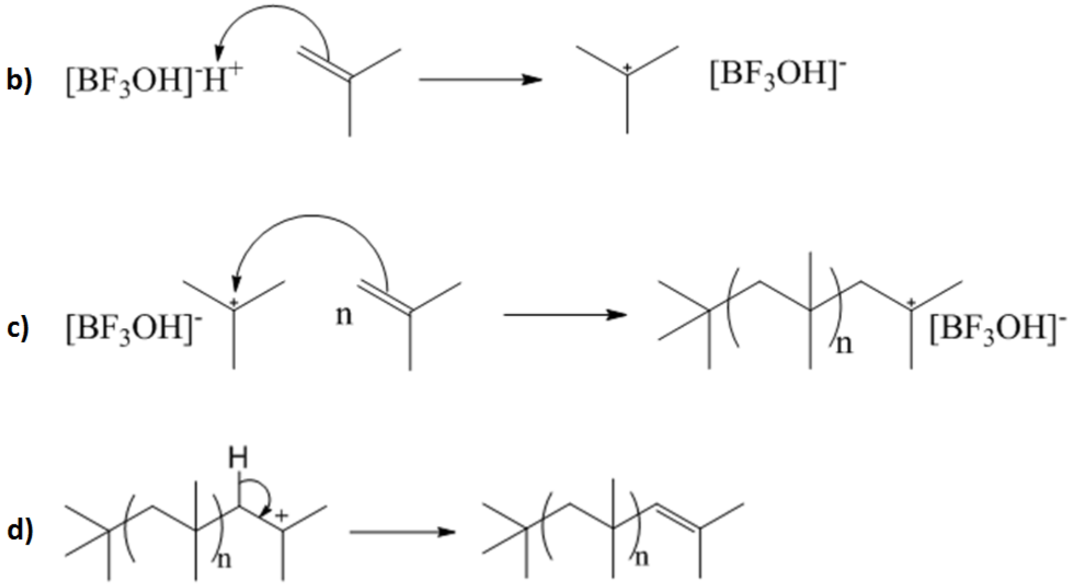

Figure 1.3: Schematic showing (a) the formation of the initiator species (b) initiation of the monomer (c) propagation and (d) termination via a unimolecular rearrangement for the cationic polymerization of isobutene using the initiator $[BF_3OH]^-H^+$.

is used as a proton donor to increase the rate of initiation. The formation of the initiator; initiation step and propagation step are shown in Figure 1.3(a-c).

Termination is still an on-going process, but unlike free-radical polymerizations it is a unimolecular process as two propagating chains have the same charge and therefore do not annihilate each other.[3] Termination now occurs via a unimolecular rearrangement with the counterion (Figure 1.3d). Chain transfer reactions can also occur either by a hydrogen abstraction from the active chain-end by the counter ion, or by a hydrogen abstraction from the active end to a monomer. The former terminates the growing chain end but regenerates the initiator-co-catalyst complex which can then initiate more chains (Figure 1.4).

These termination and chain transfer processes dominate at ambient temperatures and consequently cationic polymerizations have to be carried out at low temperatures (≤ -78 °C) to supress these side reactions. As a result the only polymer prepared commercially by cationic polymerization is polyisobutylene (or butyl rubber) which cannot be polymerized by any other technique.

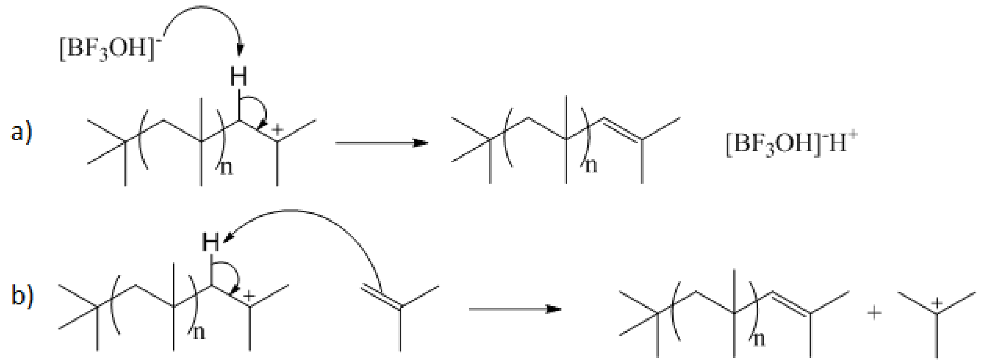

Figure 1.4: Chain transfer reactions by a hydrogen abstraction from the active chain-end by (a) the counter ion or (b) the monomer.

Ionic polymerizations are electrically neutral, and negative anions or positive cations will neutralize the charges of cationically growing chains or anionically growing chains, respectively. These counter-ions can co-exist as a variety of different species ranging from covalent species to free ions. They are known to form different complexes depending on the solvent, solvating agents present, temperature, etc. which will affect the kinetics of the polymerization. Hence, the rate of propagation can be increased in all cases by increasing the charge separation, i.e. more polar solvents or larger counter ions.

In anionic polymerizations, the initiation step can be achieved either by electron transfer (Figure 1.5) or by the use of strong anions (Figure 1.6).

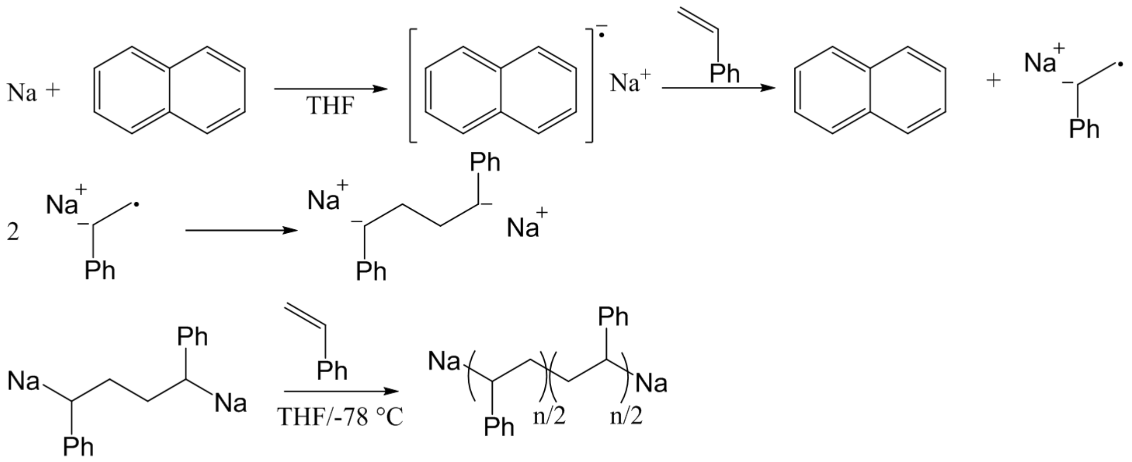

Figure 1.5: Schematic showing the anionic polymerization of styrene using sodium naphthalene as the initiator in THF.

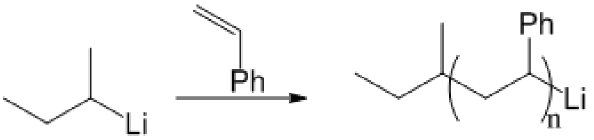

Figure 1.6: Schematic showing the anionic polymerization of styrene using *sec*-butyllithium as the initiator.

Whilst in some cases termination and chain transfer reactions can occur during anionic polymerization, either involving the monomer or the solvent, in 1956 Szwarc demonstrated it was possible to perform anionic polymerizations in the absence of termination or chain transfer.[4] These polymerizations were termed 'living' polymerizations. Furthermore, as the chains remain active even upon consumption of the monomer, a second monomer can be subsequently added which allows the synthesis of block copolymers making this technique of critical importance for sequence control. The defining criteria and consequences of living polymerizations will be discussed in the next section.

1.2.2.3. Living Polymerization

Living polymerizations are chain growth polymerizations that occur in the absence of any termination or chain transfer and usually describe polymerizations where the system remains active after the polymerization is complete. This allows a new batch of monomer to be added and therefore continue the propagation of the living chains. These polymerizations allow well-defined polymers to be synthesized with a high degree of control over composition and structure, including molecular weight, molecular weight distribution, microstructure, etc. and subsequently low degrees of compositional heterogeneity. Since the discovery of living polymerizations, various systems have been investigated, some of which can be described as pseudo-living (also termed controlled) and will be discussed later. In order that a polymerization mechanism be defined as living, a number of experimental criteria need to be met as described below[5-6]:

1) The polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.

2) The number average molecular weight, M_n (or N, the number average degree of polymerization), is a linear function of conversion.

3) The number of polymer chains (and active centres) remains constant, and is independent of conversion.

4) The molecular weight can be controlled by the stoichiometry of the reaction.

5) Block copolymers can be prepared by sequential monomer addition.

6) Chain-end functionalized polymers can be prepared in quantitative yield.

7) A plot of rate of propagation as a function of time as shown by the following equation must be linear:

$$\ln\frac{[M]_0}{[M]} = k_{obs}t \tag{1.8}$$

8) A plot of $\ln(1 - [I_0]\overline{\mathrm{DP}_n}/[M_0])$ as a function of time as shown by the following equation must be linear:

$$\ln\left(1-\frac{[I]_0}{[M]_0}\overline{\mathrm{DP}_n}\right) = -k_p[I]_0 t \tag{1.9}$$

Criterion 1 is the basis of the description of living polymerizations and the ability to continue polymerizing upon addition of additional monomer is an important characteristic of living polymerization. However this criterion alone is not sufficient to define a living polymerization.

Criterion 2 is often used to determine whether a polymerization is living, and whilst it is indeed the case that the number average molecular weight will be a linear function of conversion for a living polymerization, this still applies even if termination is occurring. This is due to the fact that the number of chains will remain constant throughout even if some chains are terminated. This is no longer the case if chain transfer is an on-going process, hence a plot of M_n versus % conversion will allow determination of whether chain transfer is occurring, but not chain termination, and thus this criterion is not an unequivocal test for a living polymerization. This criterion should be considered necessary but not sufficient criteria for a living polymerization.

Similarly with criterion 3 the number of polymer chains will remain constant regardless of chain termination; however, the number of active sites will only remain constant in the absence of chain termination.

As stated by criterion 4, for a living polymerization, the number average molecular weight should be a simple function of the degree of conversion of the monomer and the stoichiometry given by the equation:

$$M_n = \frac{\text{mass of monomer consumed (g)}}{\text{moles of initiator (mol)}} \qquad [1.10]$$

This criterion depends on the quantitative activation by the initiator before all the monomer has been consumed. This is therefore sensitive to impurities which would decrease the effective moles of initiation and consequently the number of active chain ends and overall molecular weight. In general, termination reactions will increase the molecular weight, whilst chain transfer reactions will decrease the molecular weight.

Criteria 5 and 6 are a consequence of criterion 1; as the chains remain active and can continue to propagate upon the addition of more monomer, if a second type of monomer is added a block copolymer should form. Thus this can be used to determine whether a reaction is indeed living. In the case of criterion 6, if a functionalized terminating agent is used it can quantitatively react with the active chains in a controlled termination. However, most functionalization reactions do not proceed quantitatively and this is therefore not an ideal method for testing whether a polymerization is indeed living.

The kinetics of propagation for a living polymerization should be pseudo-first-order as given by the equation:

$$R_p = \frac{-d[M]}{dt} = k_p[P^*][M] = k_{obs}[M] \qquad [1.11]$$

Provided there is no chain termination the concentration of the propagating species will remain constant and integration of equation [1.11] yields equation [1.8]:

$$\ln\frac{[M]_0}{[M]} = k_{obs}t \qquad [1.8]$$

However, as chain transfer will not affect the number of propagating species, P*, it will not affect the kinetics and this criterion is only a method of determining whether chain termination is present. It is therefore possible to use this criterion with criterion 2 to show that there is no chain termination or chain transfer and hence reveal whether the polymerization is living.

It is also possible to combine criteria 2 and 7 to form a single equation, which if linear indicates that neither chain termination nor chain transfer is present. From criterion 2 the number average degree of polymerization is a linear function of conversion, hence the following equation applies:

$$N = \frac{[M]_0 - [M]_t}{[I]_0} \qquad [1.12]$$

From criterion 7,

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = -k_p[I]_0 t \qquad [1.13]$$

Rearranging Eq. 1.12 and substituting into Eq. 1.13 provides the following equation:

$$\ln\left(1 - \frac{[I]_0}{[M]_0}\overline{\mathrm{DP}}_n\right) = -k_p[I]_0 t \qquad [1.9]$$

and therefore if a plot of the left side of Eq. 1.9 versus time, *t*, is linear then both chain transfer and termination are absent.

An additional criterion that is frequently used is that narrow-molecular-weight distribution polymers should be obtained. However, living polymerizations can produce polymers with broad molecular weight distributions in certain cases and furthermore, some non-living systems can be used to produce polymers with relatively narrow molecular weight distribution ($M_w/M_n \leq 1.1$). Hence it is more accurate to state that a consequence of living polymerizations is that narrow-molecular-weight distribution polymers can be prepared provided certain requirements are met. These following requirements were proposed by Flory,[7] and Henderson and Szwarc[5, 8]:

1) The growth of each polymer chain must proceed exclusively by consecutive addition of monomers to an active terminal group.
2) All of the active termini must be equally susceptible to reaction with monomer throughout the polymerization.
3) All active centres must be introduced at the outset of polymerization.
4) There must be no chain transfer or termination.
5) Propagation must be irreversible.

Requirement 2 is essential to ensure all the propagating chains grow at the same rate. If there is more than one type of active centre, each with a different propagation rate constant then each of these species must be in rapid equilibrium in order for all the chains to grow uniformly and for a low dispersity polymer to be obtained. This is of particular importance when polymerizing methacrylate monomers.

It follows from requirement 3 that the rate of initiation is at least competitive with the rate of propagation. This requirement ensures that all the chains grow for the same period of time, and thus prevent broadening of the molecular weight distribution.

Requirement 4 is the only requirement that relates to the living nature of the polymerization; hence even in living polymerizations if any of the other criteria are not met a narrow molecular weight distribution polymer will not be obtained.

In some living polymerizations, such as the polymerization of α-methylstyrene, there is an accessible ceiling temperature, above which depropagation becomes a competing process which broadens the molecular weight distribution. Hence propagation must be irreversible or the rate of depropagation must be insignificant in comparison with the rate of propagation in order to obtain polymers with a narrow molecular weight distribution.

1.2.2.3.1. Living Anionic Polymerization

First reported in 1956, living anionic polymerization reactions occur without any chain transfer or termination. However, whilst it is free from inherent termination, due to the reactivity of the carbanions towards oxygen, moisture, carbon dioxide and even slightly acidic protons, these reactions are very sensitive to traces of impurities. Hence these reactions must therefore be carried out under an inert atmosphere or a high vacuum, with aprotic solvents and rigorously purified reagents. Furthermore only specific monomers can be polymerized by living anionic polymerization techniques. These monomers are typically vinyl compounds with an electron withdrawing group. However, they cannot contain even slightly acidic functional groups such as alcohols, carboxylic acids or amines, etc. Preparation of polymers with these functional groups is possible by living anionic polymerization by the use of protected functional groups and functional group conversions post-polymerization.

Alkali metals, such as sodium, were the first initiators used for anionic polymerization. However, for these species initiation is a heterogeneous process which occurs on the surface of the metal. Initiation is therefore a slow process and continues to generate new active chains throughout the subsequent propagation reactions, and hence there is little control of molecular weight ($M_w/M_n = 3 – 10$).

Alkali metals can also be used with aromatic hydrocarbons in polar aprotic solvents to form stable radical anions to initiate anionic polymerizations. Indeed the discovery of living anionic polymerization by Szwarc involved a naphthalene radical anion initiator. These radical anions are only formed efficiently in polar solvents, such as tetrahydrofuran (THF), and as a result there are a number of disadvantages to these initiators. Firstly, in polar solvents polydiene microstructure is high in 1,2- and 3,4- whereas high 1,4- microstructure is inaccessible. Secondly, polar solvents accelerate the rate of propagation which can broaden the molecular weight distribution due to a fast rate of propagation relative to initiation. Furthermore, in polar solvents, an equilibrium exists between the active species (contact ion pairs, solvent-separated ion pairs, free ions, etc.) Each of these species propagates with a different rate constant, which again broadens the molecular weight distribution.

The adoption of alkyllithium initiators for anionic polymerization was of particular importance both industrially and academically. These initiators are soluble in hydrocarbon solvents and have rapid rates of initiation (with respect to propagation) which allows the synthesis of polymers with narrow molecular weight distributions. Of industrial significance was the ability to polymerize dienes such as butadiene and isoprene in non-polar hydrocarbons, this allowed the synthesis of high 1,4-polyisoprene as a synthetic alternative to natural rubber (*cis*-1,4-polyisoprene). Probably the most important difference between various alkyllithium initiators is their degree of aggregation in solution. Organolithium compounds associate into dimers, tetramers and hexamers in hydrocarbon solvents which is the underlying reason for their solubility in these solvents. The degree of association of organolithium compounds depends on the structure of the organic moiety, the solvent, the concentration and the temperature. Typically, small, unhindered, straight-chain alkyllithium compounds such as *n*-butyllithium are associated into hexamers in hydrocarbon solvents. The average degree of association can be decreased by increasing the steric hindrance of the alkyl group, hence alkyllithium compounds with branching at either the α- or β- carbon, such as *sec*-butyllitium, tend to associate into tetramers. Also, decreasing the concentration, increasing the temperature, the presence of a lewis base or substituting an aromatic solvent for an aliphatic solvent tends to decrease the average degree of association. The relative reactivity of alkyllithium compounds, and therefore the rate of initiation, is generally inversely related to the degree of aggregation. For dienes with butyllithium initiators in hydrocarbon solvent the order is *sec*-butyllithium > *tert*-butyllithium > *iso*-butyllithium > *n*-butyllithium. For styrene the order is *sec*-butyllithium > *iso*-butyllithium > *n*-butyllithium > *tert*-butyllithium. It should also be noted that it is possible to achieve living cationic polymerization, but as mentioned earlier these reactions must be carried out at low temperatures to supress side reactions which lead to termination.

1.2.2.3.2. Coordination Polymerization

Coordination polymerizations are chain growth mechanisms where propagation occurs through an organometallic active centre. The three main techniques are Ziegler-Natta, metallocene and ring opening metathesis (ROMP), and ROMP can be used to obtain living polymerizations.[9]

Ziegler-Natta polymerizations involve the formation of an active centre on the surface of the $TiCl_3$ crystals via an exchange with triethylaluminium. The monomer coordinates to the vacant site which is inserted into the titanium-ethyl bond regenerating the active site. The orientation of the monomer is determined by steric and electronic interactions at the active site which gives rise to stereoregularity. Stereoregular (isotactic or syndiotactic) polymers stack in a regular fashion and are semi-crystalline thermoplastics with excellent mechanical properties and high melting points.

In metallocene polymerizations the catalyst (two cyclopentadienyl anions bound to a metal centre) is in solution and therefore the reaction is homogeneous. Methyl aluminoxane is used as a co-catalyst and is used to bind a methyl group to the metal centre. The monomer is always inserted between the metal centre and the methyl group, and the catalyst can be used to control the stereochemistry and therefore tacticity of the polymer.

ROMP involves a metal complex (e.g. ruthenium) and often uses a co-catalyst. The monomers used in ROMP are cyclic alkenes such as cyclobutene, cyclooctadiene or norbornine. When ROMP was first discovered in the 1960’s the resulting polymers were not well controlled with broad molecular weight distributions. In the 1990’s Schrock found that molybdenum based catalysts provide better control over molecular weight, dispersity and stereoregularity but these polymerizations were sensitive to impurities. A ruthenium-carbene catalyst was developed by Grubbs in 1992 which was more stable to impurities and had a greater tolerance to functional groups but still allowed control over molecular weight, dispersity and stereoregularity.

1.2.2.3.3. Quasi-Living Polymerization

Since the discovery of living anionic polymerization by Szwarc, a variety of other mechanistic types of polymerization have been investigated to produce a living system and hence highly controlled polymers. A number of polymerizations were developed where the propagating species is in equilibrium with a dormant, non-propagating species which simulated living-like behaviour. The terminology of these systems has caused a lot of confusion throughout the literature. Whilst these polymerizations are sometimes termed 'living', herein the term 'living polymerization' will refer to an ideal living polymerization where chain termination and chain transfer are absent, whereas 'quasi-living polymerizations' or 'controlled polymerizations' will refer to polymerizations where chain termination and/or chain transfer occur but are reversible processes and hence the propagating species is in equilibrium with a dormant species. Quasi-living polymerizations have been found for a variety of systems, including free-radical and group transfer polymerizations.

1.2.2.3.3.1. Controlled Free-Radical Polymerization

Free-radical polymerization offers a lot of advantages over other types of polymerizations. It can be used to polymerize a wide range of vinyl monomers, only mild reaction conditions are required, it can be performed over a range of different temperatures and most importantly free radical polymerization is tolerant to water, although oxygen has to be excluded. However, due to inherent chain termination and chain transfer free radical polymerization does not produce well-defined polymers. The living polymerizations described in section 1.3.2.3, allow polymers to be prepared with controllable molecular weights and a narrow molecular weight distribution. Living polymerization mechanisms also allow control of chain architecture, monomer sequences and chain-end functionality. For this reason controlled free-radical polymerizations were developed in order to combine the versatility of free-radical polymerizations with the control of living polymerizations. Essentially, achieving narrow molecular weight distributions depends on the reaction kinetics: the rate of initiation must be greater than the rate of propagation, the chains must propagate at the same rate (i.e. only one propagation rate constant) and whilst ideally there must be no chain termination, provided the rate of propagation is much greater than the rate of termination, such that termination does not occur during the polymerization, then polymers with a narrow molecular weight distribution can still be obtained. It should be noted that even if termination is not significant during the timescale of the polymerization, this can still inhibit the synthesis of block copolymers. In the case of free-radical polymerizations the rate of termination, either by combination or disproportionation, is greater than the rate of propagation. However, whilst propagation is first order with respect to the concentration of the propagating chains, [P$^\bullet$], termination requires two active chains to either combine or disproportionate, and hence is second order with respect to the concentration of propagating chains, [P$^\bullet$]. It follows that the rate of propagation and the rate of termination are:

$$R_p = k_p[M][P^\bullet] \qquad [1.14]$$

and

$$R_t = k_t[P^\bullet]^2 \qquad [1.15]$$

respectively, where R_p and R_t are the rates for propagation and termination, [M] is the concentration of monomer and [$P^\bullet$] is the concentration of propagating species. Hence termination can be selectively supressed by decreasing the concentration of propagating species. This is the principle underpinning controlled free-radical polymerizations which is achieved by establishing an equilibrium between active and dormant chains, i.e. reversible chain termination and ensuring that the concentration of dormant chains is much higher than that of the propagating species, i.e. [P] >> [$P^\bullet$]. In recent years there has been extensive research into controlled free-radical polymerizations and there are now a number of different methods of reversible chain termination, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), nitroxide mediated radical polymerization (NMP) and single electron transfer (SET).

1.3. Block Copolymers

The most common block copolymer structures are AB di-block (A and B represent long sequences of monomer A and monomer B), ABA or BAB tri-block and $[AB]_n$ multi-block. The constituent blocks are usually thermodynamically incompatible and the degree of incompatibility dictates the morphology and properties of the resulting copolymers.

1.3.1. Morphology

Whilst mixtures of different homopolymers (e.g. polystyrene and polybutadiene) are usually incompatible and blends will therefore tend to phase separate, when homopolymers are covalently bonded together, i.e. in a di-block copolymer, the individual polymers are now unable to undergo macrophase separation. The thermodynamics of block copolymer melts is governed by two opposing effects: the enthalpic contribution usually favours demixing, but as this restricts the configuration of chains, the entropic contribution favours mixing. Hence at lower temperatures, the enthalpic contribution dominates, and the blocks tend to segregate by a process known as microphase separation. For a di-block copolymer consisting of monomer A and monomer B, the resulting morphology of these microphases depends on several factors: the volume fraction of monomer A, f_A; the total degree of polymerization, N, and the interaction parameter, χ, which is a phenomenological temperature dependent parameter and provides a measure of the polymer-polymer interaction. Lower values of χ and N favour disordered polymer structures, whereas higher values favour ordered structures. As χ is temperature dependent, a disordered polymer can form an ordered microphase upon cooling, and vice versa upon heating. This is known as the order-disorder-transition, ODT. The product χN expresses the enthalpic – entropic balance and the value of χN at the order-disorder-transition is known as the critical χN. The microphase structures that form are predominantly controlled by f_A, as different domain sizes determine which morphology provides the most efficient packing. For a symmetric di-block copolymer, where $f_A = 0.5$, above the critical χN value (predicted as 10.5) the microphase separates into a lamellar morphology. As f_A increases the morphology becomes either gyroid or cylindrical depending on χN,

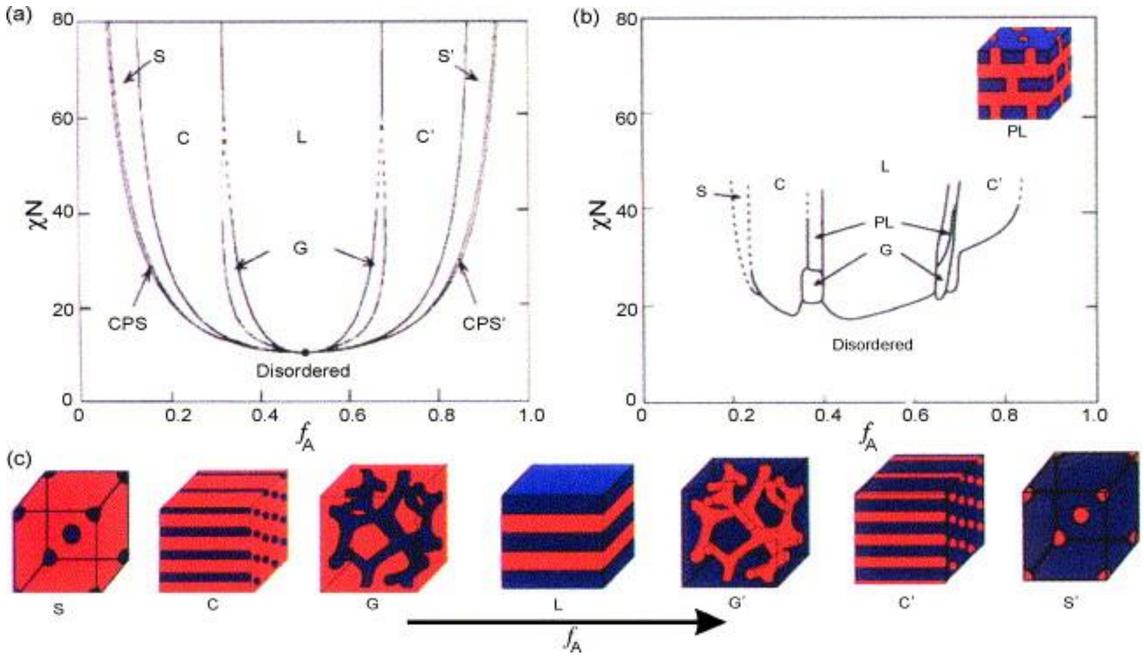

Figure 1.7: (a) Theoretical and (b) Experimental Phase diagram for a Polyisoprene-*block*-Polystyrene copolymer, and (c) microstructure schematics of (S) spherical (C) cylindrical (G) gyroid (L) lamellar and (PL) perforated layers. f_A is the volume fraction of polyisoprene, χ is the interaction parameter, N is the degree of polymerization and CPS are close packed spheres. Reprinted with permission from Bates, F. S., Fredrickson, G. H., Physics Today, Vol. 52/2, Page 32-38, 1999. Copyright 1999, American Institute of Physics.[10]

although a metastable perforated layer structure is sometimes observed. The gyroid phase is a bicontinuous morphology where each region is fully interconnected but if χN is too large then this morphology cannot form and perforated layers or cylinders form instead. Upon increasing f_A further, the gyroid or perforated layer microstructure will give way to a cylindrical morphology, and finally if f_A is increased beyond the cylindrical limits, a spherical morphology will result. Similarly, if f_A is decreased from the lamellar phase then the same morphologies will form but domains of A and B will be reversed. The morphologies as well as the theoretical and experimental phase diagrams for a polyisoprene-*block*-polystyrene (PI-*b*-PS) di-block copolymer are shown in Figure 1.7.[10-11]

1.3.2. Mechanical Properties

Block copolymers can be classified as either rigid or elastomeric. Rigid materials can either be composed of two hard segments or one hard segment with a minor fraction of a soft segment. A hard segment is a block with a T_g and/or T_M above room temperature, and a soft segment has a T_g (and possibly a T_M) below room temperature. Elastomeric block copolymers contain a soft segment and a minor fraction of a hard segment and will therefore typically have spherical or cylindrical morphology as described in the previous section. The spheres or cylinders will be formed from the hard segments, whilst the matrix will be formed by the soft segment. The flexibility of this entangled rubbery matrix gives rise to the elastomeric properties of these copolymers. It is also possible to obtain a block copolymer composed of two soft segments; however, these copolymers do not have significantly improved mechanical properties compared to other soft homopolymers.[12]

An interesting situation arises for tri-block (ABA) or multi-block $-(AB)_n-$ copolymers where A is a minor fraction of a hard segment and B is a major fraction of a soft segment. The soft rubbery matrix becomes effectively cross-linked, as a single polymer chain can span into two different hard domains (Figure 1.8). Whilst the flexible rubbery matrix is able to stretch, it is still constrained by these hard domains (comprised of spheres or cylinders) which act as physical cross-links. This creates a material with the elastomeric mechanical properties of a cross-linked rubber with the processability of a linear thermoplastic polymer. These copolymers have therefore been termed thermoplastic elastomers. Conversely tri-block copolymers (BAB) where a single hard block is connected to two soft blocks are not thermoplastic elastomers as they cannot form the physical cross-links required.

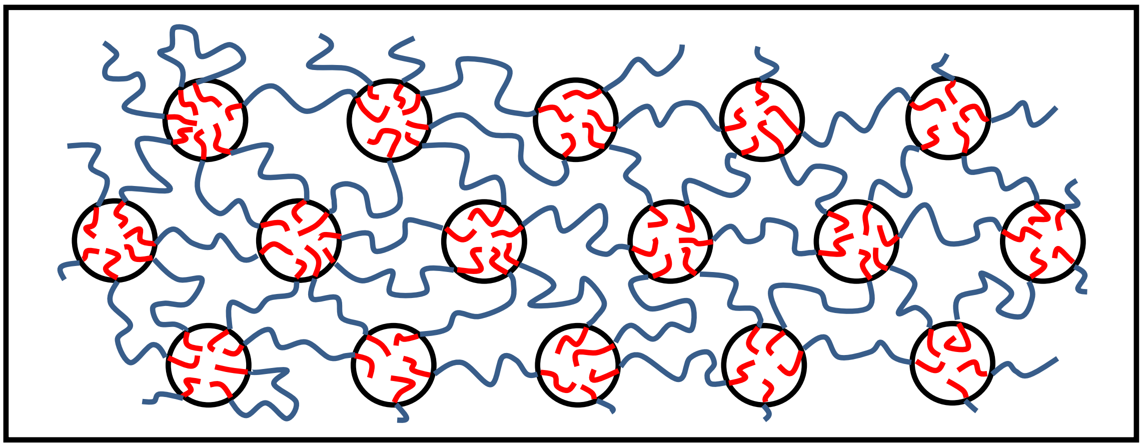

Figure 1.8: Schematic of a tri-block copolymer with spherical morphology showing physical networks formed by hard domains (red) with a soft rubbery matrix (blue).

1.3.3. Amphiphilic Copolymers

Block copolymers can self-assemble to form aggregates upon the addition of a selective solvent (i.e. a solvent that is a good solvent for only one block). Amphiphilic copolymers are block or graft copolymers which consist of a hydrophobic and a hydrophilic block. These copolymers can self-assemble in water to form various morphologies. When the hydrophobic block is much longer than the hydrophilic block there are a large variety of possible morphologies (termed 'crew-cut' aggregates) that can form depending upon the conditions. These morphologies include spherical micelles, rods, bicontinuous structures, lamellae and vesicles,[13-15] *etc*. as shown in Figure 1.9.[16] Some of the morphologies are thermodynamically stable, such as

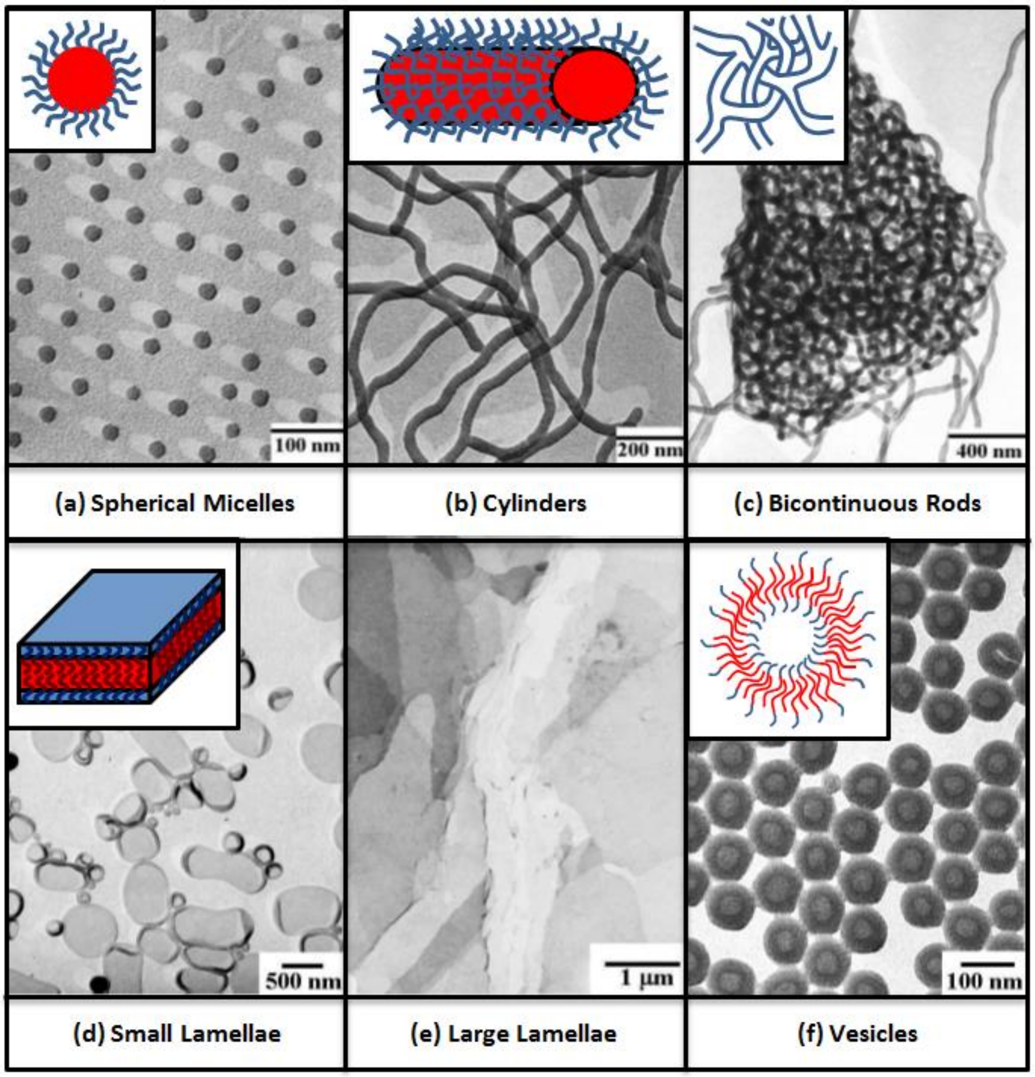

Figure 1.9: Schematic diagrams and transmission electron microscopy (TEM) images of various morphologies formed from amphiphilic block copolymers. Reprinted with permission from Cameron, N. S., Corbierre, M. K., Eisenberg, A., Can. J. Chem. –Rev. Can. Chim., Vol. 77/8, Page 1311-1326, 1999. Copyright 1999, Canadian Science Publishing.[16]

spheres, rods, bilayers, etc., whilst other morphologies such as large compound vesicles, tubules, etc. are kinetically trapped. When the hydrophilic block is longer than the hydrophobic block spherical micelles (termed 'star-like' aggregates) typically form. The formation of these structures is primarily a result of the hydrophobic effect.[17] The introduction of the solvent to the block copolymer means there are now three interaction parameters, χ_{AB}, χ_{AS}, χ_{BS}, where A and B represent the two blocks and S represents the solvent. As the water-hydrophilic block interaction is favourable and the water-hydrophobic block interaction is unfavourable, morphologies form to minimise the contact between the hydrophobic block and the water molecules. The main parameter that determines which morphology forms is the packing parameter, $p = v/a_0l$, where v is the volume of the hydrophobic block, a_0 is the area occupied by the hydrophilic block and l is the length of the hydrophobic block. A value of $p < 1/2$ favours the formation of aggregates with a high degree of curvature such as micelles and cylinders; when $1/2 < p < 1$ the formation of less curved bilayer structures is favoured such as vesicles and lamellae; $p = 1$ favours planar lamellae and $p > 1$ inverted structures.[18] Typically, decreasing the length of the hydrophilic block will decrease the curvature of the aggregates; hence a smaller hydrophilic block will promote the formation of vesicles and lamellae.

Spherical micelles are usually the first aggregates to form, from which other morphologies develop. The micelles contain a spherical hydrophobic core surrounded by hydrophilic chains which comprise the corona (Figure 1.9a). The hydrophobic core allows the encapsulation of drugs, or fluorescent probes and hence micelles can be used for drug delivery and biological imaging. The radius of the micelle core is determined by the aggregation number (i.e., the average number of polymer chains per aggregate), N_{agg}, and the length of the hydrophobic chains. Increasing the aggregation number is energetically favourable as it reduces the overall number of aggregates, and hence the total interfacial area. However, increasing N_{agg} results in an entropic penalty due to stretching of the hydrophobic blocks and is also hindered by repulsion between the hydrophilic blocks. For larger hydrophilic blocks, the interchain repulsion will more strongly limit the core size. As the length of the hydrophilic block is reduced, the repulsion among the coronal chains decreases allowing larger core sizes with a larger value of N_{agg}. However, this increases the stretching in the hydrophobic blocks which then becomes the limiting factor on core growth. Eventually when the entropic penalty for stretching the hydrophobic blocks becomes too high, the micelles begin to adopt other morphologies such as cylinders and lamellae in order to minimize the total free energy further. Cylinders (also termed rods or wormlike micelles) contain a hydrophobic cylindrical core surrounded by a corona of hydrophilic chains (Figure 1.9b) and have possible applications in providing a template for aligning metal, semiconducting or magnetic nanoparticles. The cylinder diameter is similar to that of micelles (*ca*. 30 nm), whilst the length can greatly vary in size and can be over 10 µm long. Lamellae are flat or slightly curved bilayers (Figure 1.9d and Figure 1.9e) and vesicles are closed bilayers which contain a hollow core with a hydrophobic layer sandwiched between two hydrophilic coronas (Figure 1.9f). Other possible morphologies include bicontinuous rods (Figure 1.9c), hexagonally packed hollow hoop structures and large compound micelles.

1.4. Monomer Sequence Control in Polymer Synthesis

When a polymer consists of two or more monomers it is possible to obtain a wide variety of different compositions as discussed in Section 1.1.2. Whilst the synthesis and properties of different polymer architectures has been extensively studied, sequence controlled polymers have largely been neglected. The co-monomer sequence of a polymer has a significant effect on the polymer properties. For example, an alternating copolymer will possess a T_g which is between that of the two monomers which comprise the polymer; whereas a block copolymer will have two T_g values; each corresponding to one block. Furthermore natural polymers, such as proteins, rely on the polymer sequence rather than the architecture to control the polymer properties. The primary structure (i.e. order of monomers) dictates the overall 3D structure and therefore the form and function of the protein. The monomer (amino acid) sequence allows the proteins to perform advanced and complicated tasks including controlling other chemical reactions. In nature the sequence control is perfect and all protein molecules are self-similar in both sequence order and chain length. This absolute control is unlikely to be possible for man-made polymers. However, it may not be necessary to precisely control the sequence in order to synthesize functional materials.

In recent years there has been growing interest in synthesis of sequence controlled polymers and there are a number of groups utilizing different strategies to influence the co-monomer sequence.

1.4.1. Sequence Control in Step Growth Polymerization

Step growth polymerization can involve co-monomers containing two different functional groups (i.e. XaY + XbY, where X and Y are the reactive functional groups and a and b are the co-monomers), or co-monomers containing one distinct type of functional group (i.e. XaX + YbY). The former case will typically produce copolymers with a random or statistical structure, whereas in the latter case a perfectly alternating sequence will be obtained. The introduction of a third monomer usually yields a statistical copolymer. Whilst it is possible to control the sequence by single monomer addition, this methodology is time consuming as it requires a number of additional steps. In some specific cases, such as the copolymerization of nitroisophthalic acid, bis(2,4,6-trichlorophenyl) isophthalate and 4-aminobenzyhydrazide, it is possible to obtain a polymer with an ABC ordered sequence due to the specific monomer reactivities.[19] More generally, a combination of protection/deprotection group chemistry with step-growth polymerizations can be used to prepare perfect monomer sequences. This is the current methodology for the synthesis of biopolymers such as peptides and oligonucleotides which can be prepared either in solution or on solid-phase support.[20] However each monomer addition requires a number of time-consuming steps and as a result this is a very expensive approach.

1.4.2. Sequence Control in Chain Growth Polymerization

Whilst it is much more challenging to control the monomer sequence in chain growth polymerizations, these polymerizations are much more versatile and can be used to prepare polymers with a narrow dispersity and controllable high molecular weights, and therefore have many advantages over step growth polymerizations. Recently there have been a number of methods investigated for controlling monomer sequence distribution in chain growth copolymerizations which include post polymerization sequence modification, controlled monomer insertion, templating and kinetic control.

1.4.2.1. Post Polymerization Sequence Modification

Typically the copolymer sequence is determined during the polymerization; however, Nishikubo *et al.* demonstrated a method of sequence modification post polymerization.[21] This involves the insertion of thiirane motifs into poly(s-aryl thioester) chains to provide a copolymer with a repeating ACBC sequence as shown in Figure 1.10.

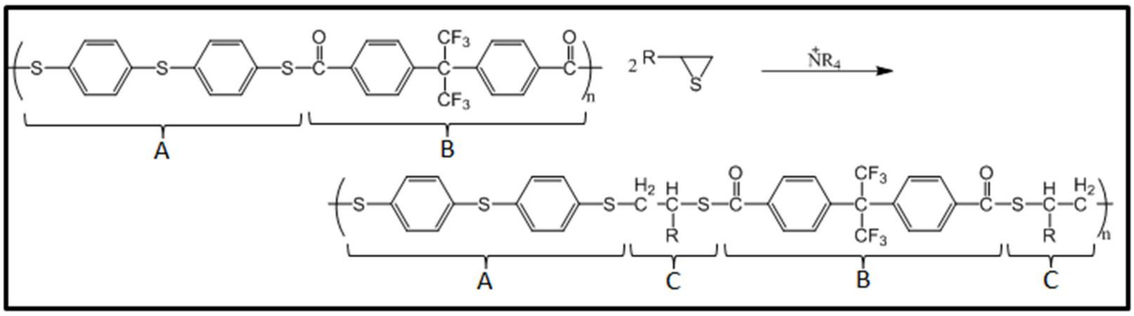

Figure 1.10: Synthetic scheme showing the synthesis of a sequence controlled copolymer by the monomer insertion of an ethylene sulfide derivative.[21]

1.4.2.2. Template Controlled Sequence Distribution

One technique for controlling monomer sequences is by the use of a template to control monomer addition. In essence this is how nature controls sequences in natural polymers, where the template (enzymes, RNA, etc.) ensures that only the desired monomer is available at the active site. However, these templates are often very complex molecules whereas simple templates are more desirable from a synthetic viewpoint. Hillmyer *et al*. reported a novel approach to prepare regioselective terpolymers or quaterpolymers by ring opening metathesis polymerization (ROMP) of multi-substituted cyclooctenes.[22] This template monomer unfolds to create a perfectly ordered copolymer structure with high regio- and stero-control; however, it does require the complex synthesis of a multi-functional cyclooctene monomer. Another strategy involving the use of template monomers was reported by Sawamoto *et al*. in which one unit of methyl methacrylate and one unit of methyl acrylate were each attached to the *peri*-position of a naphthalene template. The monomers were then polymerized by ATRP to prepare an alternating copolymer (Figure 1.11).[23] In a similar fashion Sawamoto *et al*. also used a palladium template attached to three monomers (two units of 4-aminomethylstyrene and one unit of 4-vinylpyridine) to prepare a

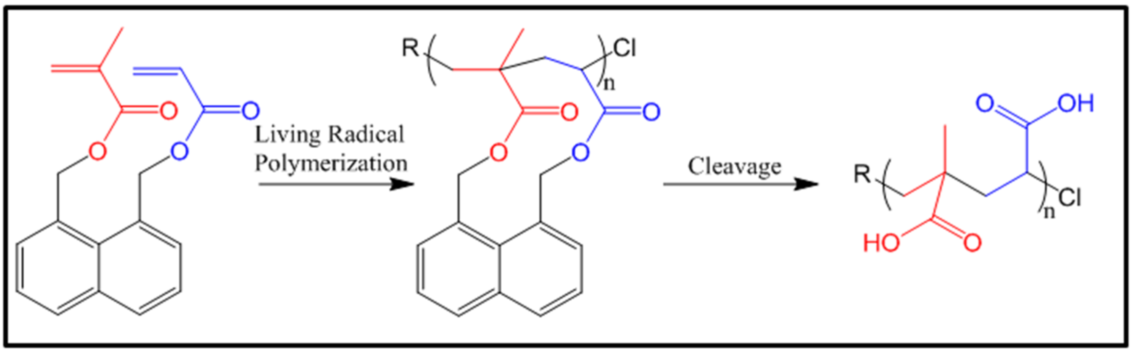

Figure 1.11: Synthetic scheme showing a sequence controlled living radical polymerization using a template monomer.[23]

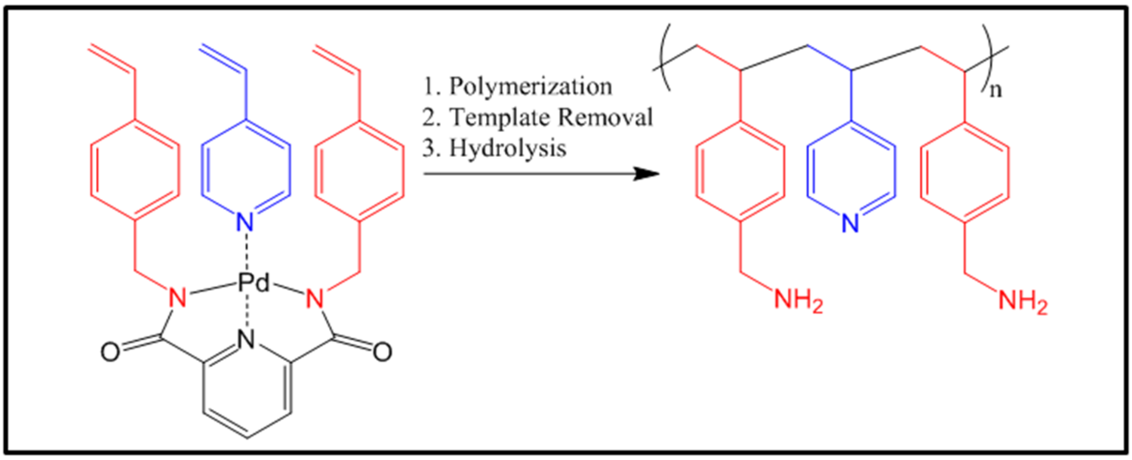

Figure 1.12: Synthetic scheme showing a sequence controlled living radical polymerization using a three-monomer template.[24]

copolymer with repeating ABA monomer sequences (Figure 1.12).[24] By using different monomers, this approach can be used to prepare ABC and other triple-unit alternating sequences.

An alternative template strategy is to use the initiator as a template to control the addition of monomers. To demonstrate a proof of concept, Sawamoto *et al*. designed a template initiator that allows preferential consumption of methacrylic acid over methyl methacrylate. The template contains an initiating site for metal mediated living radical polymerization. Pendent amino groups enable template controlled monomer insertion in which methacrylic acid was ‘recognized’ and reacted in preference to methyl methacrylate (Figure 1.13).[25-26]

Following on from this work Sawamoto *et al*. investigated using crown ether groups to provide a different type of recognition site into the template, which subsequently

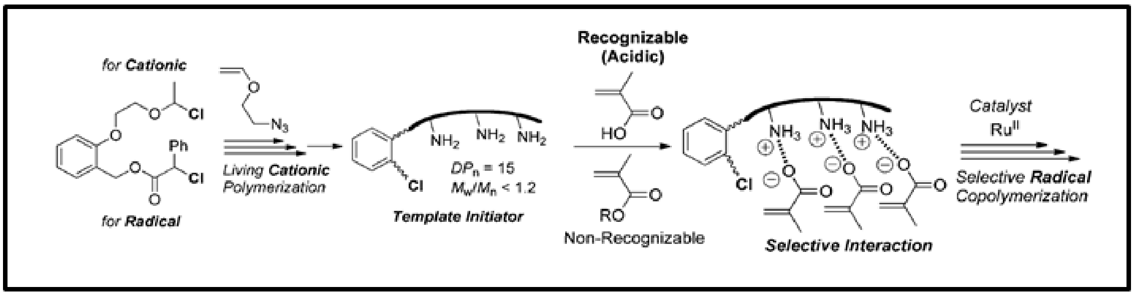

Figure 1.13: Synthesis of the template macroinitiator and ruthenium-catalyzed radical copolymerization. Reprinted with permission from Ida, S. Ouchi, M. Sawamoto, M., Vol. 32/2, Page 209-214, 2011. Copyright 2011, Wiley-VCH Verlag GmbH & co.[25]

recognizes and specifically reacts with sodium methacrylate in preference to methacryloxyloxyethyltrimethylammonium chloride which proved to be more reactive when using a template-free initiator.[27] It is also possible to use natural products as the template which was shown by O'Reilly *et al*. who used DNA to control the sequences of oligomers.[28] O'Reilly *et al*. have also polymerized a nucleobase-containing vinyl monomer in the presence of a complementary self-assembled block copolymer to yield a polymer with high molecular weight and low dispersity.[29] Although this preliminary polymerization has only been used for a homopolymerization and therefore does not currently provide sequence control, it is a promising approach for future attempts to synthesize sequence controlled copolymers with high molecular weight.

1.4.2.3. Kinetically Controlled Sequence Distribution

Whilst template controlled polymerization is a very exciting and promising approach to obtain sequence controlled polymers, the simple technique of exploiting kinetic control over co-monomer sequences during the polymerization has the advantage of being experimentally easier and more economical and hence much more applicable from an industrial perspective. Living polymerizations are of particular importance to kinetic control as the absence of chain termination allows the formation of uniform chains with near-identical sequences, i.e. it is possible to prepare a tapered block copolymer in living polymerization conditions, whereas if chain termination was an ongoing process, only small sequences of homopolymers would be obtained. If two monomers are copolymerized, there are four potential propagation reactions and therefore four propagation rate constants that will affect the copolymer sequence

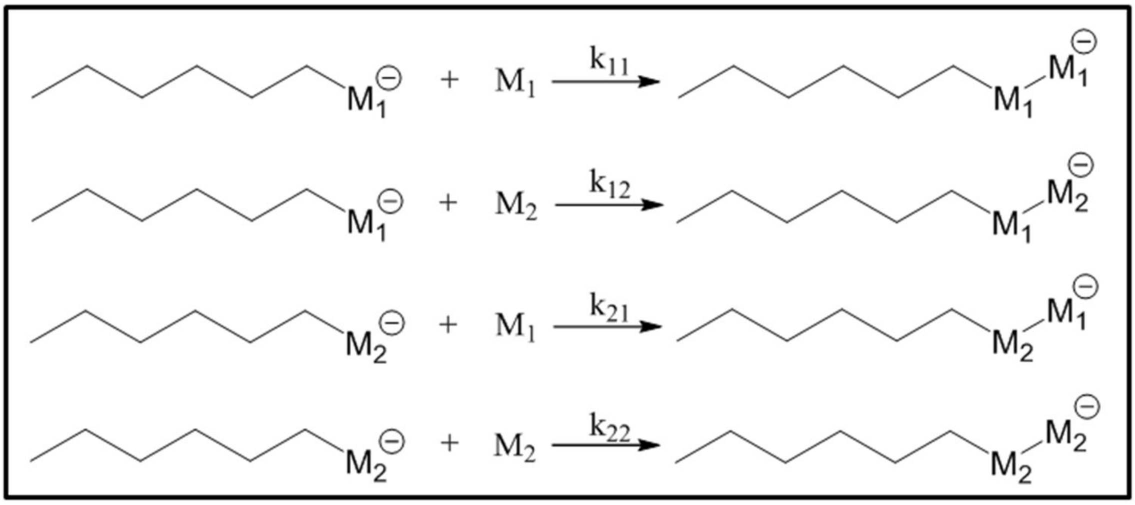

Figure 1.14: Four propagating rate constants for the copolymerization of two monomers assuming the reactivity of the chain end only depends on the last unit.

(Figure 1.14). The resulting copolymer sequence is governed by the ratios of the self-propagating rate constants relative to the cross-propagating rate constants. If $k_{11} > k_{12}$, then the reactivity ratio, r_1, is greater than 1 ($r_1 = k_{11}/k_{12} > 1$) and monomer 1, M_1, will prefer to homopolymerize. Similarly if $k_{22} > k_{21}$ ($r_2 = k_{22}/k_{21} > 1$), then monomer 2, M_2 also prefers to homopolymerize and in the absence of chain termination or chain transfer a ‘blocky’ copolymer will be obtained (i.e. a copolymer with long sequences of each monomer). Other possible sequences include: alternating copolymers ($r_1 = r_2 = 0$); random copolymers ($r_1 = r_2 = 1$); statistical copolymers ($0 < r_1,r_2 < 1$) and tapered copolymers ($r_1 << r_2$). One of the simplest examples of sequence control is alternating copolymers. If the right co-monomer pair can be found it is possible to obtain perfectly controlled alternating sequences. One of the first reported examples was the free radical copolymerization of maleic anhydride with styrene to form an alternating copolymer.[30] This monomer combination was exploited by Hawker *et al*. who used an excess of styrene with maleic anhydride to prepare a block copolymer of poly(styrene-*alt*-maleic anhydride)-*block*-polystyrene by controlled free radical polymerization.[31] Lutz *et al*. expanded on this idea of exploiting the reactivity ratios, but combined it with sequential addition of monomers to prepare a multi-block copolymer.[32] In this innovative method an excess of styrene is copolymerized with a variety of maleimide monomers. The controlled radical polymerization by ATRP of styrene is interrupted by the addition of an aliquot of maleimide co-monomer to the reaction. Given the reactivity ratios, a short sequence of alternating styrene-maleimide units is introduced until the maleimide derivative has been consumed at which point the homopolymerization of styrene can resume. A second maleimide derivative can be subsequently added and a second short alternating sequence is introduced. This procedure was repeated for two more maleimide derivatives to prepare a polystyrene polymer containing four short alternating styrene-maleimide sequences. This elegant approach relies on manual intervention or 'intelligent-design' rather than any intrinsic sequence control.

1.4.2.3.1. Kinetically Controlled Sequence Distribution using 1,1-Diphenylethylene

There are a number of examples of alternating copolymers prepared by controlled free radical,[33-36] ROMP,[37] cationic[38] and living anionic copolymerization.[39-44] Of particular interest to living anionic copolymerizations is the monomer 1,1-diphenylethylene (DPE). Due to steric constraints, DPE is unable to homopolymerize and has therefore been used with alkyllithium initiators to initiate and end-cap anionic polymerizations (i.e. as either the first or last monomer unit in the chain).[45-49] It is particularly useful for controlling the initiation of acrylate and methacrylate monomers as the ester carbonyl group on these monomers can undergo side reactions with the initiator. The steric bulk of 1,1-diphenylhexyllithium (generated from reacting DPE with butyllithium) inhibits the attack on the carbonyl group. DPE can also be used to end-cap another propagating species such as styryl lithium before the addition of methyl methacrylate to prepare a polystyrene-*block*-poly(methyl methacrylate) copolymer.[45-46] Whilst DPE is unable to homopolymerize, it can copolymerize with other monomers, and provided a suitable co-monomer is found it can be used to prepare alternating copolymers analogous to the copolymerizations of maleic anhydride with styrene in free-radical copolymerizations. It should also be noted that reaction conditions (particularly the solvent) can have a large impact on the reactivity ratios (see Section 1.4.2.3.4.). In the 1960's Yuki *et al*. explored the copolymerization of DPE with styrene;[43] butadiene;[41] isoprene;[42] 2,3-dimethylbutadiene[40, 44] and methoxystyrene.[39] ^{1}H NMR analysis suggested the formation of alternating or nearly alternating copolymers in all cases when THF was used as the reaction solvent, however only styrene, 2,3-

Table 1.1: Monomer Reactivity Ratio, r_1, for anionic copolymerization of 1,1-Diphenylethylene (M_2) with various co-monomers (M_1) in polar and apolar solvents.

M_1	r_1 in THF	Temp/°C	r_1 in Benzene	Temp/°C	Ref.
Styrene	0.13	30	0.7	30	43
p-MeOSt	~0	0	<0.3	40	39
o-MeOSt	~0	0	20	40	39
Butadiene	0.13	0	54	40	41
Isoprene	0.11	0	37	40	42
2,3-Dimethyl-butadiene	0	22	0.23	40	40, 44
p-Divinylbenzene	2.5	-20	16*	-20	50-51
m-Divinylbenzene	1.2	-20	2.5*	-20	50-51

* In toluene

dimethylbutadiene and *p*-methoxystyrene formed nearly alternating copolymers in benzene. Butadiene, isoprene and *o*-methoxystyrene showed a very strong tendency to homopolymerize in the presence of DPE when using non-polar solvents. The reactivity ratios obtained by Yuki are shown in Table 1.1. Hatada *et al*. investigated the copolymerization of DPE with *m*- and *p*- divinylbenzene (DVB).[50-51] They found *p*-DVB had a reactivity ratio, r_1 = 16 in toluene and 2.5 in THF, and hence *p*-DVB has a tendency for self-propagation when copolymerized with DPE. *m*-DVB had a reactivity ratio, r_1 = 2.5 in toluene and 1.2 in THF and hence *m*-DVB has a slight tendency for self-propagation rather than cross-propagation. In comparison, styrene has a reactivity ratio, r_1 = 0.4 in toluene and 0.13 in THF. Whilst the incorporation of DPE can be increased by using a large excess of DPE, *m*- and *p*-DVB are not ideal co-monomers for preparing alternating copolymers.

Until recently all attempts to copolymerize DPE by cationic copolymerization were unsuccessful, however, in 2012 Yasuoka *et al*. successfully managed to copolymerize a high molecular weight copolymer of DPE with *p*-methylstyrene with a narrow molecular weight distribution and a DPE content of 26 mol. %.[52]

1.4.2.3.2. Sequence Control with Functionalized derivatives of 1,1-Diphenylethylene

Functional derivatives of DPE have been used to introduce functionality at various positions in the polymer chain. These functional derivatives often involve masked functionality due to the sensitivity of living anionic polymerizations. There have also been a number of studies involving derivatives of DPE (such as 1-phenyl-1-(1′-pyrenyl)ethylene) as a fluorescent labelling group.[53-57] Amino-derivatives such as 1-(4-dimethylaminophenyl)-1-phenylethylene and 1-(4-(*N*,*N*-Bis(trimethylsilyl)amino)-phenyl)-1-phenylethylene have been used to place amino groups at the beginning of the chain,[58] the chain terminus,[58-59] at the interface between two blocks[58] or to prepare telechelic copolymers by the use of sequential addition and stoichiometric amounts of the functionalized DPE.[58] Li *et al*. copolymerized 1,1-bis(4-dimethylaminophenyl)ethylene with styrene[60] and also with butadiene[61] to prepare statistical copolymers, Quirk *et al*. reported the copolymerization of 1-(4-dimethylaminophenyl)-1-phenylethylene with styrene,[62] and Hayashi attempted to use the reactivity ratios to prepare a sequence controlled telechelic copolymer of poly(styrene-*co*-butadiene) end-capped at both ends with 1,1-bis(4-dimethylaminophenyl)ethylene.[63] Summers *et al*. have reported the use of amino-derivatives of DPE to prepare a variety of different telechelic copolymers by ATRP involving stoichiometric amounts and sequential addition of the DPE-derivative.[64-67] Telechelic copolymers with carboxylic acid end groups were synthesized by Summers *et al*. using either *N*,*N*-diisopropyl-4-(1-phenylethenyl)benzamide[68] or 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxalone[69] and deprotecting the carboxylic acid groups post polymerization. Similarly DPE derivatives have been used to add phenol groups at the chain terminus[70-71] or at the interface between two styrene blocks.[72] Hutchings *et al*. used 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene to end-cap polystyrene and prepare hyperbranched polymers (HyperMacs).[73-74]

Hutchings *et al*. also investigated the copolymerization of styrene with the deactivated DPE monomer, 1,1-bis(4-tert-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) and also with the activated DPE monomer, 4-cyanodiphenylethylene (DPE-CN).[75-76] The deactivated monomer DPE-OSi was found to be weakly incorporated into a predominantly styrene containing polymer, whereas the activated monomer DPE-CN formed perfectly alternating oligomers but could not be used to prepare higher molecular weight copolymers due to the slow cross-over from DPE-CN to styrene.[75-76]

1.4.2.3.3. Kinetically Controlled Block Copolymers

Block copolymers can also be prepared by kinetic control. When $r_1 > r_2$ and if $0 < r_2 < 1$ then monomer 1 will preferentially homopolymerize in the first instance, and if it does cross to monomer 2, then monomer 2 will preferentially cross-propagate back to monomer 1. Only upon high conversions of monomer 1 will monomer 2 begin to homopolymerize. A well-known example of this is styrene and butadiene in non-polar solvents.[77] Initially butadiene is consumed ($r_1 = 10.8$ and $r_2 = 0.04$ in benzene),[5] then as the concentration of butadiene decreases a middle block propagates which is initially richer in butadiene but changes in composition until it becomes richer in styrene, this is followed by a final block of styrene which occurs after complete consumption of butadiene. This type of copolymer is termed a gradient or tapered copolymer.

When styrene is copolymerized with DPE it increases the T_g from about 100 °C to approximately 170 °C,[78-79] thereby extending the operational temperature of the polymer. For this reason DPE is ideal for increasing the T_g of a glassy block in a block copolymer; however, there are only four examples in literature of block copolymers containing DPE – three of poly(styrene-*co*-DPE)-*block*-polybutadiene[78, 80-81] and one of poly(styrene-*co*-DPE)-*block*-polyisoprene.[82] In all of these cases the block copolymers are prepared by sequential addition of monomers; first copolymerizing styrene with DPE followed by the addition of either butadiene or isoprene. However, the reactivity ratios indicate that a situation resembling that of the copolymerization of styrene and butadiene in non-polar solvents should occur. Namely that a simultaneous terpolymerization of styrene, butadiene and DPE should proceed by the initial polymerization of butadiene followed by a styrene-*co*-DPE block and therefore creating a sequence controlled tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE). This hypothesis is investigated herein.

1.4.2.3.4. Solvents, Additives and Temperature Effects on Reactivity Ratios

It is possible to influence the reactivity ratio by changing the solvent, temperature or by the addition of additives. The solvent polarity can have the most significant effect on the reactivity ratios; and generally the reactivity ratios will not differ greatly from one non-polar solvent to another. Using the copolymerization of butadiene (M_1) and styrene (M_2) (at 25 °C) as an example, the reactivity ratios, r_1 and r_2, have been reported as 10.8 and 0.04 in benzene; 15.5 and 0.04 in cyclohexane and 12.5 and 0.03 in hexane and hence will all form a tapered copolymer of polybutadiene-*co*-polystyrene.[5] However, in the case of the polar solvent THF, polystyryllithium becomes preferentially stabilized relative to polybutdienyllithium, and the reactivity ratios, r_1 and r_2, are reported to be 0.3 and 4.0 at 25 °C, hence a tapered copolymer of polystyrene-*co*-polybutadiene would now form.[5]

Temperature effects have also been reported to influence the reactivity ratios, however the effects are not usually so pronounced as changing the polarity of the solvent. Again using the copolymerization of butadiene (M_1) and styrene (M_2) as an example, when hexane is used as the solvent the reactivity ratios, r_1 and r_2, are reported as 13.3 and 0.03 at 0 °C; 12.5 and 0.03 at 25 °C and 11.8 and 0.04 at 50 °C.[5]

It should be noted the solvent and temperature have other affects upon the copolymerization, including upon the rate of polymerization and microstructure. Polar solvents and higher temperatures will increase the rate of polymerization whereas non-polar solvents and lower temperatures will tend to decrease it. More importantly in the case of butadiene, polar solvents such as THF increase the 1,2-polybutadiene content which can be disadvantageous as 1,4-polybutadiene is usually more commercially desirable.

Polar additives were investigated as a method of forming a random copolymer of butadiene and styrene, i.e. $r_1 \approx r_2 \approx 1$, ideally with a relatively high 1,4-polybutadiene content. The addition of one equivalent of TMEDA ([TMEDA]/[Li] = 1) has been reported to be used to prepare a near-random copolymer of butadiene (M_1) and styrene (M_2) in toluene, $r_1 = 0.86$ and $r_2 = 0.91$, however, the resulting copolymer had a microstructure of 65 % 1,2-polybutadiene.[83] Alkali metal alkoxides (other than lithium) have been used to promote the incorporation of styrene without significantly increasing the amount of 1,2-polybutadiene microstructure. Potassium *tert*-butoxide in particular has been used to promote the incorporation of styrene, and, by adjusting the molar feed ratio relative to the butyllithium initiator, can be used to maintain a constant incorporation of styrene throughout the reaction. Furthermore at low molar feed ratios of potassium *tert*-butoxide (less than 0.1 mole equivalents relative to butyllithium) the 1,2-polybutadiene microstructure is reported to be less than 20 %.[84]

1.5. Aims and Objectives

The aims and objectives of this project are to investigate the copolymerization and terpolymerization of styrene, butadiene, DPE and derivatives of DPE under various reaction conditions. Of particular interest is the simultaneous copolymerization of two or more monomers whereby the resulting monomer sequences are controlled by reactivity ratios – termed a ‘fire and forget’ strategy.

An initial aim is to explore the two component (binary) systems involving DPE, particularly the copolymerization of styrene with DPE and that of butadiene with DPE. The use of state-of-the-art techniques such as MALDI-ToF mass spectrometry (MS) will enable an in-depth analysis and confirmation of the resulting copolymer sequences. A full analysis of these binary systems will allow for a better understanding when analysing more complicated systems, for example in a terpolymerization.

A key aim is to investigate the synthesis of terpolymers containing styrene, butadiene and DPE using both butyllithium and a difunctional initiator and to ascertain the resulting monomer sequences. Moreover, a comparison between these materials (synthesized by a ‘fire and forget’ approach) and analogous copolymers made via the more traditional sequential addition of monomers approach will be carried out. In particular this will include an investigation of the impact of synthetic methodology and the resulting monomer sequence on physical properties including the thermal behaviour and the phase separated morphology. The reaction conditions, such as choice of solvent and monomer molar feed ratios, will also be investigated to determine the impact upon the resulting monomer sequence.

Another key aim of this research is to investigate the use of DPE derivatives as a method of both introducing functionality and manipulating the monomer reactivity. This work will build upon research undertaken by Hutchings *et al*. and will involve derivatives of DPE that contain either an electron withdrawing or an electron donating group. Of particular interest is whether the reactivity ratios can be controlled to allow various monomer sequences to be formed, ranging from alternating to telechelic. Again, the use of various state-of-the-art analytical techniques, including MALDI-ToF MS will be exploited to analyse the monomer sequence of these copolymers.

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CHAPTER 2

Sequence Controlled Copolymers Containing 1,1-Diphenylethylene

2. Sequence Controlled Copolymers containing 1,1-Diphenylethylene

1,1-Diphenylethylene (DPE) is a very useful monomer for preparing sequence controlled copolymers. The large sterically bulky phenyl rings prohibit this monomer from homopolymerization.[1-3] However, DPE can copolymerize by living anionic polymerization with other monomers such as styrene and butadiene, with which it can form perfectly alternating copolymers.[2, 4-8] Yuki *et al*. reported that the copolymerization of DPE with either styrene or butadiene in tetrahydrofuran, THF, resulted in an almost perfectly alternating copolymer.[2, 6] When benzene was used as the solvent the copolymerization of DPE with styrene resulted in near-alternating copolymers whereas the copolymerization of DPE with butadiene resulted in DPE being almost entirely excluded from the reaction.[2, 6] Herein the synthesis of a variety of DPE containing copolymers is reported, including terpolymers with monomer sequences controlled by kinetics (reactivity ratios). Simultaneous copolymerizations, which are referred to herein as a 'fire and forget' approach, are more facile than the more commonly used sequential addition of monomers and the resulting copolymers are often comparable in terms of structure and properties.

2.1. Copolymerization of Styrene and 1,1-Diphenylethylene

The analysis of copolymer sequences becomes less trivial as the number of co-monomers increase. Hence it was decided that prior to investigating terpolymerizations with DPE as a co-monomer, the simple copolymerizations involving DPE and one other monomer would first be explored. Yuki *et al*. first reported in 1964 the living anionic copolymerization of DPE with a variety of co-monomers.[2, 4-9] Furthermore, depending upon the feed ratio, the solvent and co-monomer, apparently perfect alternating copolymers could be prepared if the rate constant for cross-propagation to DPE (M_2) is significantly higher than the rate constant for self-propagation of the non DPE co-monomer (M_1), $k_{12} << k_{11}$. One such co-monomer is styrene which can form alternating copolymers with DPE, but the propensity for alternation is highly dependent upon solvent polarity.[2] Yuki *et al.* used ^{1}H NMR spectroscopy and mass balance (yield) calculations to estimate the amount of DPE in the resulting copolymer and therefore postulate the co-monomer sequences.[2]

However, nearly 50 years later, using a combination of high field (700 MHz) NMR spectroscopy and MALDI-ToF mass spectrometry (MS) it is possible to distinguish the exact composition of a series of poly(styrene-*co*-DPE) copolymers, (P(S-*co*-D)), and therefore establish whether the monomer sequence in these copolymers is perfectly alternating or not.

A series of P(S-*co*-D) copolymers were synthesized and the composition and molecular weight data are shown in Table 2.1 and 2.2 respectively. The ^{1}H NMR spectroscopy for one such P(S-*co*-D) copolymer (PSD-4) synthesized in benzene with a 0.65 : 1.00 molar feed ratio of styrene : DPE is shown in Figure 2.1. The copolymer composition was determined from the ^{1}H NMR spectrum by comparing the integrals of the aliphatic protons (0.0 – 2.5 ppm) relative to the aromatic protons (5.0 – 7.3 ppm). The sharp peak at 7.26 ppm is the trace of the $CHCl_3$ present in $CDCl_3$, and the sharp peak at 2.37 ppm is from toluene. The integrals of $CHCl_3$ and toluene have been subtracted from the integrals of the polymer signals. As toluene contains 5 aromatic protons (present "underneath" the polymer aromatic protons at 5.0 – 7.3 ppm) and 3 protons (Ar-CH_3) at 2.37 ppm, these have also been subtracted from the aromatic polymer signals. The $CDCl_3$ was dried with molecular sieves and the sample prepared under dry nitrogen to reduce the signal of water (expected at 1.56 ppm). Since styrene contains 5 aromatic protons per monomer repeat unit and DPE contains 10 aromatic protons, the following equation can be used:

$$5x + 10y = 2.81 \qquad [2.1]$$

where *x* : *y* is the ratio of styrene : DPE present in the copolymer and 2.81 is the integral of the aromatic region in the spectrum. As styrene contains 3 aliphatic hydrogen atoms, and DPE contains only 2, the following relationship also applies:

$$3x + 2y = 0.98 \qquad [2.2]$$

Solving these simultaneous equations gives the styrene : DPE ratio in the final copolymer as 1.18 : 1.00 i.e. styrene is in slight molar excess. This method was used to determine the composition for the other poly(styrene-*co*-DPE) copolymers, however, this approach could not be used to determine the composition of low molecular

Table 2.2: Monomer Reactivity Ratios, ***r_1***, for the anionic copolymerization of styrene and 1,1-diphenylethylene.

Sample	Sty : DPE feed ratio	Solvent	Temp/ °C	Sty : DPE Composition in copolymer (from ^{1}H NMR)	r_1
PSD-1	1.50 : 1.00	Benzene	RT	2.02 : 1.00	-
PSD-2	0.97 : 1.00	Benzene	50	1.37 : 1.00	0.60
PSD-3a	0.65 : 1.00	Benzene	30	1.17 : 1.00	-
PSD-3b	0.65 : 1.00	Benzene	30	1.17 : 1.00	-
PSD-3c	0.65 : 1.00	Benzene	30	1.22 : 1.00	0.57
PSD-4	0.65 : 1.00	Benzene	RT	1.18 : 1.00	0.46
PSD-5	0.97 : 1.00	Benzene	50	-	-
PSD-6	0.65 : 1.00	Benzene	50	-	-
PSD-7	0.95 : 1.00	Toluene	25	1.24 : 1.00	0.37
PSD-8	0.63 : 1.00	Toluene	25	1.20 : 1.00	0.54
PSD-9	0.95 : 1.00	THF	0	1.11 : 1.00	0.15

Table 3.2: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.196) for the anionic copolymerization of styrene and 1,1-diphenylethylene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PSD-1	9,000	9,900	1.10
PSD-2	10,700	12,200	1.14
PSD-3a	7,800	9,000	1.16
PSD-3b	21,400	25,600	1.20
PSD-3c	91,800	105,500	1.15
PSD-4	40,100	43,800	1.09
PSD-5	1,900	2,100	1.10
PSD-6	1,900	2,100	1.11
PSD-7	57,200	62,300	1.09
PSD-8	71,600	84,900	1.19
PSD-9	60,000	66,000	1.10

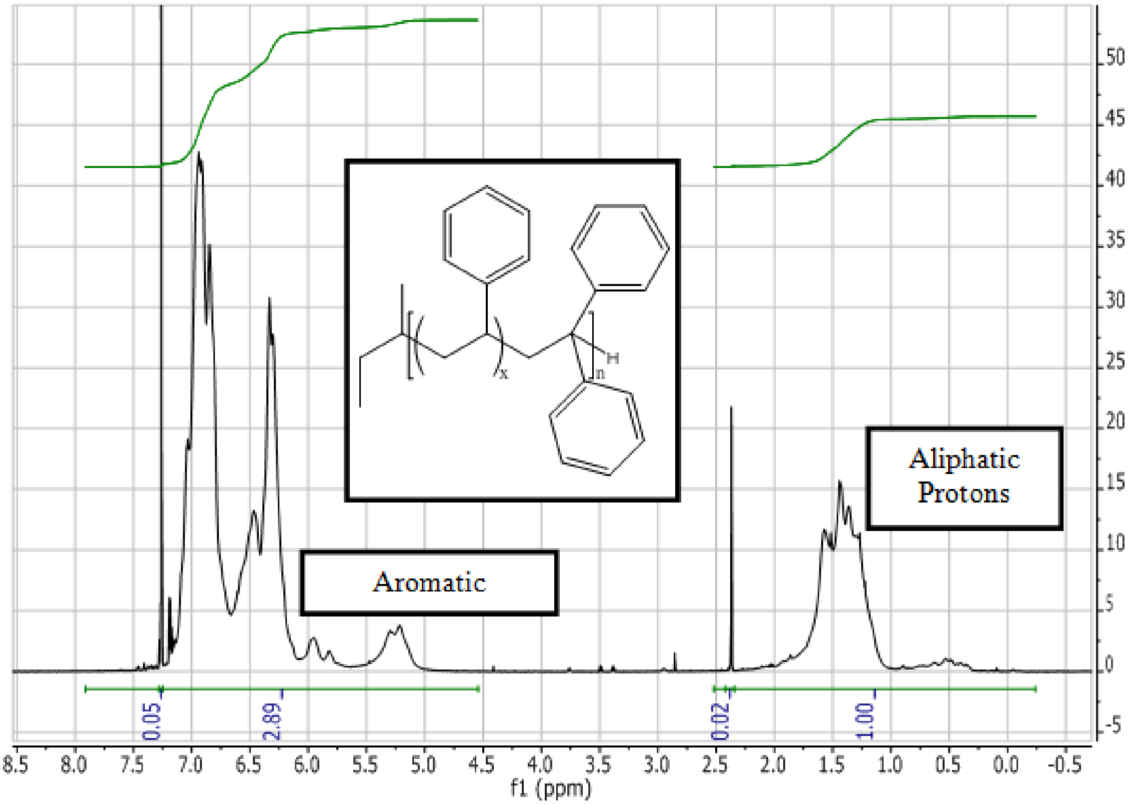

Figure 2.15: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(styrene-*co*-DPE), PSD-4, synthesized in benzene with a molar feed ratio of 0.65 : 1.00 styrene : DPE.

weight samples of poly(styrene-*co*-DPE) copolymers (PSD-5 and PSD-6) since the *sec*-butyl end-group will significantly contribute to the aliphatic protons.

The reactivity ratios, r_1, (listed in Table 2.1) were calculated by an iterative process using the following equation:

$$\ln\frac{[M_2]}{[M_2]_0}+\frac{1}{r_1-1}\ln\left[\frac{[M_1]_0}{[M_2]_0}(r_1-1)+1\right]=0 \qquad [2.3]$$

derived by Yuki *et al.* from the Mayo-Lewis equation, where $[M_2]$ is the final concentration of DPE, $[M_1]_0$ and $[M_2]_0$ are the initial monomer concentrations of styrene and DPE respectively, $r_1 \neq 1$, the reaction must have gone to completion and $[M_2] \neq 0$.[2] In order to calculate the reactivity ratio, the instantaneous monomer feed ratios are required. However, as the monomer feed ratios vary throughout the reaction, reactivity ratios are typically calculated at low monomer conversion when the monomer feed ratio is close to the initial monomer feed ratio.[10] When DPE is used as a co-monomer it is possible to calculate the reactivity ratio at complete conversion provided there is unreacted DPE monomer present at the end of the reaction. Upon consumption of the non-DPE co-monomer, the polymerization will end as DPE cannot homopolymerize. At this point it is possible to calculate the final concentration of DPE monomer, determine the final monomer feed ratio and therefore calculate the reactivity ratio. However, if the DPE monomer is consumed first, the other co-monomer will continue to homopolymerize regardless and the final composition will always be equal to the molar feed ratio. For this reason the reactivity ratios have only been calculated when the molar feed ratio of DPE was equimolar or in excess of the co-monomer. Furthermore, if the reaction had not reached completion, as in the case of PSD-3a and 3b, then it is also not possible to calculate the reactivity ratio as the concentration of the non-DPE co-monomer will not be equal to 0 and the instantaneous molar feed ratios cannot be determined.

The values in Table 2.1 show that for each copolymerization when benzene is the solvent, the reactivity ratio (r_1) is less than 1.0, indicating that styrene has a preference for cross-propagation, however, the values are not so low as to promote perfect alternation – even when DPE is present in excess of styrene. The reactivity ratios obtained for the copolymerization of styrene and DPE in benzene are approximately between 0.5 – 0.6, which are close to the value obtained by Yuki *et al*. who found a reactivity ratio of 0.7.[2] Reactivity ratios have been reported to vary with temperature;[3] however, in this case there does not appear to be a significant variation in the reactivity ratio obtained from the copolymerization at 30 °C and that at 50 °C.

The MALDI-ToF MS analysis was performed on low molecular weight copolymers (M_n ~ 2,000 g mol^{-1}) as it is often difficult to obtain MALDI-ToF mass spectra for high molecular weight polymers[11] and because at higher molecular weight the mass resolution is insufficient to separate individual chains and results in a continuous distribution.[12] Using MALDI-ToF MS, the mass corresponding to each individual copolymer chain could be found, from which it was possible to calculate the number of styrene and DPE units in a given chain. Since it is not possible for two DPE units to be adjacent to each other, it is possible to establish if the copolymer has a perfectly alternating sequence as shown in Figure 2.2. It should be noted that the intensities of individual peaks are not 100 % quantitative, since some copolymer chains may be less prone to ionization.[13] Regardless, the MALDI-ToF mass spectrum in Figure 2.2 provides an excellent indication of the copolymer composition and suggests that the polymerization of an almost equimolar feed ratio in benzene results in a copolymer which is highly but not perfectly alternating. Figure 2.2 shows that many of the individual chains are perfectly alternating with equal numbers of styrene and DPE units; for example the largest peak with an m/z of 1588 mass units corresponds to 5 units of styrene (5 × 104.15 m/z) + 5 units of DPE (5 × 180.25 m/z) + the counter ion, Ag+ (107.87 m/z) + the *sec*-butyl end-group (57.11 m/z) + the hydrogen end-group (1.01 m/z). The difference between this peak and the peak at 1303 mass units, labelled 4 : 4, is exactly 284 m/z; corresponding to one styrene + one DPE unit. The majority of the peaks correspond to perfect alternating sequences, containing equal numbers of styrene and DPE units (blue lines), or ratios of styrene : DPE = n : n+1 (red lines), or n : n-1 (green lines), in the case of chains with the same monomer unit at both chain ends (see inset Figure 2.2). It is possible that the blue line could also correspond to chains with a DPE at both ends and one styrene-styrene imperfection, and similarly the green line could correspond to a chain with a DPE unit at one or both ends and one or two styrene-styrene imperfections. However, the sequences highlighted by the red lines can only correspond to perfectly alternating sequences. There are also a few, low intensity peaks indicating a low concentration of chains which are not perfectly alternating, highlighted with red circles. Thus the reactivity ratio r_1 is indeed less than 1.0 – indicating that styrene shows a preference for undergoing cross-propagation reactions – but not so low as to avoid any sequence imperfections. It will subsequently be shown that solvent polarity can be used to change the reactivity ratios and promote alternation, but the resulting composition can of course also be controlled by the monomer feed ratio. Thus, by increasing the amount of DPE in the monomer feed ratio to give a feed ratio of 0.65 : 1.0 (styrene : DPE) the likelihood of styrene-DPE cross-propagation can be increased and alternation enhanced. The MALDI-ToF mass spectrum in Figure 2.3 confirms this and shows chains which are predominantly alternating copolymers with only a very few imperfections – the peaks corresponding to imperfections being highlighted with red circles. The difference between Figures 2.2 and 2.3 clearly demonstrates the impact that increasing the feed ratio of DPE has upon the resulting monomer sequence and shows a near-perfect alternating copolymer can be obtained even when the reactivity ratio is not 0.

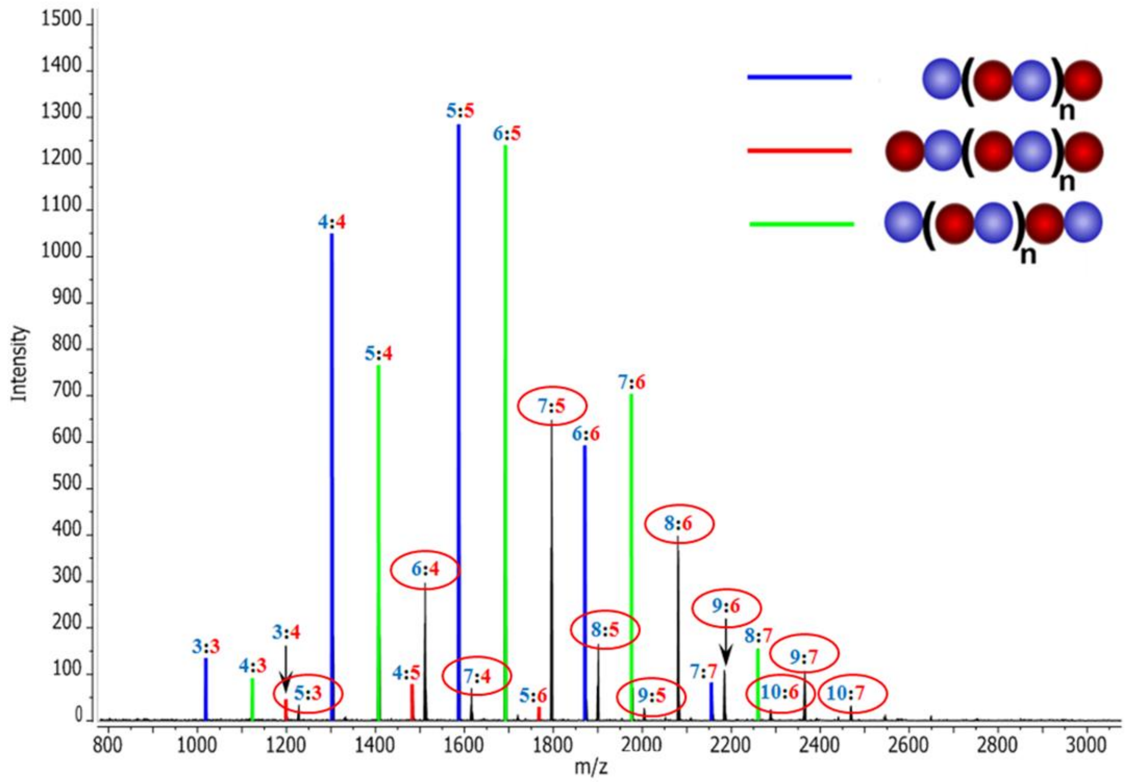

Figure 2.16: MALDI-ToF mass spectrum for the copolymer PSD-5 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 0.97 : 1.00). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

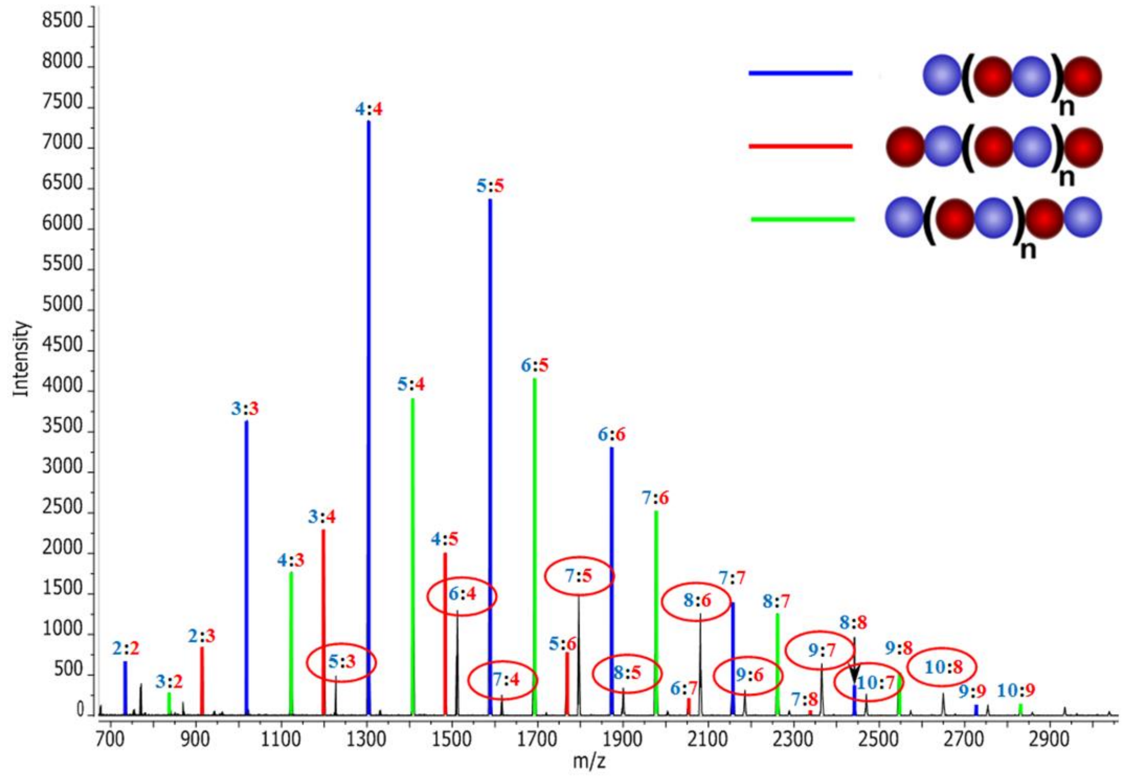

Figure 2.17: MALDI-ToF mass spectrum for the copolymer PSD-6 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 0.65 : 1.00). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

2.1.1. Impact of Solvent Polarity on Reactivity Ratios

The reactivity ratios are often strongly dependent on the polarity of the solvent. It has been reported that a copolymerization of styrene with DPE in toluene yields a reactivity ratio, r_1, of 0.44 (molar feed ratio of styrene : DPE = 1.0 : 1.0) whereas in benzene a reactivity ratio, r_1, of 0.71 was obtained (molar feed ratio of styrene : DPE = 0.9 : 1.0).[2] Switching from a non-polar solvent to a polar one often yields a much more dramatic effect on the reactivity ratios, and indeed in THF the reactivity ratio, r_1, was reported to be 0.13 (molar feed ratio of styrene : DPE = 1.0 : 1.0).[2]

The copolymerization of styrene and DPE in both toluene and THF was investigated and the composition of the resulting polymers analysed by ^{1}H NMR spectroscopy. Comparing the copolymerization of styrene and DPE in toluene (PSD-7 and 8) with analogous reactions in benzene indicates that in toluene the reactivity ratio, r_1, is between 0.4 – 0.5 whereas in benzene r_1 is observed to be 0.5 – 0.6 and again in excellent agreement with Yuki *et al*. who reported a reactivity ratio (in toluene) r_1 = 0.44.[2] This indicates that changing the solvent from benzene to toluene may slightly decrease the reactivity ratio but does not have a significant effect.

Switching to the more polar solvent THF, had a much greater effect on the relative reactivities. PSD-9 (Table 2.1), a copolymerization of (almost) equimolar amounts of DPE and styrene polymerized in THF at 0 °C resulted in a copolymer with an (almost) equimolar composition of DPE and styrene and a reactivity ratio r_1 = 0.15, much lower than the reactivity ratios calculated for reactions carried out in benzene and toluene and in good agreement with previously reported data by Yuki *et al*. who found a reactivity ratio r_1 = 0.13.[2]

A low molecular weight copolymer of poly(styrene-*co*-DPE) was prepared in THF and analysed by MALDI-ToF MS (Figure 2.4). Every visible peak in the MALDI-ToF mass spectrum of the poly(styrene-*co*-DPE) copolymer prepared in THF can be attributed to a perfectly alternating co-monomer sequence. The blue lines indicate alternating copolymers with equal numbers of styrene and DPE units – this is the major distribution present. The second most populous distribution is of alternating chains with one more DPE unit than styrene, indicating alternating copolymers with DPE units

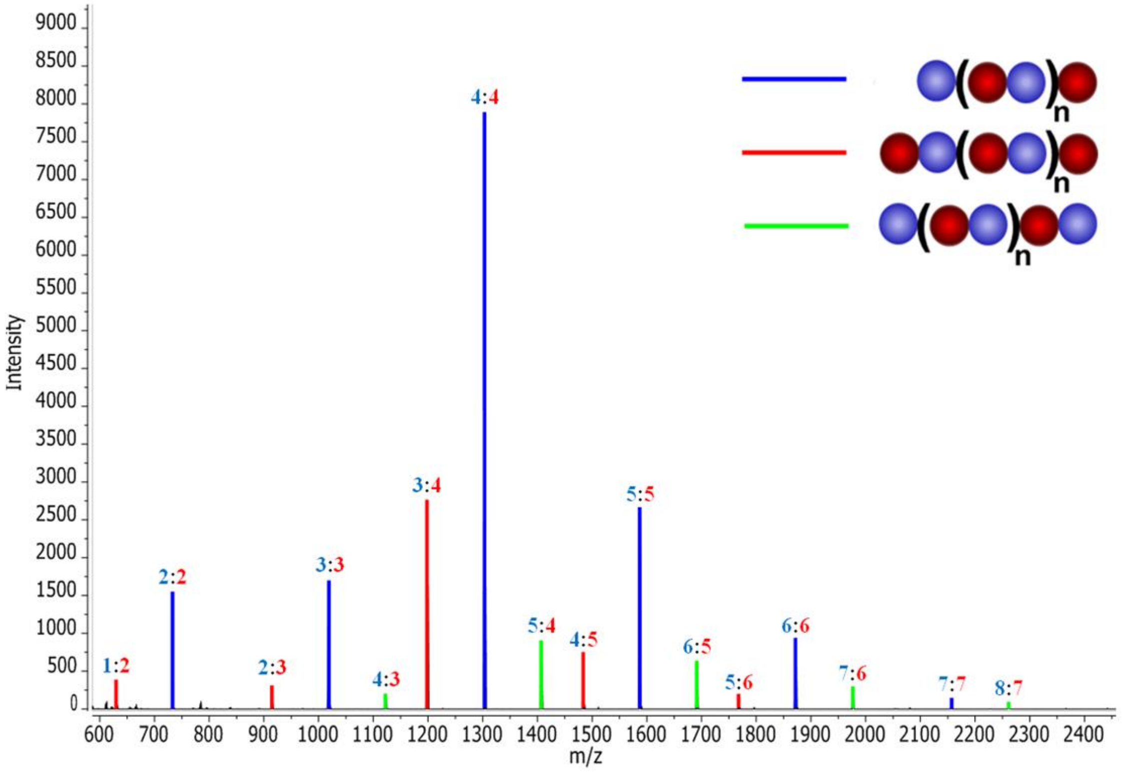

Figure 2.18: MALDI-ToF mass spectrum for the copolymer PSD-10 prepared by the anionic copolymerization (in THF) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 0.95 : 1.00). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

at each chain end, and finally there is a distribution of chains which are alternating with styrene units at each end of the chain, indicated by the green lines. MALDI-ToF MS is unique in being able to reveal this level of detail about not only sequence distribution but also end-groups.

2.2. Copolymerization of Butadiene and 1,1-Diphenylethylene

The effect of changing from a non-polar solvent to a polar one is much more significant on the copolymerization of butadiene with DPE. In non-polar solvents, such as benzene, the copolymerization of butadiene and DPE results in a homopolymer of polybutadiene due to the high r_1 value (54 in benzene)[6] and DPE is almost entirely excluded from the reaction. However, in polar solvents such as THF, the behaviour of these monomers is very different. Yuki *et al*. previously reported a reactivity ratio r_1 = 0.13 in THF and the formation of an almost perfectly alternating copolymer.[6] In the current work a high and low molecular weight copolymer of poly(butadiene-*co*-DPE) were synthesized using THF as the solvent. The composition and molecular weight data for these copolymers are shown in Table 2.3 and Table 2.4 respectively. The

Table 2.4: Monomer reactivity ratios, r_1, for the anionic copolymerization of butadiene and 1,1-diphenylethylene in THF.

Sample	Bd : DPE feed ratio	Solvent	Temp/ °C	Bd : DPE Composition in copolymer (from ^{1}H NMR)	% 1,4-PBd	r_1
PBdD-1	1.04 : 1.00	THF	0	1.05 : 1.00	64	< 0.05
PBdD-2	0.97 : 1.00	THF	0	1.03 : 1.00	64[a]	0.04

[a] Assuming the same 1,4-PBd content as PBdD-1

Table 2.5: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.189) for the anionic copolymerization of butadiene and 1,1-diphenylethylene

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdD-1	40,600	43,400	1.07
PBdD-2	2,100	2,300	1.11

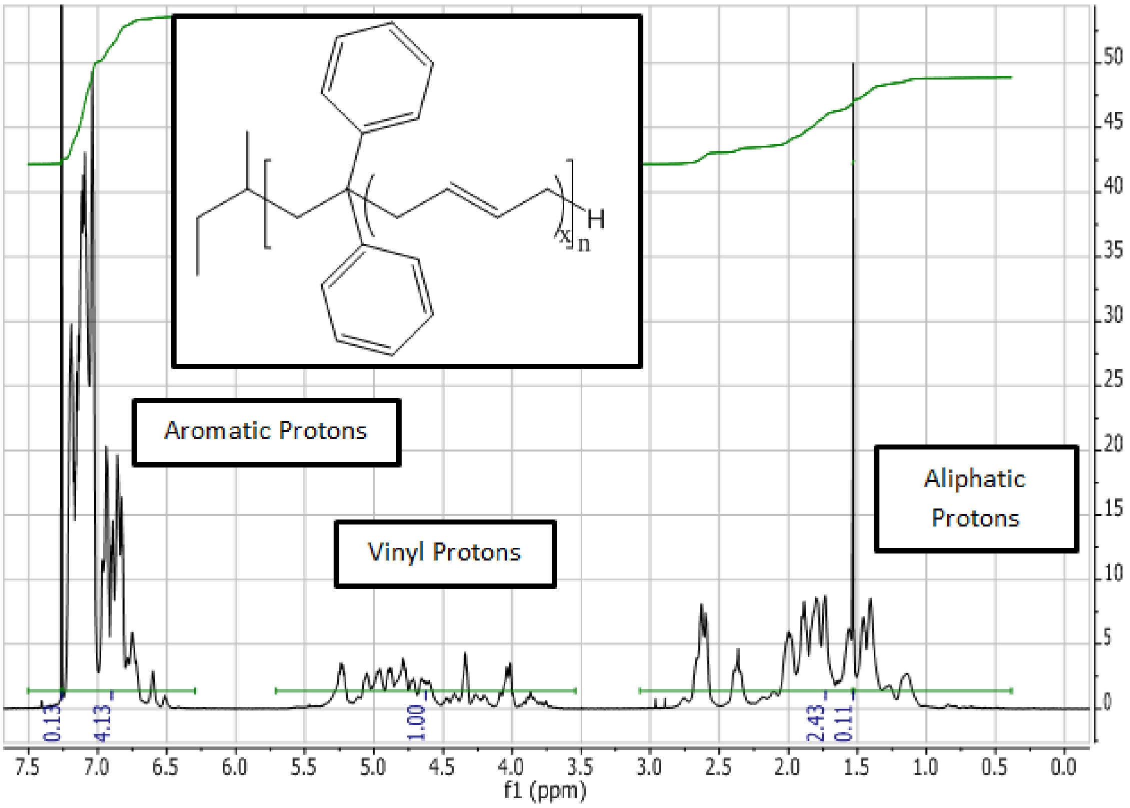

Figure 2.19: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-DPE), PBdD-1, synthesized in THF with a molar feed ratio of 1.04 : 1.00 butadiene : DPE.

composition of these copolymers was determined from high resolution ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum for PBdD-1 synthesized in THF with a 1.04 : 1.00 molar feed ratio of butadiene : DPE is shown in Figure 2.5.

The copolymer composition can be determined by comparing the integrals of the aliphatic protons (0.0 – 2.9 ppm); the alkene protons (3.6 – 5.6 ppm) and the aromatic protons (6.4 – 7.3 ppm). The sharp peak at 7.26 ppm is from the trace of $CHCl_3$ present in $CDCl_3$, and the sharp peak at 1.5 ppm is from H_2O present in $CDCl_3$, both of these have been deconvoluted and subtracted from the integral. If z : y is the ratio of butadiene : DPE present in the copolymer then, as butadiene contains no aromatic protons and DPE contains 10, y can be found from the integral of the aromatic region ($10y$ = 4.00). As 1,2-polybutadiene contains 3 alkene protons and 1,4-polybutadiene contains 2 alkene protons, this leads to the following equation:

$$3z_{1,2} + 2z_{1,4} = 1.00 \tag{2.4}$$

where $z_{1,2}$: $z_{1,4}$ is the ratio of 1,2-polybutadiene : 1,4-polybutadiene (cis, trans) respectively and:

$$z = z_{1,2} + z_{1,4} \tag{2.5}$$

The final equation arises from the aliphatic region, where DPE contributes 2 protons, 1,2-polybutadiene contributes 3 protons and 1,4-polybutadiene contributes 4 protons, such that:

$$2y + 3z_{1,2} + 4z_{1,4} = 2.32 \tag{2.6}$$

Solving these simultaneous equations gives y = 0.40; $z_{1,2}$ = 0.16; $z_{1,4}$ = 0.26 and z = 0.42. This indicates a copolymer composition of butadiene : DPE = 1.05 : 1.00, and a 1,4-polybutadiene content of 62 %. A 62 % 1,4-polybutadiene microstructure is high for polybutadiene when polymerized in THF, and the reason for this will be explained later. As stated earlier, in order to accurately calculate the reactivity ratio r_1, an equimolar or excess molar feed ratio of DPE is required. However, in this reaction butadiene was in a slight molar excess and as a result some butadiene may have been incorporated after complete consumption of DPE. The reactivity ratio will be discussed later but it is therefore possible that the reactivity ratio obtained for PBdD-1 could be slightly overestimated.

It is also possible to calculate the butadiene : DPE ratio using just the alkene and aromatic protons in the ^{1}H NMR spectrum. This requires ascertaining which peaks correspond to 1,2-polybutadiene and which correspond to 1,4-polybutadiene. This was determined by 2D NMR spectroscopy and the spectra are shown in Figures 2.6 – 2.9. The HSQCAD spectrum (Figures 2.6 and 2.7) shows how the ^{13}C NMR spectrum relates to the ^{1}H NMR spectrum (i.e. which protons are bound to which carbon atoms). The red spots represent a CH or a CH_3 group whereas blue spots represent a CH_2 group. Hence the peaks at 3.8 – 4.6 ppm in the ^{1}H NMR spectrum can be assigned to the CH_2 groups on 1,2-polybutadiene ($CH_2CHCH{=}C\mathbf{H_2}$).

The COSY NMR spectrum (Figures 2.8 and 2.9) shows that the 1,2-polybutadiene CH_2 protons (3.8 – 4.6 ppm) couple to a peak at 5.2 – 5.4 ppm which can be assigned to the 1,2-polybutadiene CH group ($CH_2CHC\mathbf{H}{=}CH_2$). Finally the peaks from 4.5 – 5.2 ppm can be assigned as the CH groups on 1,4-polybutadiene ($CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$). Whilst the integral of the 1,2-polybutadiene CH_2 protons should be exactly double that of the 1,2-polybutadiene CH protons, the ratio of 1,2-polybutadiene CH_2 : CH = 2.32 : 1.00 which is probably due to overlapping signals. Using the CH protons to determine the polybutadiene microstructure indicates 62.2 % 1,4-polybutadiene; using the CH_2 protons indicates 64.6 % 1,4-polybutadiene and using an average indicates 63.9 % 1,4-polybutadiene. Hence the PBdD-1 copolymer has a microstructure comprising of approximately 64 % 1,4-polybutadiene, which is in good agreement with the value obtained using equations 2.4 – 2.6. Using the integrals of the alkene region and the aromatic region the butadiene : DPE ratio was calculated as 1.05 : 1.00 which is exactly the same value as that obtained using equations 2.4 – 2.6.

Whilst it was not possible to obtain an accurate ratio of styrene : DPE by ^{1}H NMR spectroscopy for low molecular weight samples of poly(styrene-*co*-DPE) due to contributions from the end-groups, in the case of poly(butadiene-*co*-DPE), PBdD-2, the alkene and aromatic region can be used to determine the DPE content and thereby

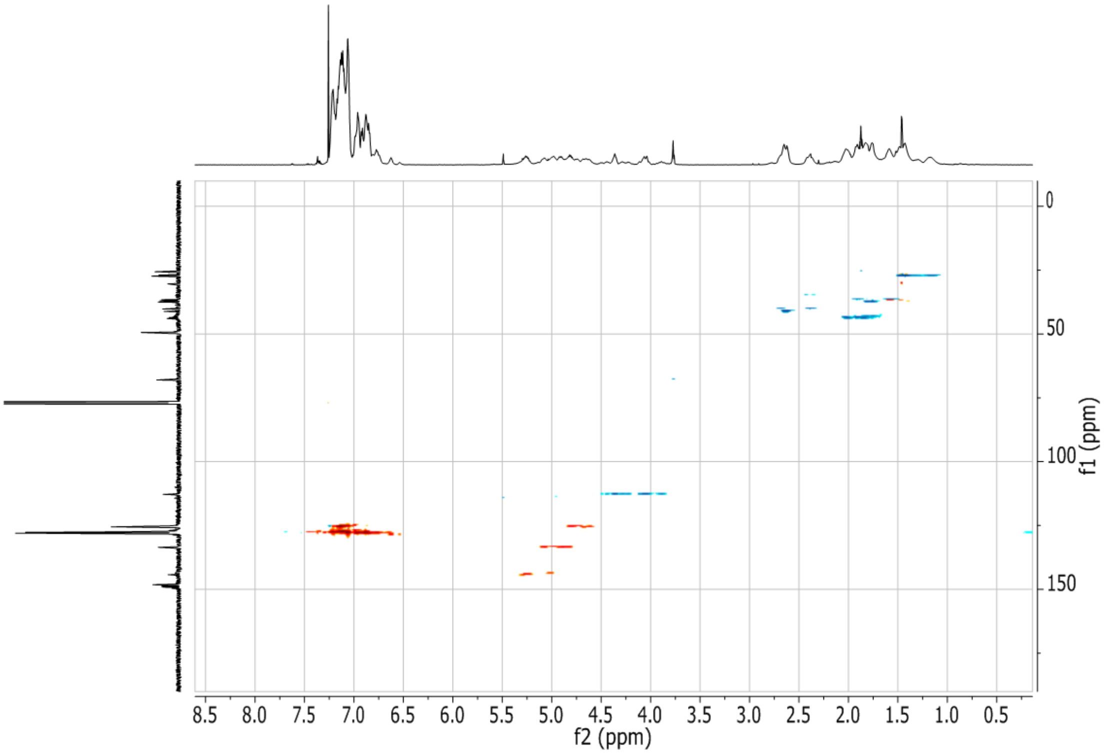

Figure 2.20: HSQCAD NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE), PBdD-1.

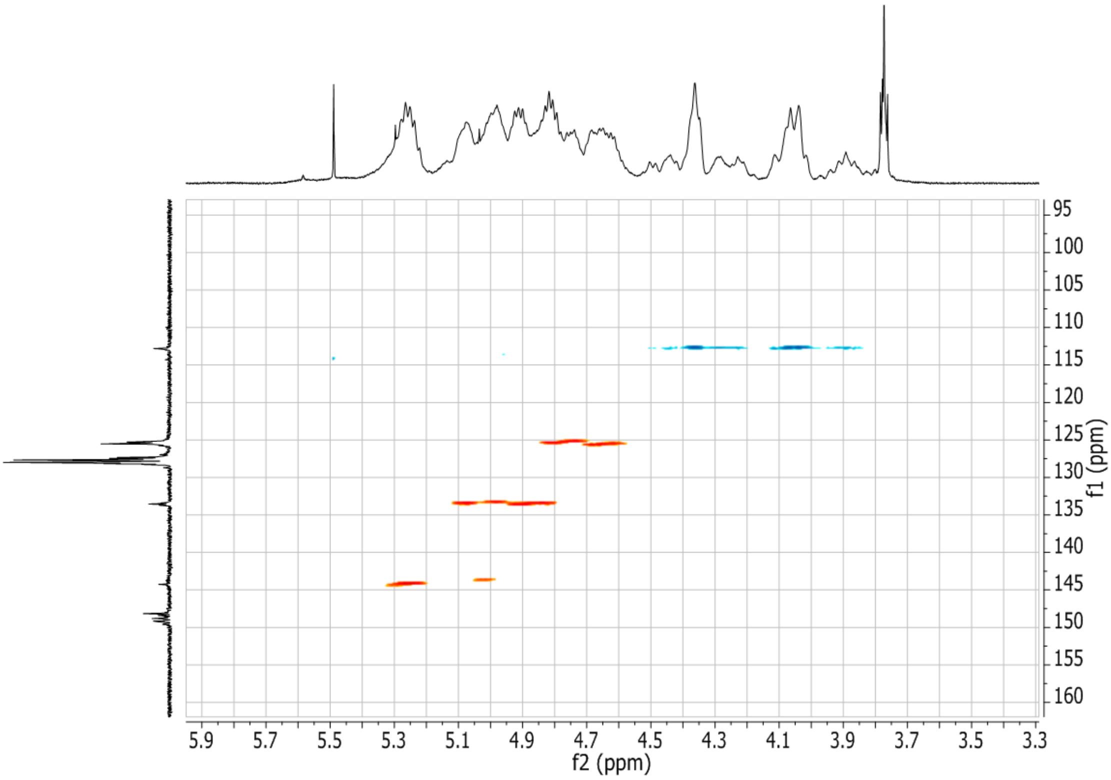

Figure 2.21: HSQCAD NMR spectrum (in $CDCl_3$) of the alkene region of poly(butadiene-*co*-DPE), PBdD-1.

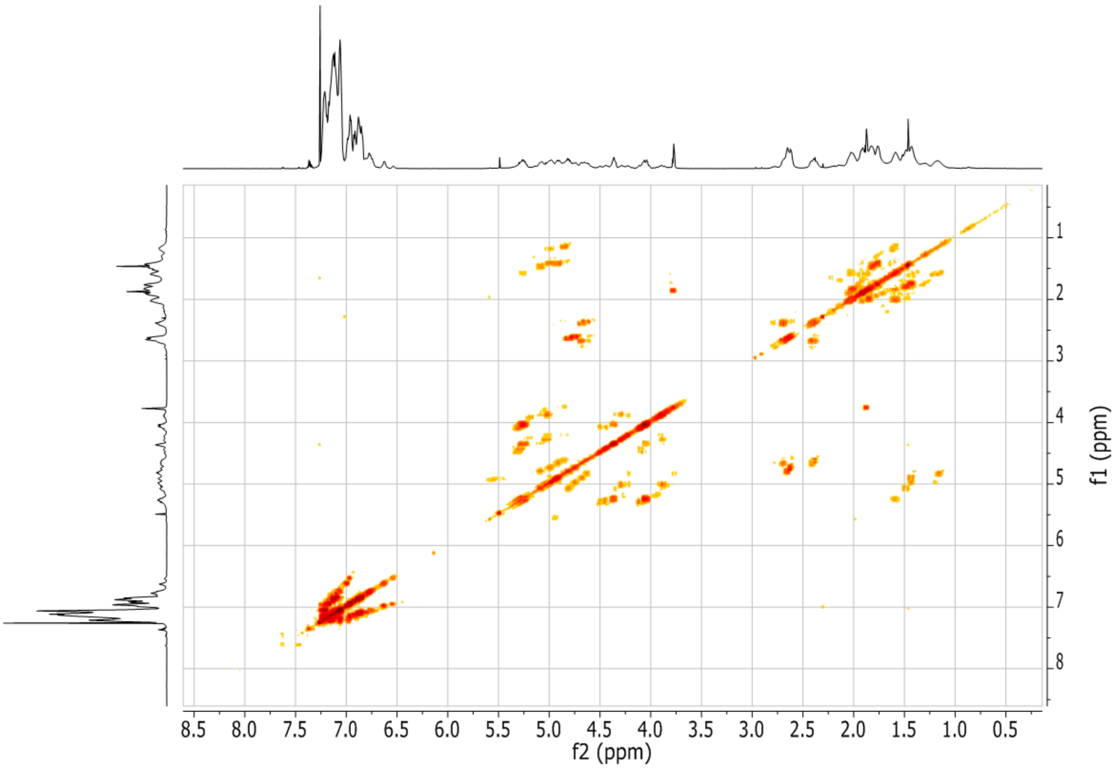

Figure 2.22: COSY NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE), PBdD-1.

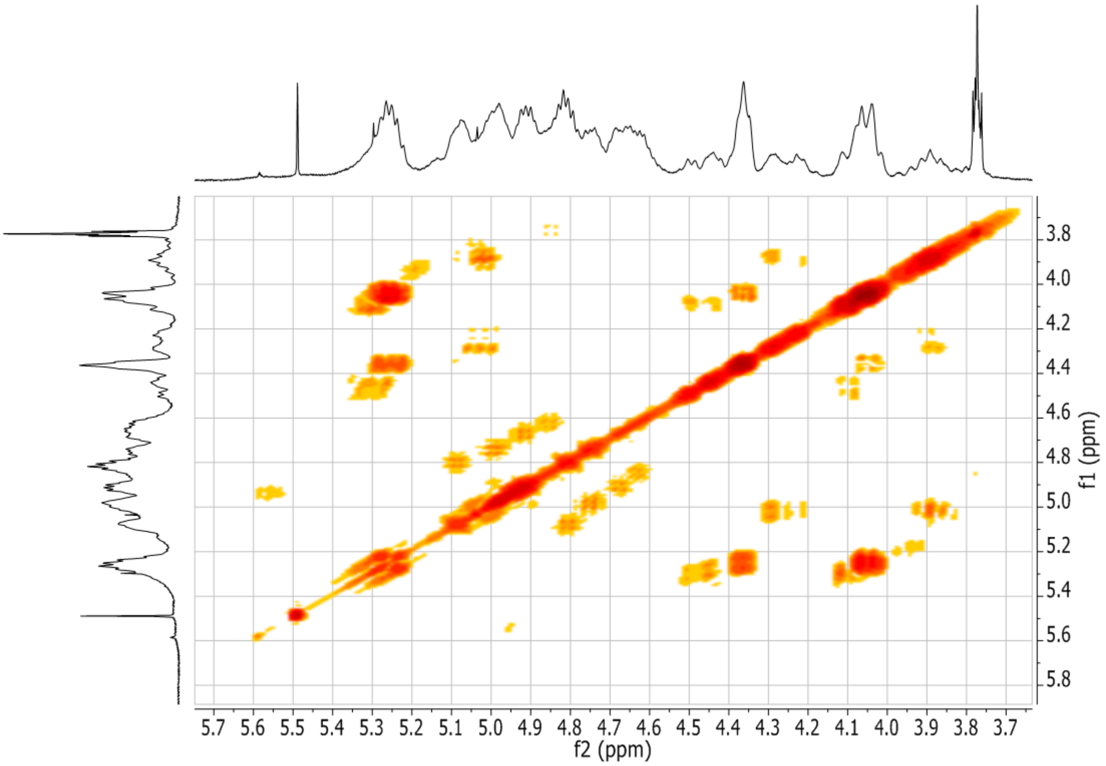

Figure 2.23: COSY NMR spectrum (in $CDCl_3$) of the alkene region of poly(butadiene-*co*-DPE), PBdD-1.

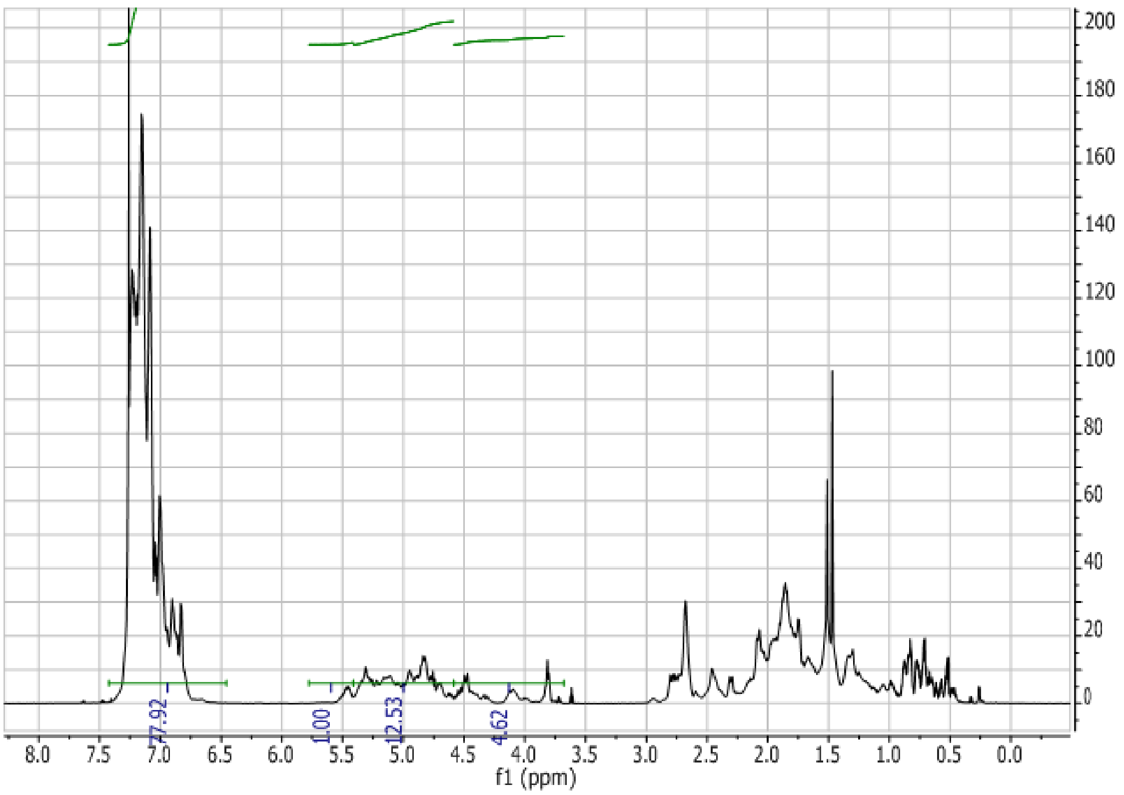

Figure 2.24: ^{1}H NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE), PBdD-2, synthesized in THF with a molar feed ratio of 0.97 : 1.00 butadiene : DPE.

avoid the contribution of the end-groups which occurs in the aliphatic region (Figure 2.10). The peaks in the alkene region are not identical to that of the high molecular weight sample, PBdD-1, as there is now more overlap between the signals. In this case it now appears that the 1,4-polybutadiene protons overlap with both the 1,2-polybutadiene CH and CH_2 signals (Figures 2.11 – 2.14). The butadiene : DPE ratio was therefore estimated to equal 1.03 : 1.00 assuming the same 1,4-polybutadiene content as for PBdD-1 (64 %).

From the butadiene : DPE ratio, determined by ^{1}H NMR spectroscopy, an r_1 value of 0.05 and 0.04 was calculated for PBdD-1 and PBdD-2 respectively. However, the r_1 value calculated for PBdD-1, which used an excess of butadiene monomer with respect to DPE, means it is possible that all the DPE monomer had been consumed before the reaction was completed and this value of r_1 may therefore be an overestimate.

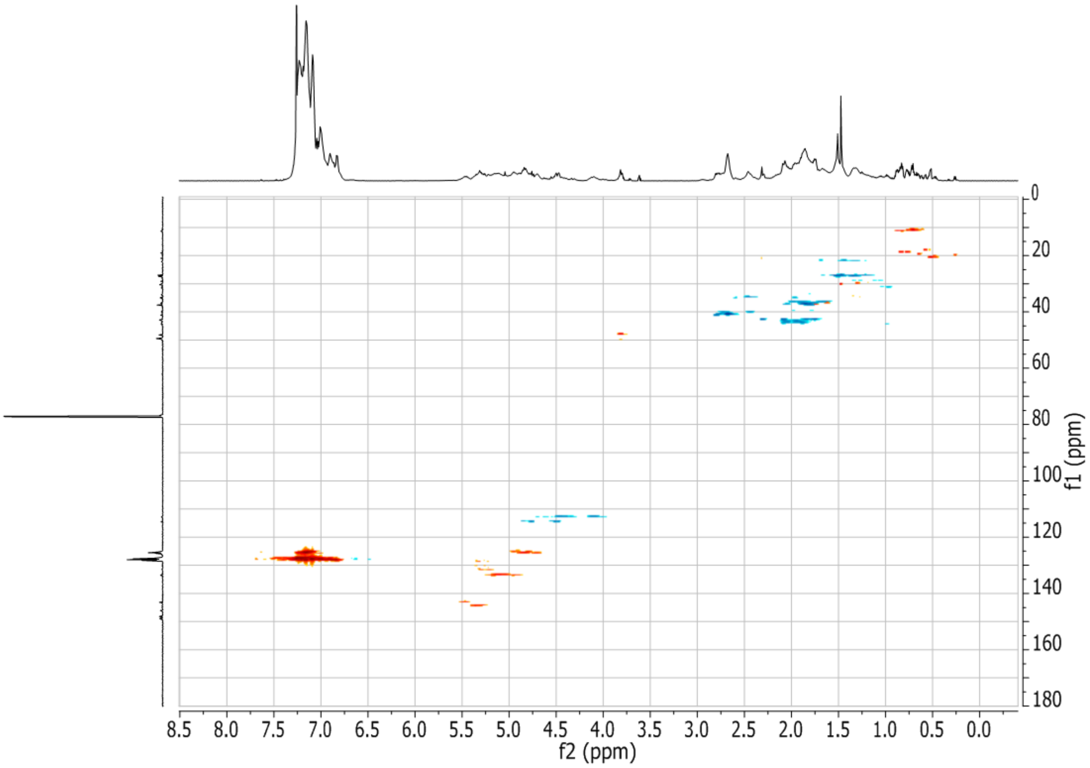

Figure 2.25: HSQCAD NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE), PBdD-2.

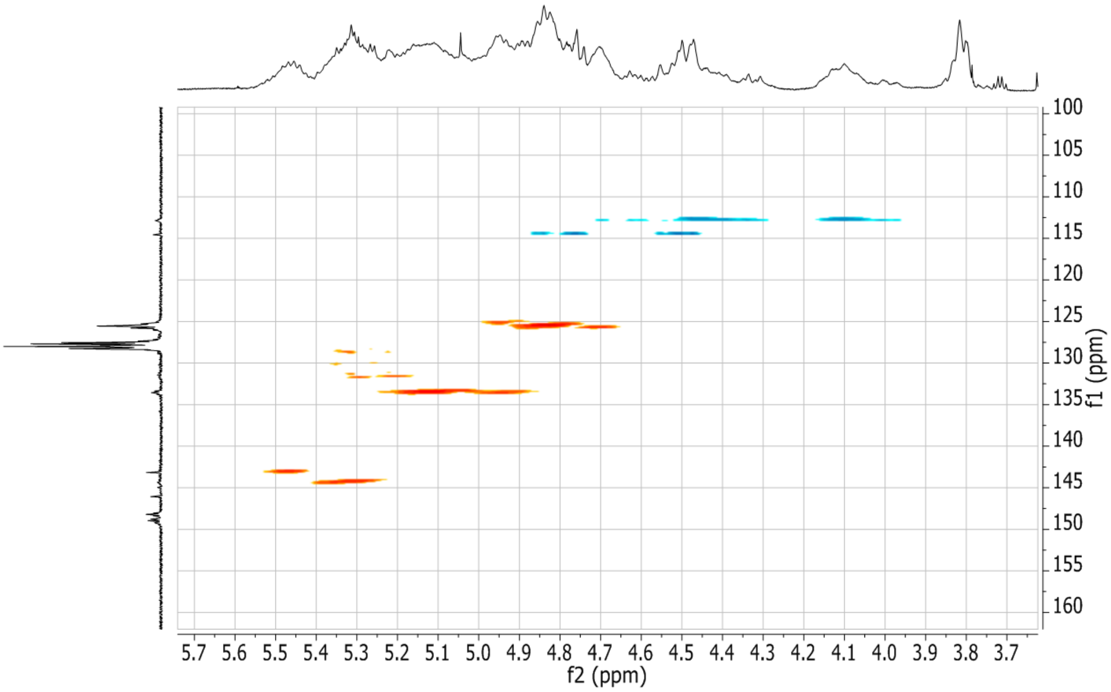

Figure 2.26: HSQCAD NMR spectrum (in $CDCl_3$) of alkene region of poly(butadiene-*co*-DPE), PBdD-2.

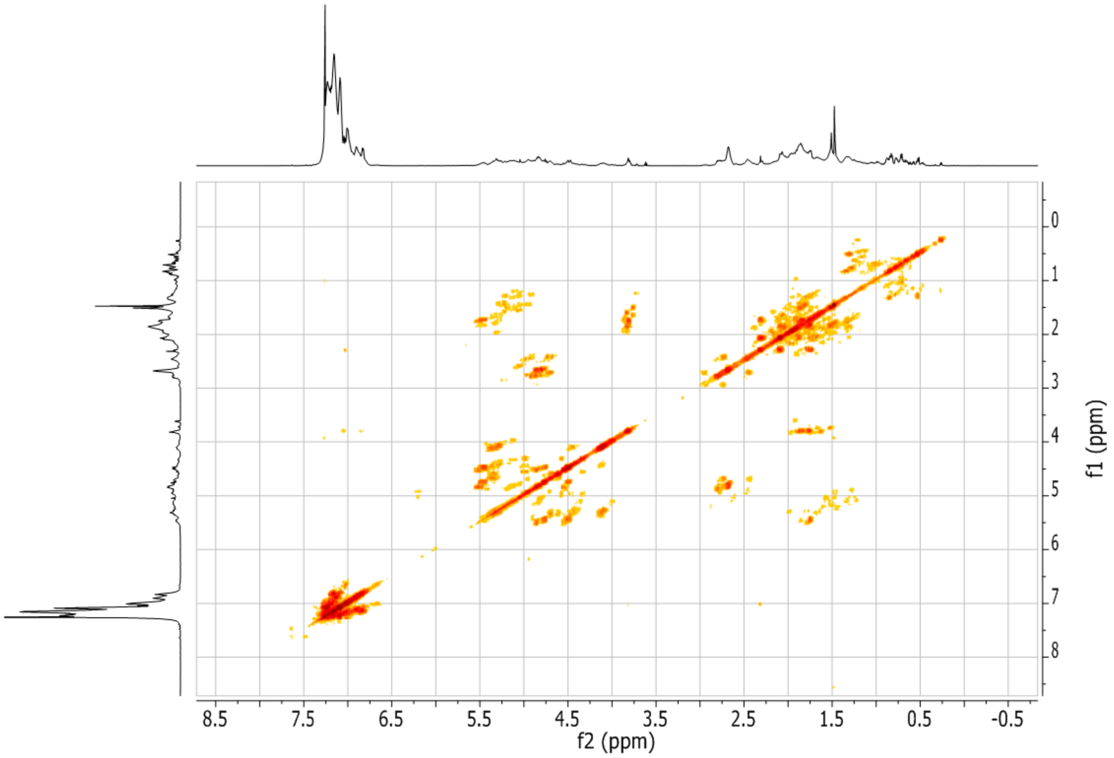

Figure 2.27: COSY NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE), PBdD-2.

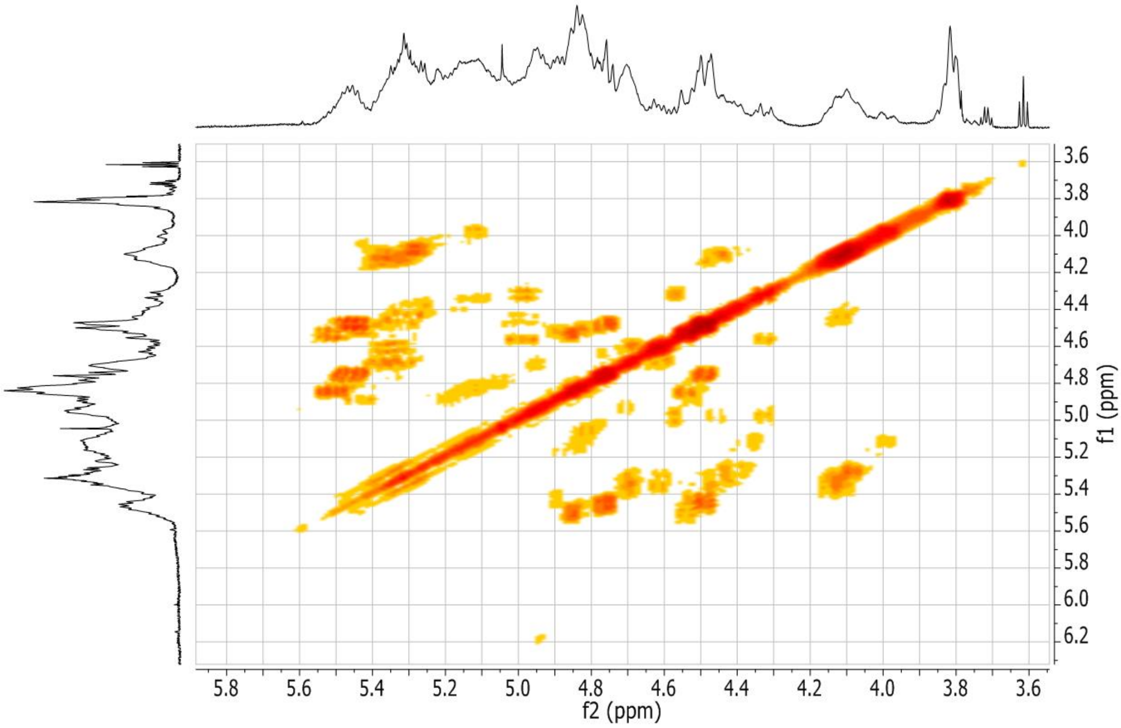

Figure 2.28: COSY NMR spectrum (in $CDCl_3$) of the alkene region of poly(butadiene-*co*-DPE), PBdD-2.

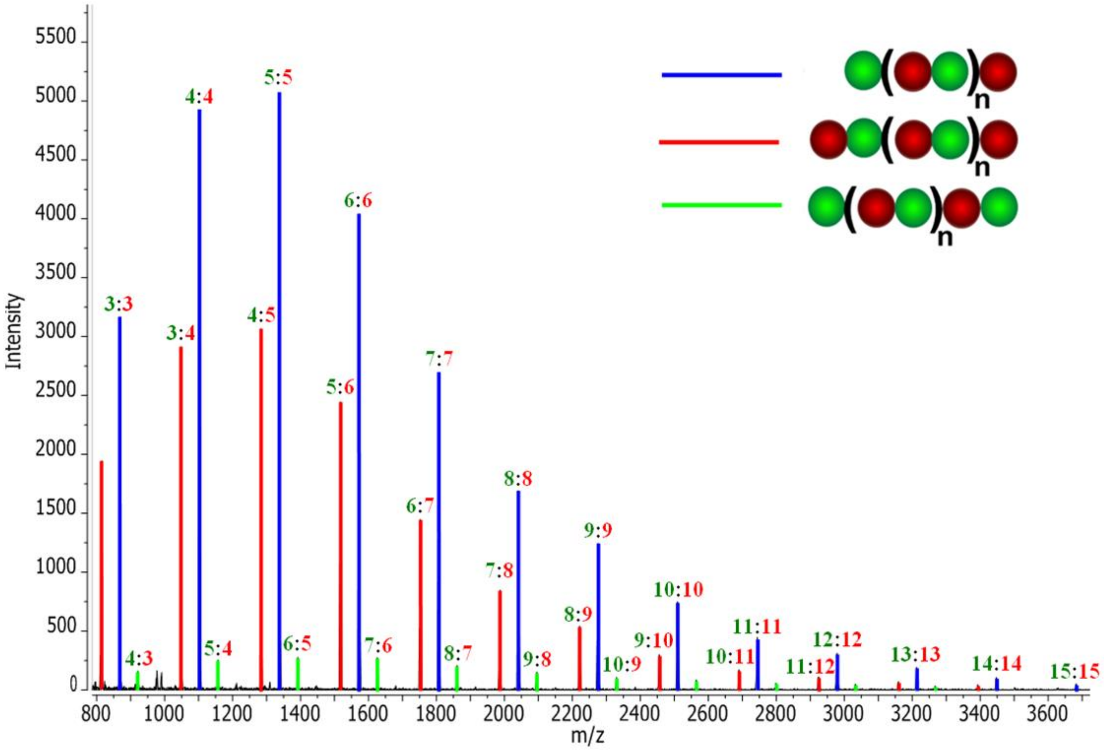

Figure 2.29: MALDI-ToF mass spectrum for the copolymer PBdD-2 prepared by the anionic copolymerization (in THF) of butadiene and DPE (monomer molar feed ratio of butadiene : DPE = 0.97 : 1.00). The mole ratio of butadiene : DPE for any given chain is labelled with butadiene in green and DPE in red.

The MALDI-ToF mass spectrum indicates a perfectly alternating sequence (Figure 2.15) with three distinct distributions of chains, differing only in the nature of the terminal repeat units. In common with the perfectly alternating copolymer of styrene and DPE (Figure 2.4) the MALDI-ToF mass spectrum for butadiene and DPE in THF indicates that the most prevalent distribution is that of chains containing equal numbers of butadiene and DPE units – the blue lines, followed by chains with DPE units at either chain end (the red lines), and finally the least common chains are those with butadiene units at either chain end (the green lines).

A further interesting point is that the P(Bd-*co*-D) copolymer (PBdD-1) prepared in THF contains polybutadiene units with a microstructure comprising 64 % 1,4-PBd whereas a homopolymer of butadiene prepared in THF has a microstructure with nearly 90 % 1,2-enchainment.[14] The anomalously high degree of 1,4 enchainment observed in the nearly alternating P(Bd-*co*-D) copolymer is likely due to the steric crowding caused by the two phenyl groups on DPE when the butadienyl lithium chain end reacts with the

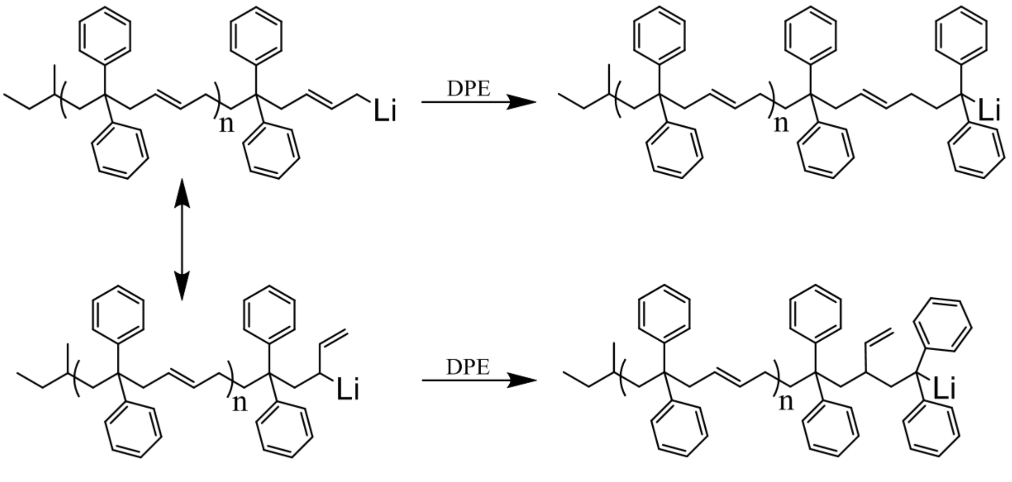

Figure 2.30: Impact of DPE steric crowding upon the microstructure of butadiene units.

incoming DPE monomer. The propagating butadiene chain end can either react via the 2-carbon on the butadiene unit or the 4 carbon. The latter being a primary carbon will experience considerably less steric crowding and will be favoured in spite of the fact that THF usually strongly promotes 1,2-enchainment (Figure 2.16).

2.2.1. Copolymerization of Butadiene and 1,1-Diphenylethylene in Benzene

Dienes, in particular butadiene and isoprene, are very important commercially as the resulting polymers contain cross-linkable alkene functionality and, due to the typically low glass transition temperatures can provide flexible, rubbery polymers.[3, 15-16] Hence these polymers are used for a large variety of different applications such as in tyres, footwear and moulded goods.[3, 15-16] It was hypothesized that the copolymerization of butadiene, styrene and DPE in non-polar solvents would result in a tapered copolymer that is initially rich in butadiene. In order for this terpolymer to have a rubbery butadiene block with a low glass transition temperature, T_g, a low incorporation of both DPE and styrene into the initial butadiene-rich section is required. For this reason the copolymerization of butadiene with DPE in benzene was also investigated in order to determine the extent of incorporation of DPE. Yuki *et al.* used mass balance/yield calculations and ^{1}H NMR analysis to determine that the copolymerization of butadiene and DPE in benzene results in DPE being almost entirely excluded from the reaction ($r_1 = 54$).[6] In the current study the sequence analysis of this copolymerization was explored using MALDI-ToF MS. A low molecular weight copolymer of poly(butadiene-*co*-DPE) was synthesized with a butadiene : DPE molar feed ratio of 3.26 : 1.00 using

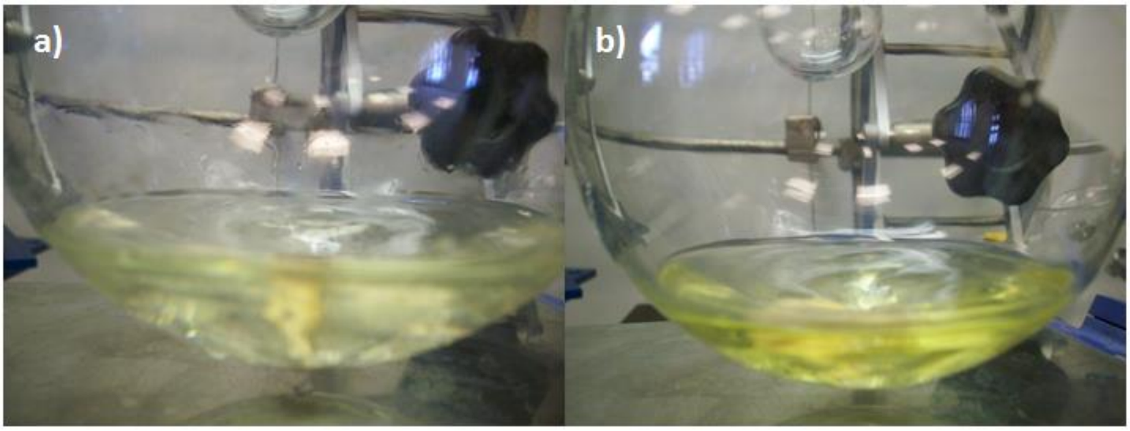

Figure 2.31: Photographs for the copolymerization of butadiene and DPE in benzene, PBdD-3, taken at (a) 1 minute after initiation and (b) 19.7 hours after initiation.

benzene as the solvent. Upon initiation, the reaction mixture became yellow, similar to the colour of the reaction mixture in Figure 2.17b. Within one minute the colour of the reaction faded to a pale yellow colour indicative of butadienyl lithium as shown in Figure 2.17a. The initial darker yellow colour may indicate that *sec*-butyllithium was also reacting with DPE. Indeed it has been reported that when styrene and butadiene are copolymerized in non-polar solvents, butyllithium reacts more rapidly with styrene which is the less reactive monomer.[3] It is therefore quite plausible that *sec*-butyllithium may react preferentially with the styrenic DPE monomer. After 1.9 hours the reaction mixture was still pale yellow at which time a sample was removed (PBdD-3a) for analysis. After approximately 19 hours (Figure 2.17b) the reaction had reverted back to the yellow colour observed upon initiation which may indicate the presence of some diphenylethyl lithium, which will be discussed later. The reaction was stirred for a further 0.7 hours before termination to yield PBdD-3b. A yield of 38 % (based on consumption of both monomers) was obtained, however, it was expected that DPE would be predominantly excluded from the copolymerization, and if the DPE is removed from the yield calculation then the yield of PBdD-3 becomes 81 %. The compositions of PBdD-3a and 3b were determined from high resolution ^{1}H NMR spectroscopy and MALDI-ToF MS. The ^{1}H NMR spectra for PBdD-3a and 3b synthesized in benzene with a 3.26 : 1.00 molar feed ratio of butadiene : DPE are shown in Figures 2.18 and 2.19. The copolymer composition can be determined by comparing the integrals of the alkene protons (4.9 – 5.6 ppm) and the aromatic protons (7.1 – 7.3 ppm).

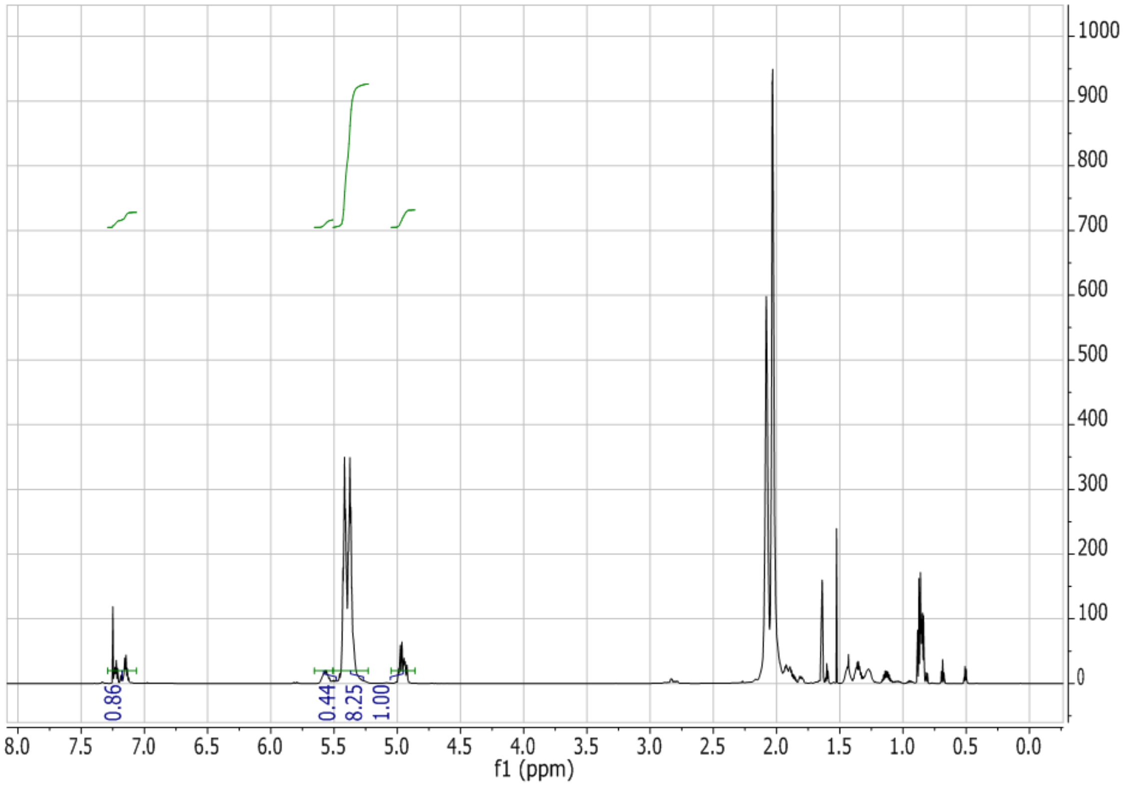

Figure 2.32: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-DPE), PBdD-3a, synthesized in benzene with a molar feed ratio of 3.26 : 1.00 butadiene : DPE and terminated after 1.9 hours.

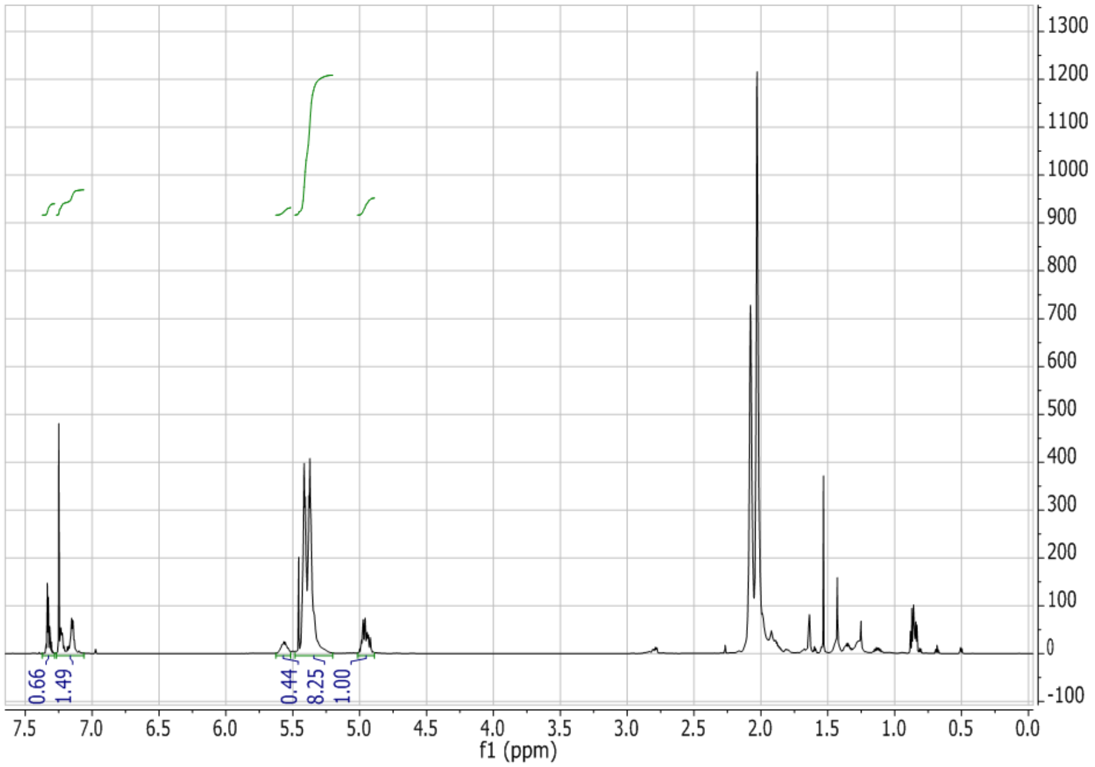

Figure 2.33: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-DPE), PBdD-3b, synthesized in benzene with a molar feed ratio of 3.26 : 1.00 butadiene : DPE and terminated after 19.7 hours.

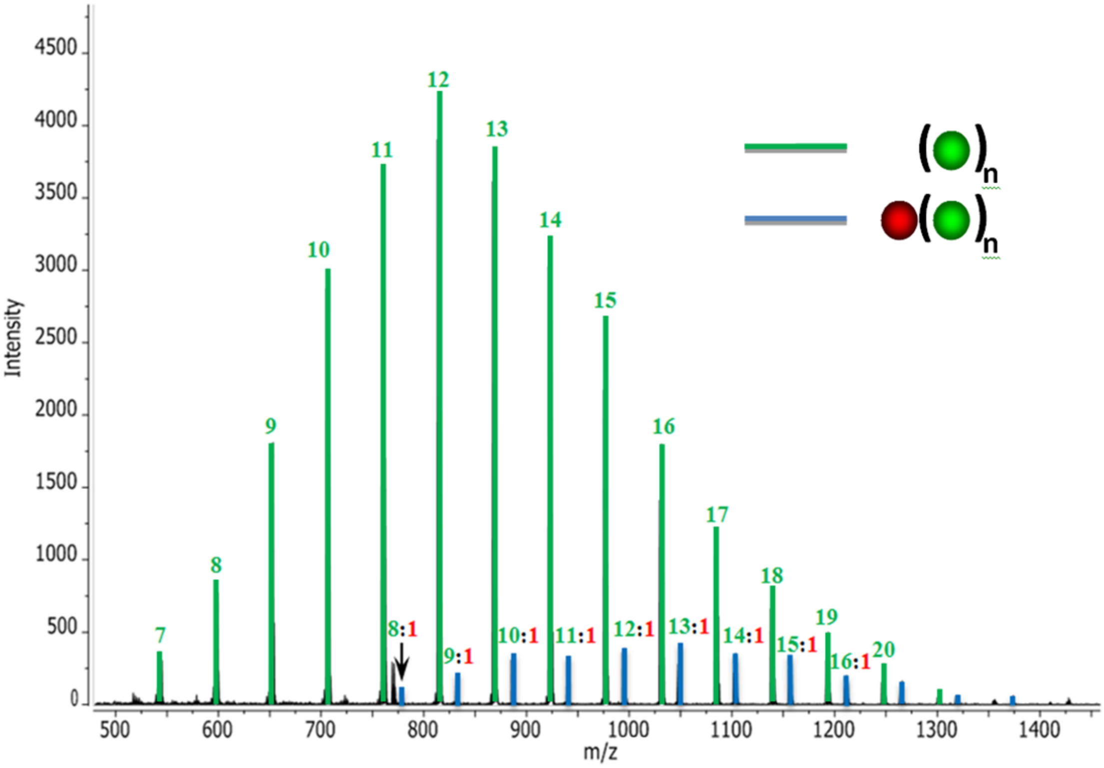

Figure 2.34: MALDI-ToF mass spectrum for the copolymer PBdD-3a prepared by the anionic copolymerization (in benzene) of butadiene and DPE (monomer molar feed ratio of butadiene : DPE = 3.26 : 1.00) after 1.9 hours. The mole ratio of butadiene : DPE for any given chain is labelled with butadiene in green and DPE in red.

The signals corresponding to $CHCl_3$ in Figures 2.18 and 2.19 and those corresponding to DPE monomer in Figure 2.19 (5.47 ppm and 7.31 – 7.37 ppm) were subtracted from the integrals of the aromatic signals (7.1 – 7.3 ppm) and the alkene signals (4.9 – 5.7 ppm) respectively. The ratios of butadiene : DPE were found to be 63.4 : 1.0 and 38.1 : 1.0 for PBdD-3a and PBdD-3b respectively. In both cases the 1,4-polybutadiene content was 89 %. The MALDI-ToF mass spectrum (Figure 2.20) of PBdD-3a shows that only a few chains contain a single DPE unit (highlighted as blue lines), whilst the vast majority of chains contain only butadiene (highlighted as green lines). As the reaction mixture was a more intense yellow colour at the start of the reaction, this may suggest that the single unit of DPE present in some chains was incorporated at the start of the reaction due to *sec*-butyl lithium reacting with the DPE monomer in preference to butadiene. Regardless, both the ^1H NMR spectrum and the MALDI-ToF MS analysis suggest that the overwhelming majority of chains correspond to polybutadiene homopolymer. Figure 2.21 shows the results of the MALDI-ToF mass spectrum of PBdD-3b after 19.7 hours of the polymerization. In this case the peaks corresponding to chains containing one unit of DPE (highlighted in blue) are much more

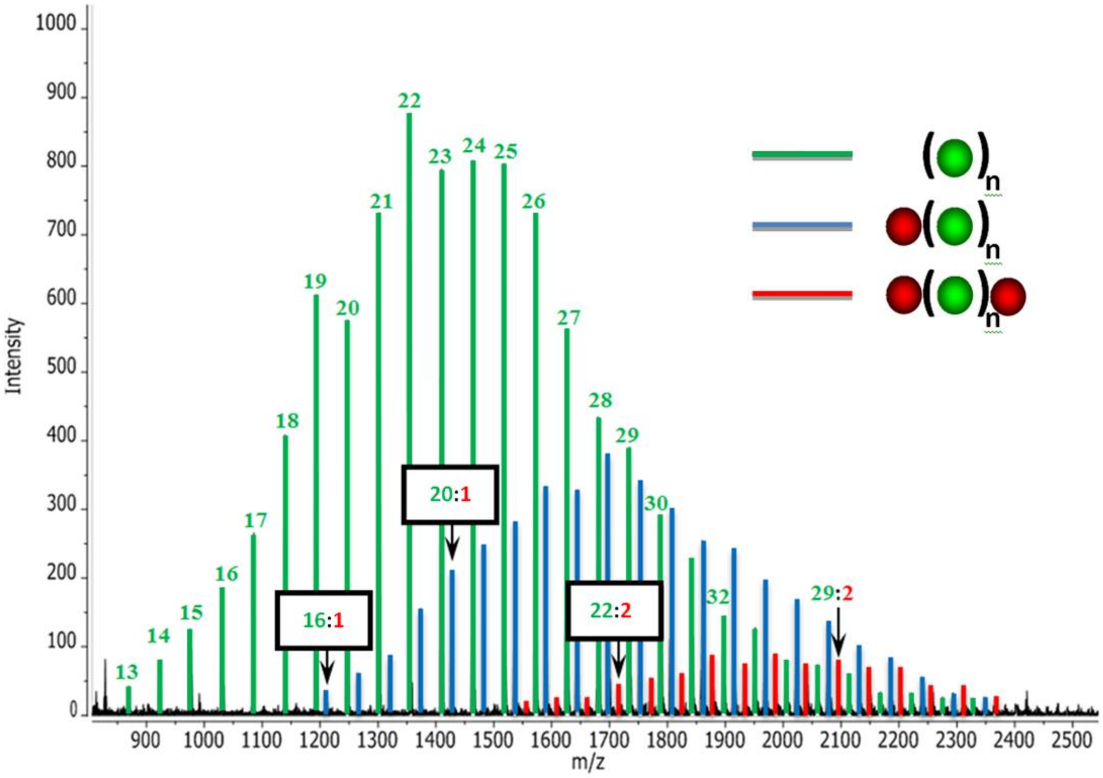

Figure 2.35: MALDI-ToF mass spectrum for the copolymer PBdD-3b prepared by the anionic copolymerization (in benzene) of butadiene and DPE (monomer molar feed ratio of butadiene : DPE = 3.26 : 1.00) after 19.7 hours. The mole ratio of butadiene : DPE for any given chain is labelled with butadiene in green and DPE in red.

intense than in Figure 2.20 and there are some chains with 2 units of DPE (highlighted in red). This is likely due to the fact that once all the butadiene has been consumed the only remaining monomer is DPE, and therefore the only possible reaction is for any living polybutadienyl chains to react with DPE and effectively end-cap the polymer. The ^{1}H NMR spectra and MALDI-ToF mass spectra are consistent with the reactivity ratio, r_1, found by Yuki *et al*. of 54.[6] Indeed there are 63 units of butadiene per unit of DPE in the first sample and 38 units of butadiene per unit of DPE in the final sample but the final sample is likely to be skewed by the end-capping of the polymer chains with unreacted DPE.

2.3. Monte Carlo Simulations of MALDI-ToF Mass Spectra

It is possible to run a simulation of a living polymerization and therefore simulate the MALDI-ToF mass spectrum. The program Initiator[17] was used to simulate MALDI-ToF mass spectra corresponding to the actual poly(styrene-*co*-DPE) and poly(butadiene-*co*-DPE) copolymers analysed by MALDI-ToF MS in Sections 2.1 and 2.2. The parameters that are entered into the program are the number of initiator molecules; the volume of solvent; the moles of the initiator; the moles of both monomers; the formula and length (i.e. number of bonds built into the main chain) of the initiator and monomers; the monomer reactivity ratios and the reactivity preference (reactivity ratio) of the initiator for each monomer. To simulate the MALDI-ToF mass spectrum of PSD-5 (i.e. the copolymerization of styrene and DPE in benzene with a styrene : DPE molar feed ratio of 0.97 : 1.00) 1000 initiator molecules (i.e. 1000 chains); 50 ml of solvent; 0.0035 moles of initiator; 0.0186 moles of styrene; 0.0192 moles of DPE and a reactivity ratio of r_1 = 0.5 were used with no preference of *sec*-butyl lithium for either monomer. The simulation of the MALDI-ToF mass spectrum is shown in Figure 2.22a. Whilst there are some similarities between the simulation and experimental data, such as the same sequences appearing in both spectra, the simulated data has more peaks present, and generally a wider range of sequences. As the experimental data was performed on a sample that had been precipitated into methanol, it is likely that some lower molecular weight chains may have been lost during precipitation. Furthermore the differences in the high m/z region could be a result of the sensitivity of MALDI-ToF MS diminishing at higher molecular weights; hence the difference between simulated and experimental data may be a consequence of the experimental limitations. The other significant difference between the two spectra is that the simulated data predicts a much higher contribution from the sequence corresponding to styrene : DPE = n : n+1. There are a number of possible reasons why the experimental data is different in this respect. For example the *sec*-butyllithium might exert a preference in reactivity towards styrene over DPE. Alternatively MALDI-ToF MS may result in preferential ionization of various sequences or finally, the difference may arise if the experimental polymerization was terminated prior to the end-capping of any polystyryl lithium with residual DPE monomer in contrast to the simulation which was run until every possible monomer had been consumed.

Figure 2.23a shows a simulation of PSD-6 using 1000 initiator molecules; 65 ml of solvent; 0.00406 moles of initiator; 0.0213 moles of styrene; 0.0329 moles of DPE; a reactivity ratio of r_1 = 0.5 and no preference of *sec*-butyllithium for either monomer. Similarly to the previous simulation, the sequence of styrene : DPE = n : n+1 appears to

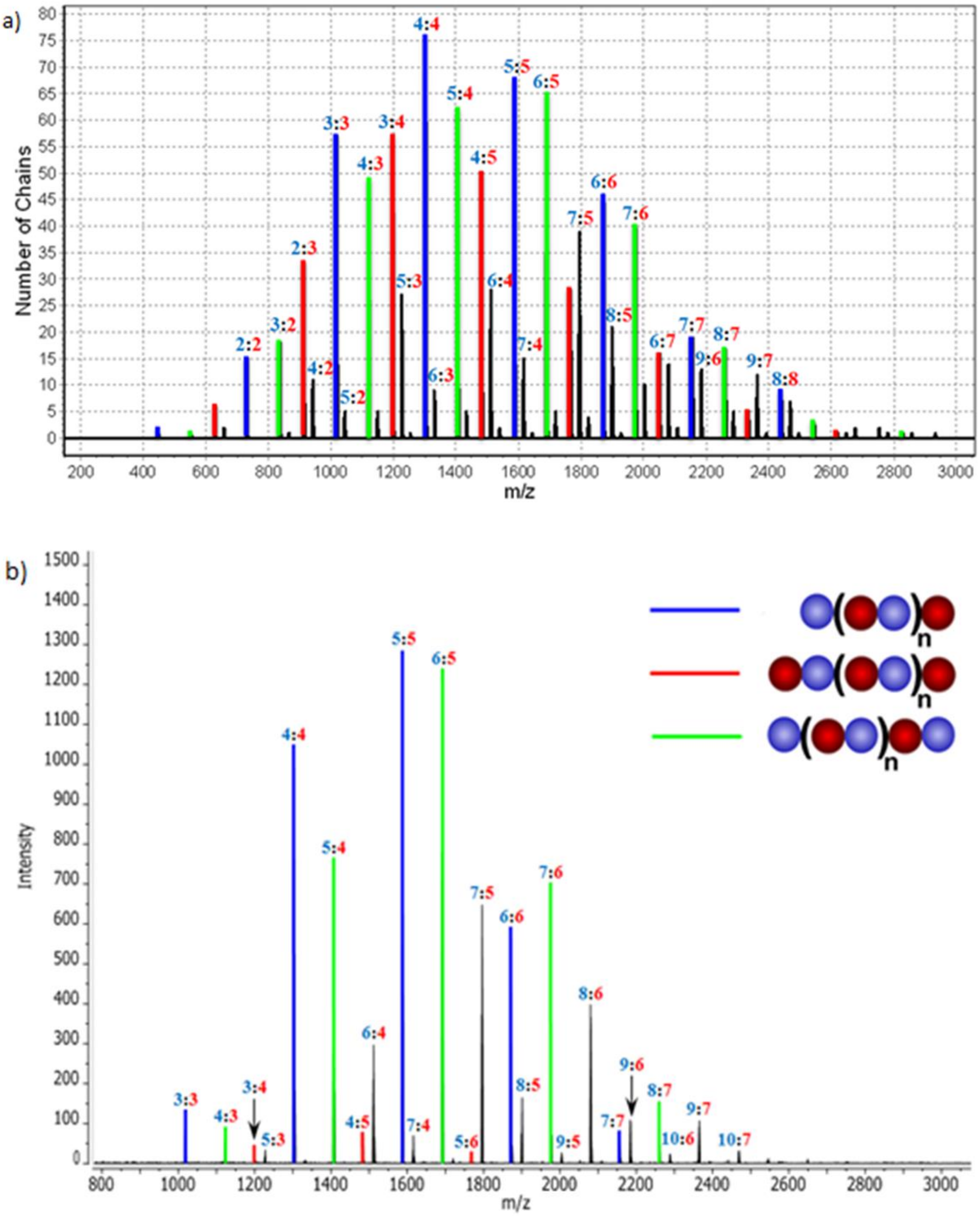

Figure 2.36: (a) Simulated versus (b) experimental MADLI-ToF data for the copolymer PSD-5 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 0.97 : 1.00). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

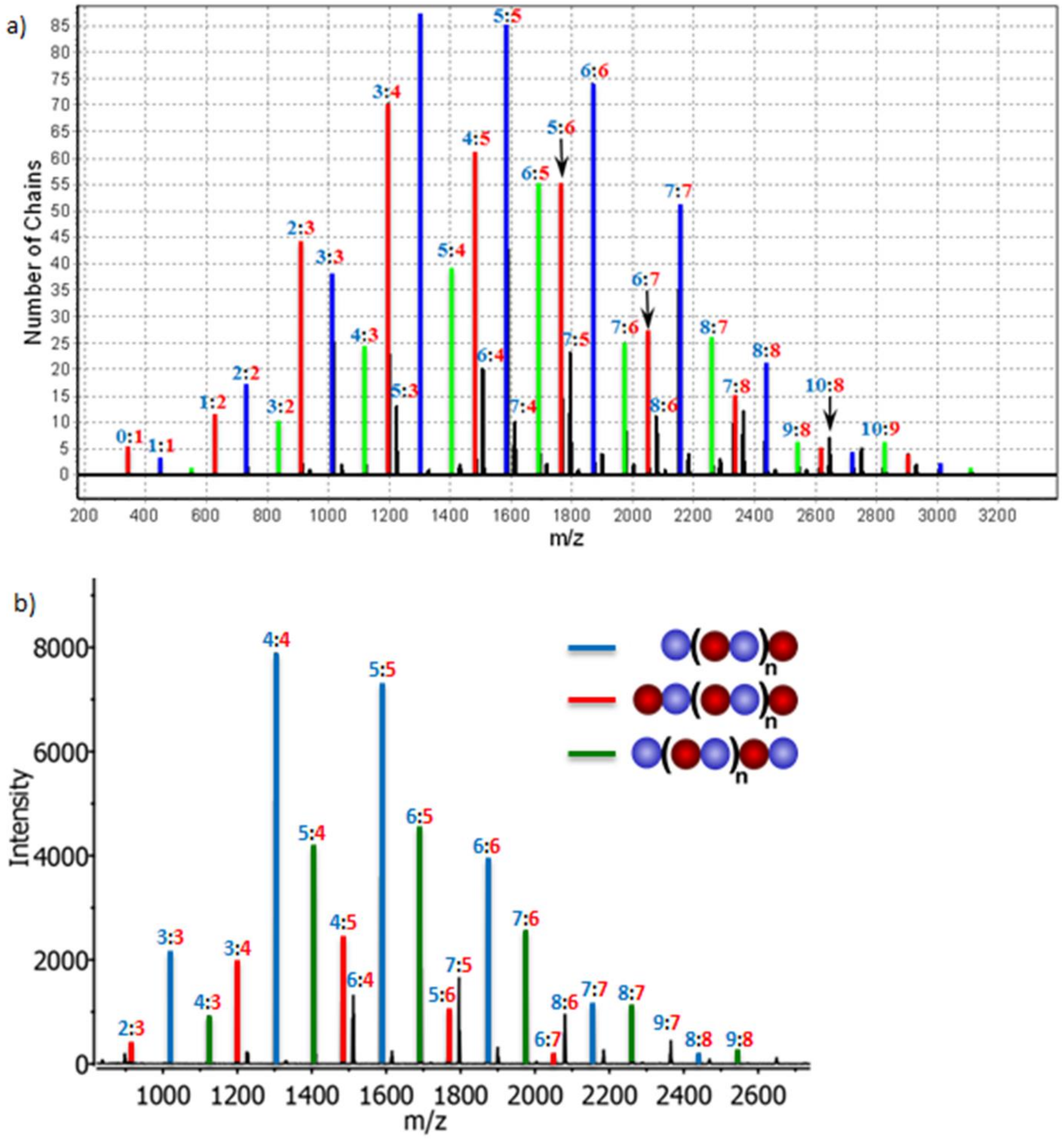

Figure 2.37: (a) Simulated versus (b) experimental MADLI-ToF data for the copolymer PSD-6 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 0.65 : 1.00). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

be too much in abundance compared to experimental data. However, the other sequences all appear in approximately the right ratios.

The simulation of the copolymerization of butadiene and DPE which was carried out in THF, PBdD-2, (Figure 2.24) was run using 1000 initiator molecules; 50 ml of solvent; 0.00504 moles of initiator; 0.0240 moles of butadiene; 0.0247 moles of DPE; a reactivity ratio of r_1 = 0.05 and no preference of *sec*-butyllithium for either monomer.

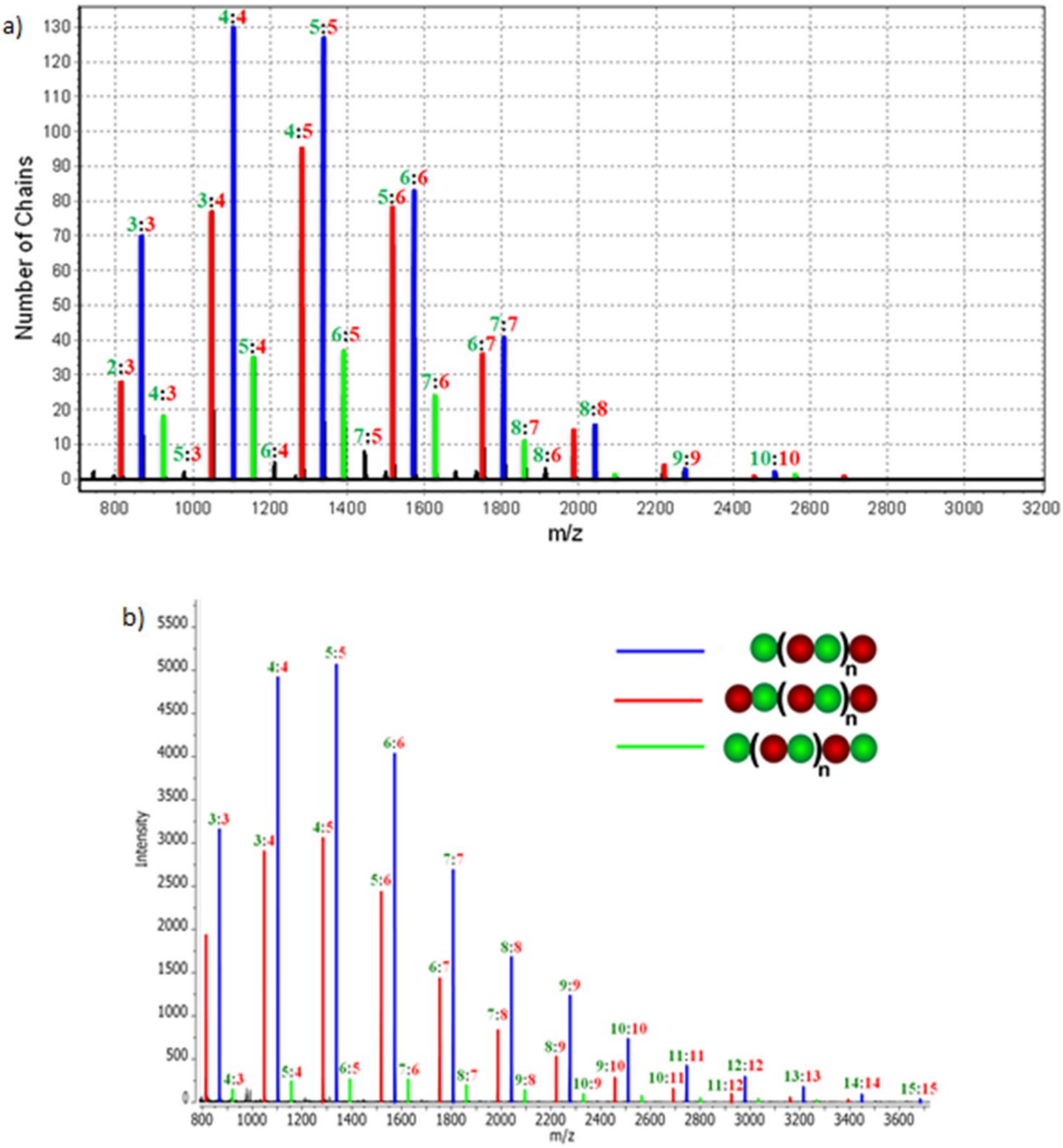

Figure 2.38: (a) Simulated versus (b) experimental MADLI-ToF data for the copolymer PBdD-2 prepared by the anionic copolymerization (in THF) of butadiene and DPE (monomer molar feed ratio of butadiene : DPE = 0.97 : 1.00). The mole ratio of butadiene : DPE for any given chain is labelled with butadiene in green and DPE in red.

In this case the experimental data indicates a much more alternating sequence than that obtained by the simulation, even with a reactivity ratio r_1 of 0.05. The simulated data contains some chains containing imperfect alternating sequences whilst the experimental data only contains perfectly alternating sequences. This is most likely due to *sec*-butyllithium having a preferential reactivity with DPE over butadiene. Regardless of these few differences, in the case of poly(butadiene-*co*-DPE) the resulting simulation is very close to that obtained experimentally. These simulations are part of an on-going comprehensive study which includes an investigation into initiator preferences, the results of which will be published elsewhere.

2.4. Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene

The simultaneous terpolymerization of styrene, butadiene and DPE under various conditions was investigated with the aim of preparing a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE). It has been shown earlier (see Section 2.1) that styrene and DPE can copolymerize in non-polar solvents, and if DPE is in molar excess, then the sequences can be driven to be nearly alternating. It is also well-known that during the copolymerization of styrene and butadiene in non-polar solvents, butadiene will preferentially undergo homopolymerization, with significant incorporation of styrene only occurring upon depletion of the butadiene monomer.[18] This type of copolymer is termed a tapered or gradient copolymer and in this case consists of a butadiene rich block; a middle block which is initially butadiene-rich with a gradual increase in styrene until it becomes rich in styrene; and a final block which is predominantly styrene. These copolymers are statistical and the length of the tapered section will vary depending on the composition. It is also known that DPE will be almost entirely excluded from a copolymerization with butadiene in non-polar solvents,[6] hence it was hypothesized that if styrene, butadiene and DPE were copolymerized in a non-polar solvent, such as benzene, then butadiene would initially homopolymerize before crossing over to styrene and DPE to form a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE). This would allow control over the sequence in a terpolymerization using monomer reactivity ratios and herein will be described as a ‘fire and forget’ approach. Furthermore a styrene-*co*-DPE block would have a higher T_g than a styrenic block which would allow this glassy block to maintain good mechanical properties up to higher temperatures and therefore extend the operating temperature range of the polymer (see Chapter 3). This is beneficial for a wide range of applications such as thermoplastic elastomers, hot melt adhesives, in tyres, footwear and mechanical goods.[3]

It is, of course, possible to prepare a copolymer of polybutadiene-*block*-poly(styrene-*co*-DPE) by the sequential addition of monomers which is the generally accepted approach and is commonly used in industry. In this case, as the rate of crossover from polystyryllithium to butadiene is faster than that of polybutadienyllithium to styrene, it is preferable to polymerize the styrene and DPE first and then add butadiene. The reason for this is that the rate of crossover needs to be at least competitive with the rate of propagation of the next monomer to ensure the second block grows uniformly to prevent broadening of the molecular weight distribution and therefore ensure a lower dispersity. There are only three reported examples of poly(styrene-*co*-DPE)-*block*-polybutadiene in the literature,[19-21] and one of poly(styrene-*co*-DPE)-block-polyisoprene,[22] and in each case they were prepared by the sequential addition of the diene monomer. The 'fire and forget' approach in which all three monomers are simultaneously copolymerized, is however, a much more facile approach, easily scalable, with obvious potential benefits for industrial production. Moreover, the resulting statistical copolymers may have similar properties to a traditional block copolymer. In the next section both of these synthetic routes is investigated.

2.4.1. Copolymerization in Benzene of Styrene and 1,1-Diphenylethylene followed by the Sequential Addition of Butadiene

A series of block copolymers were prepared in two steps. Firstly styrene and DPE were simultaneously copolymerized followed by the addition of butadiene to prepare a second block. The composition of these copolymers was determined by ^{1}H NMR spectroscopy (Table 2.5) and the molecular weight of these copolymers was determined by SEC (Table 2.6). The ^{1}H NMR spectrum of P(SD)-PBd-3, a P(S-*co*-D)-*b*-PBd copolymer, with a 1.00 : 1.55 : 2.36 molar feed ratio of styrene : DPE : butadiene is shown in Figure 2.25. The peaks at 4.9 – 5.0 ppm; 5.1 – 5.5 ppm and 5.5 – 5.6 ppm are characteristic of the alkene groups of polybutadiene (1,2-PBd CH=C**H₂**; 1,4-PBd C**H**=C**H** and 1,2-PBd C**H**=CH$_2$ respectively),[23] and the peak at 2.0 – 2.2 ppm corresponds to the CH$_2$ groups of the polybutadiene backbone. The composition can then be determined using the intensity of the integrals of these alkene peaks relative to the integrals of the aromatic peaks. If x : y : z is the ratio of styrene : DPE : butadiene in the resulting copolymer, then as a sample of the initial poly(styrene-*co*-DPE) block was extracted prior to the addition of butadiene (Figure 2.1) the ratio of styrene : DPE (x : y) is known from this first block to be 1.18 : 1.00, which provides the following equation:

$$x = 1.18y \qquad [2.7]$$

As the aromatic signals are comprised of 10 protons from DPE and 5 from styrene, this leads to the equation:

$$5x+10y=52.4 \qquad [2.8]$$

where 52.4 is the integral of the aromatic signal (after the integral of $CHCl_3$ has been subtracted). Substituting equation 2.7 into 2.8 gives y = 3.30 and x = 3.89. The value of z can be obtained from the total amount of 1,4-polybutadiene ($z_{1,4}$) and 1,2-polybutadiene ($z_{1,2}$), i.e. $z = z_{1,4} + z_{1,2}$. An average for the content of 1,2-PBd can be obtained from the two signals at 4.9 – 5.0 ppm and 5.5 – 5.6 ppm:

$$z_{1,2}=\frac{\frac{2.21}{2}+1.00}{2}=1.05 \qquad [2.9]$$

The 1,4-PBd content is then found from the signal at 5.1 – 5.5 ppm:

$$z_{1,4}=\frac{19.78}{2}=9.89 \qquad [2.10]$$

Table 2.6: Composition of poly(styrene-*co*-DPE)-*b*-polybutadiene copolymers synthesized by the sequential addition of butadiene in benzene.

Sample	Sty : DPE : Bd feed ratio	Temp/ °C	Sty : DPE : Bd Composition in copolymer (from ^{1}H NMR)	% 1,4-PBd
P(SD)-PBd-1	1.00 : 0.67 : 4.39	RT	1.00 : 0.50 : 3.93	90
P(SD)-PBd-2	1.00 : 1.03 : 1.70	50	1.00 : 0.73 : 1.63	89
P(SD)-PBd-3	1.00 : 1.55 : 2.36	50	1.00 : 0.85 : 2.28	89
P(SD)-PBd-4	1.00 : 1.03 : 5.33	50	1.00 : 0.73 : 4.76*	89
P(SD)-PBd-5	1.00 : 1.54 : 4.42	50	1.00 : 0.85 : 4.70*	88
P(SD)-PBd-6	1.00 : 1.57 : 11.7	25	1.00 : 0.85 : 14.29*	90
P(SD)-PBd-7	1.00 : 1.58 : 11.3	25	1.00 : 0.85 : 10.89*	90
P(SD)-PBd-8	1.00 : 1.60 : 8.01	25	1.00 : 0.85 : 7.78*	89

* Styrene : DPE ratio determined from previous experiments

Table 2.7: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(styrene-co-DPE)-b-polybutadiene copolymers synthesized by the sequential addition of butadiene in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
P(SD)-PBd-1	16,800	17,800	1.06
P(SD)-PBd-2	16,100	17,800	1.10
P(SD)-PBd-3	66,600	71,100	1.07
P(SD)-PBd-4	3,300	3,500	1.07
P(SD)-PBd-5	3,600	4,400	1.08
P(SD)-PBd-6	97,900	102,000	1.04
P(SD)-PBd-7	49,500	53,400	1.08
P(SD)-PBd-8	135,500	142,200	1.05

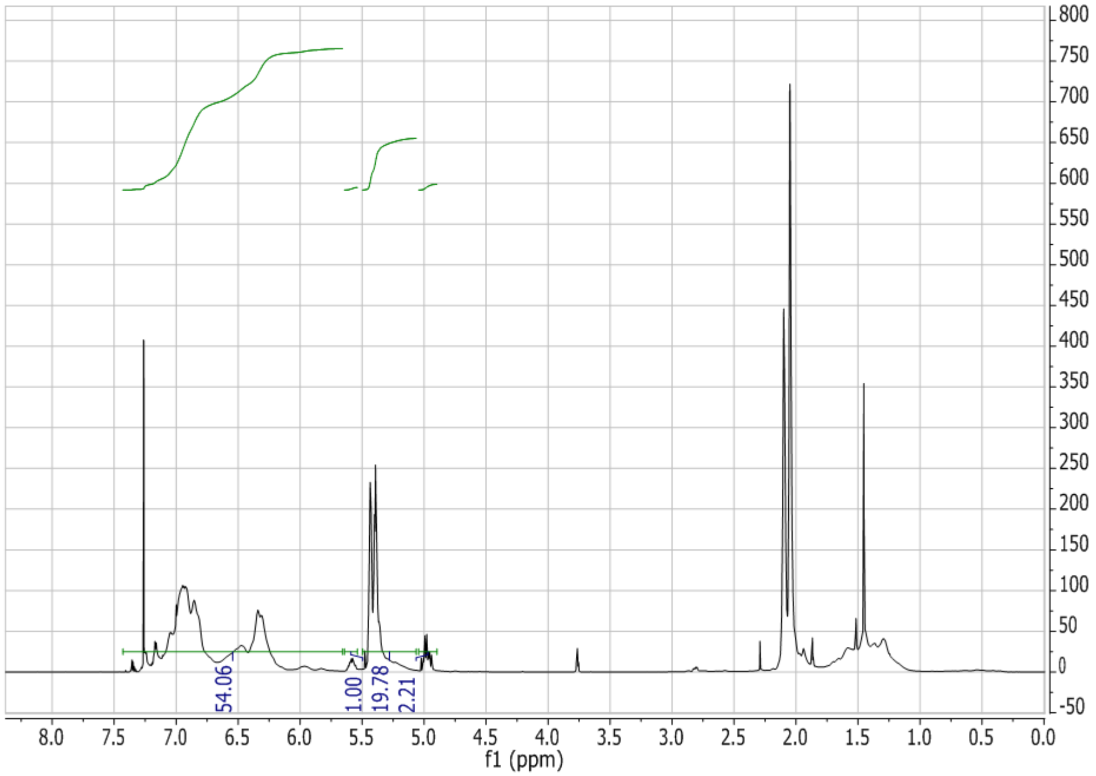

Figure 2.39: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(styrene-*co*-DPE)-*block*-polybutadiene, P(SD)-PBd-3, sequentially synthesized in benzene with a molar feed ratio of 1.00 : 1.55 : 2.36 styrene : DPE : butadiene.

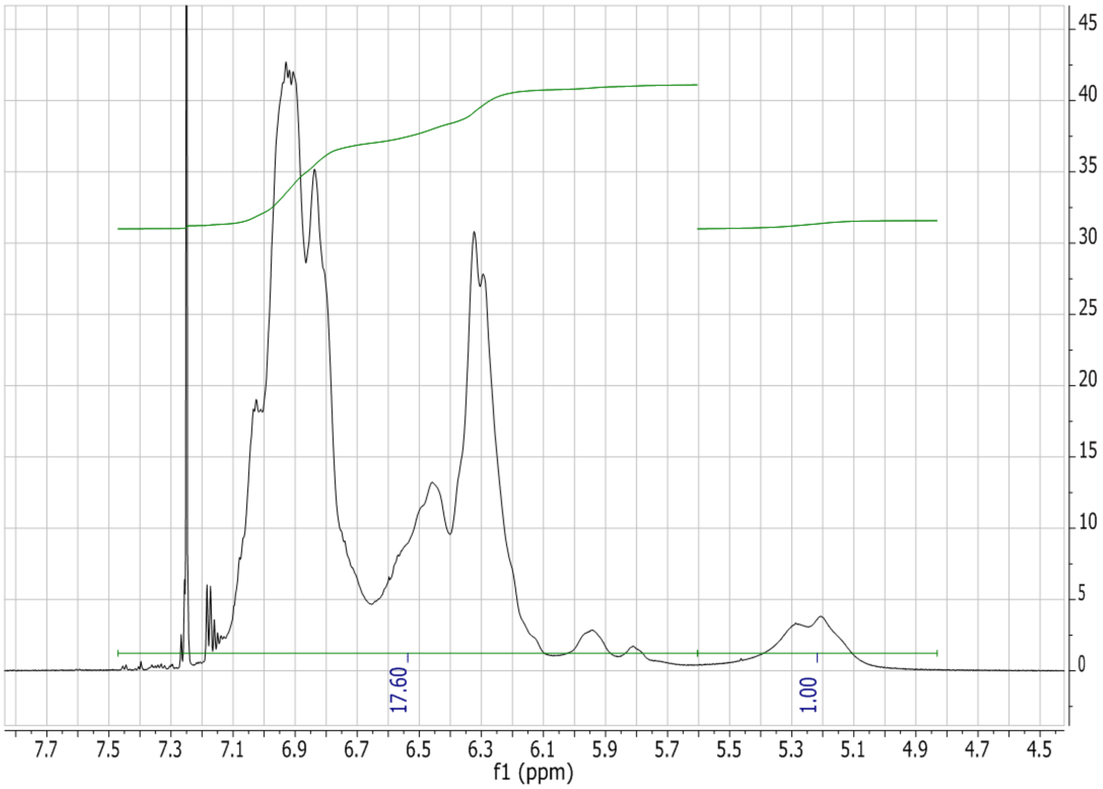

Figure 2.40: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(styrene-*co*-DPE), PSD-4, synthesized in benzene with a molar feed ratio of 1.00 : 1.55 styrene : DPE (the aromatic region).

The overall content of polybutadiene, *z*, is therefore equal to 10.94. Using these values for *x*, *y* and *z* gives a styrene : DPE : butadiene ratio of 1.00 : 0.85 : 2.81 in the resulting copolymer. The discrepancy between the ratio of styrene : butadiene in the resulting copolymer and the ratio of styrene : butadiene molar feed ratio may be due to the overlap between the aromatic and the alkene signals. The ^{1}H NMR spectrum of poly(styrene-*co*-DPE), PSD-4, (Figure 2.26) shows there is a peak at 4.9 – 5.6 ppm equivalent to approximately 5 % of the area of the other aromatic signals. By calculating the ratio of this peak to the other aromatic signals, the integrals for the P(S-*co*-D)-*b*-PBd copolymer can be corrected. This means that the integral of the aromatic signals is increased by 3.03, whilst that of the 1,4-polybutadiene signal is decreased by 3.03. Using these corrections the styrene : DPE : butadiene composition ratio is calculated as 1.00 : 0.85 : 2.28 which is consistent with the molar feed ratios. From the alkene signals the 1,4-polybutadiene content can be determined to be 89 %, which is consistent with the literature values for the living anionic polymerization of butadiene in benzene.[24] A series of polymers with various molecular weights were prepared by the method described above and each one shows good consistency between the final co-monomer composition in the copolymer and the co-monomer molar feed ratio, and the 1,4-polybutadiene content is consistently between 88 – 90 % (see Table 2.5). These poly(styrene-*co*-DPE)-*block*-polybutadiene copolymers were synthesized for comparison with the poly(butadiene-*co*-styrene-*co*-DPE) copolymers as will be discussed later. Copolymers P(SD)-PBd-1 and 2 were synthesized to analyse the resulting polymer structures, predominantly by ^{1}H NMR spectroscopy; P(SD)-PBd-3 was synthesized to investigate the thermal properties of the resulting copolymers; P(SPDE)-PBd-4 and 5 were synthesized to analyse the sequences by MALDI-ToF MS and P(SD)-PBd-6 to 8 were prepared to investigate the morphology by TEM.

In all eight reactions, upon the addition of *sec*-butyllithium to the solution of benzene, styrene and DPE, a red colour was observed which is characteristic of a mixture of diphenylethyl and styryl carbanions. Upon addition of butadiene to the living polymer, the colour instantly faded to a pale yellow colour, and in all cases except P(SD)-PBd-1 and P(SD)-PBd-4, the colour reverted back to the red colour after a few days. Whilst all the styrene should be consumed prior to the addition of butadiene, there will be, in most cases, residual DPE monomer after the copolymerization of the first block. The colour change from pale yellow to red after the polymerization of the butadiene block is indicative that some, and potentially all, chains are end-capped with DPE. Whilst this is only a single unit, the end-groups of polymers can often have significant effects on the properties.[25] The reason P(SD)-PBd1 and P(SD)-PBd-4 had not reverted back to the red colour is likely due to the fact they were terminated before the cross-over from butadienyl carbanions to diphenylethyl carbanions. Additionally, P(SD)-PBd-1 was synthesized with a molar excess of styrene with respect to DPE and therefore in this case there may have been no residual DPE present to react with butadienyl carbanion upon depletion of butadiene. When these copolymers are prepared using a 'fire and forget' simultaneous terpolymerization (see later), the butadiene is consumed first, which avoids "end-capping" of the diene block with DPE which is preferable.

A significant issue which arises from the sequential addition of monomer methodology is that upon the addition of the second batch of monomer, butadiene in this case, some chains of poly(styrene-*co*-DPE) are inevitably terminated by the introduction of environmental impurities with the butadiene monomer. Evidence of this can be seen

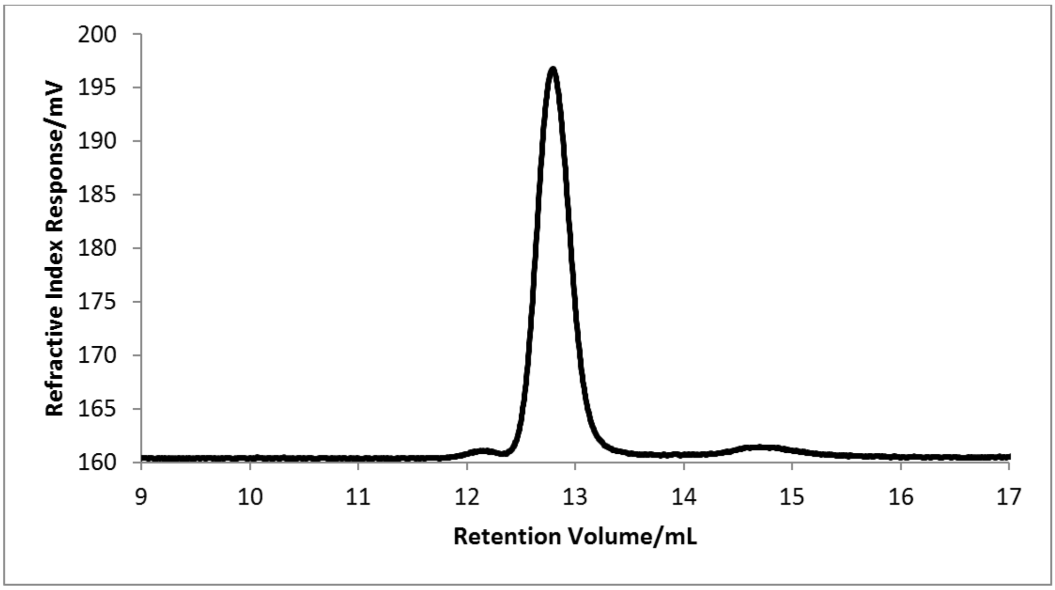

Figure 2.41: SEC chromatogram (refractive index) for poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer, P(SD)-PBd-7.

in the SEC chromatogram (Figure 2.27). The largest peak at a retention volume of 12.4 – 13.3 ml corresponds to the final block copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene, the peak at 11.9 – 12.4 ml corresponds to the cross-coupled material (due to termination and coupling by environmental impurities (oxygen and carbon dioxide) added during the termination by methanol) and the peak at 14.2 – 15.1 ml corresponds to inadvertently terminated poly(styrene-*co*-DPE). This is a significant disadvantage for the described sequential monomer addition methodology but does not present a problem for a simultaneous copolymerization of all three monomers.

The low molecular weight samples, P(SD)-*b*-PBd-4 and P(SD)-*b*-PBd-5, were synthesized to allow analysis by MALDI-ToF MS and the MALDI-ToF mass spectra are shown in Figures 2.28 and 2.29. However, the spectra are much more complicated than those of the poly(styrene-*co*-DPE) copolymers. This is due to distributions arising from both blocks, creating a distribution of distributions, and also due to overlapping molecular weights from different compositions. As a result it is not possible to identify the composition or compositions of a particular peak. However, it is possible to identify chains which differ in mass by a single butadiene unit (as shown in Figure 2.8b) and chains which differ in mass by a single unit of DPE. However, as the mass of two butadiene units (2 x 54.092 g mol^{-1} = 108.18 g mol^{-1}) differs only from one styrene unit

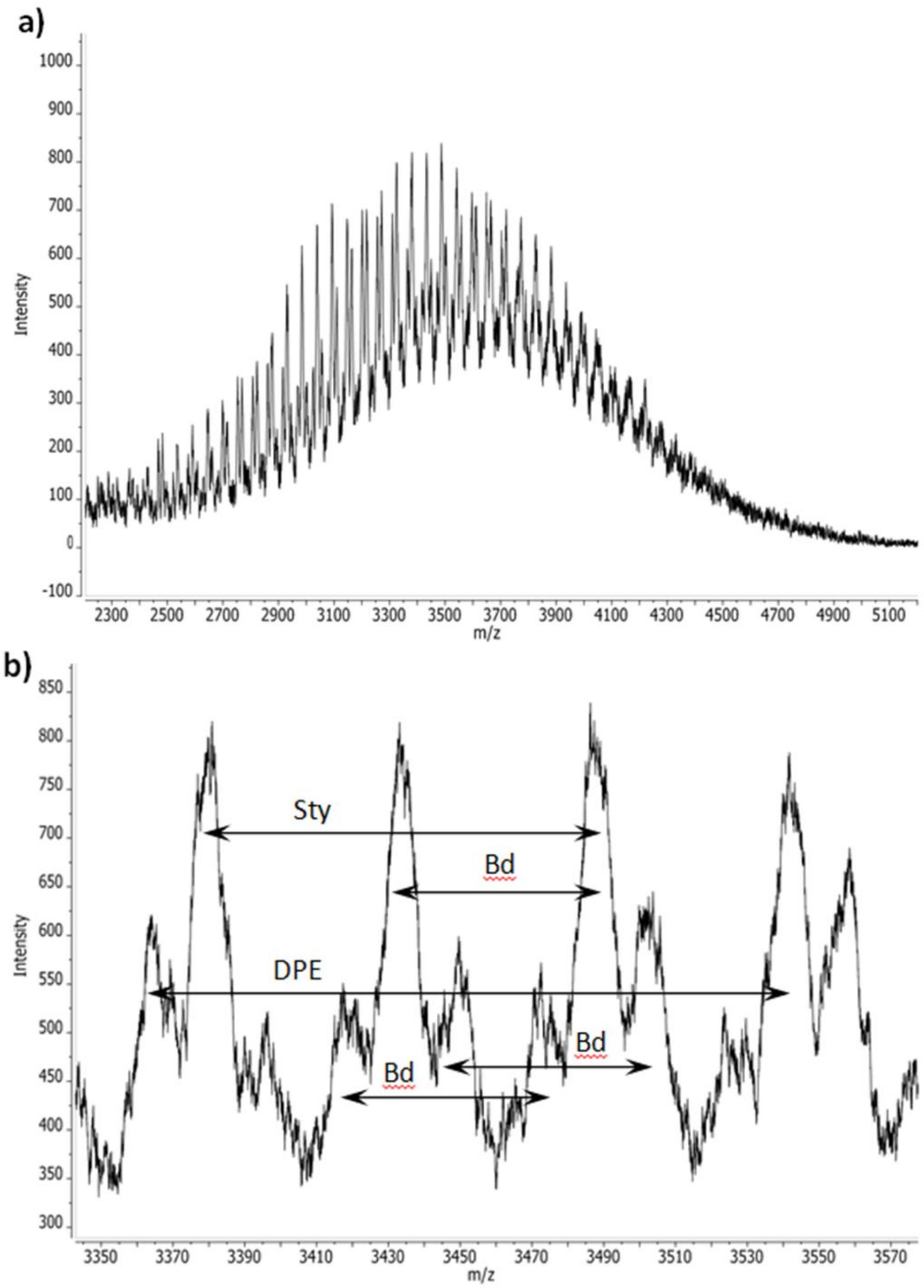

Figure 2.42: (a) MALDI-ToF mass spectrum and (b) expansion over the range m/z = 3350 – 3570 for the copolymer P(SD)-PBd-4 prepared by sequential addition of butadiene to a copolymerization (in benzene) of styrene and DPE using living anionic polymerization (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.03 : 5.33).

(104.15 g mol^{-1}) by about 4 g mol^{-1}, it is not trivial to distinguish with any certainty whether chains differ in mass by a single styrene unit or two units of butadiene.

In the case of P(SD)-*b*-PBd-5 (Figure 2.29) the signal is much weaker and only repeat units of butadiene can be identified. Hence MALDI-ToF MS is not an appropriate method for analysing block copolymers comprised of three monomers.

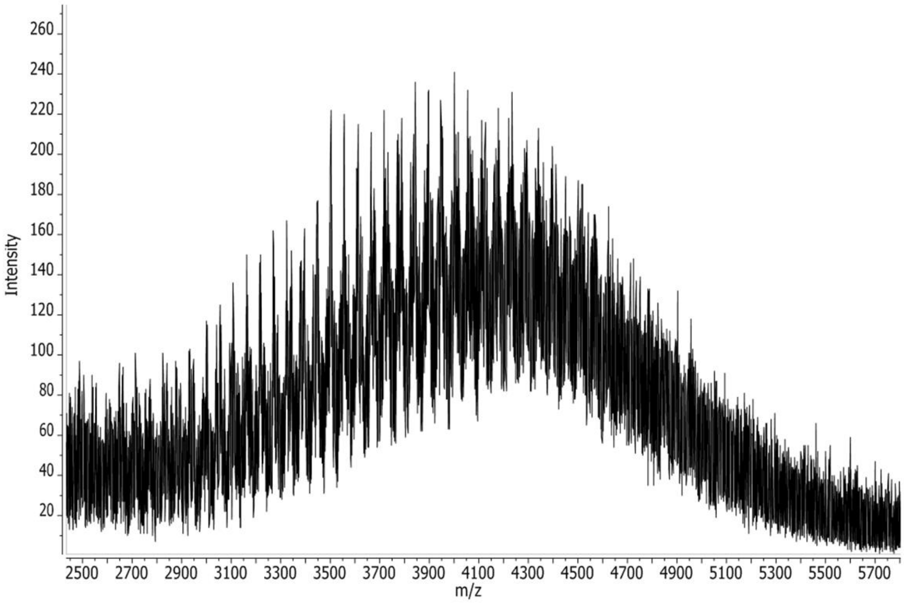

Figure 2.43: MALDI-ToF mass spectrum for the copolymer P(SD)-PBd-5 prepared by sequential addition of butadiene to a copolymerization (in benzene) of styrene and DPE using living anionic polymerization (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.54 : 4.42).

2.4.2. Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in Benzene

Although the sequential addition of monomer is the most common approach to make block copolymers both in academia and in industry there are some unavoidable disadvantages of this approach – the most noticeable of which is the inevitable termination of some chains upon the addition of the second batch of monomer. In light of that it was hypothesized that a 'fire and forget' terpolymerization of styrene, butadiene and DPE would result in a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE) where the first section would be rich in butadiene and the later section would be rich in both styrene and DPE, and the resulting copolymer may contain comparable properties to those prepared by the sequential addition of monomer. Whilst there are only four rate constants for a copolymerization of two monomers (k_{11}, k_{12}, k_{22} and k_{21}), for a terpolymerization there are now nine rate constants (k_{11}, k_{12}, k_{13}, k_{22}, k_{21}, k_{23}, k_{33}, k_{31} and k_{32}) to consider.

If butadiene is monomer 1, styrene is monomer 2 and DPE is monomer 3, then it is known from the binary copolymerizations that $\frac{k_{11}}{k_{12}}$ = 10 and $\frac{k_{11}}{k_{13}}$ = 54, or alternatively $\frac{k_{12}}{k_{11}}$ = 0.1 and $\frac{k_{13}}{k_{11}}$ = 0.02.[2-3, 6] It is a reasonable assumption that the rate constant for the self-propagation of butadiene is the same in the presence of styrene as in that of DPE (i.e. k_{11} is a constant),[26] then as $\frac{k_{12}}{k_{11}} > \frac{k_{13}}{k_{11}}$ it follows that $k_{12} > k_{13}$, therefore $k_{11} > k_{12} > k_{13}$ and butadiene is most likely to self-propagate in the terpolymerization. It is also more likely that butadiene will cross-propagate to styrene in preference to DPE. If styrene is the propagating species then it is known from the binary copolymerizations that $\frac{k_{22}}{k_{21}} = 0.035$ and $\frac{k_{22}}{k_{23}} = 0.7$,[2-3] therefore $k_{21} > k_{23} > k_{22} = 0$, and styrene is most likely to cross-propagate to butadiene in preference to either styrene or DPE, although styrene is more likely to cross-propagate to DPE in preference to self-propagating. If the propagating species is DPE then in copolymerizations with styrene and butadiene, DPE will always cross-propagate, $\frac{k_{33}}{k_{31}} = \frac{k_{33}}{k_{32}} = 0$.[2, 6] As $k_{11} > k_{12}$ and $k_{21} > k_{22}$ it is more likely that DPE will cross-propagate to butadiene (i.e. it is expected that butadiene is more reactive as a monomer than styrene). Therefore in the terpolymerization it is expected butadiene will preferentially self-propagate, and if butadienyl lithium does at any point cross-propagate to DPE, or more likely styrene, then both DPE and styrene are more likely to cross-propagate back to butadiene. Upon consumption of butadiene it is more likely that butadiene will cross-propagate to styrene, and then styrene and DPE will both continue to preferentially cross-propagate to prepare a tapered section of poly(styrene-*co*-DPE).

To test this hypothesis a series of terpolymers were prepared by the simultaneous copolymerization of styrene, DPE and butadiene in benzene. The composition of each resulting terpolymer was determined by ^{1}H NMR spectroscopy and is reported in Table 2.7. The molecular weight data of each terpolymer was determined by SEC and is reported in Table 2.8. The ratio of styrene : DPE could not be calculated from the ^{1}H NMR spectrum as the protons from the butadiene units dominate in the aliphatic region. For this reason the composition was calculated using the final ratio of styrene : DPE from analogous reactions carried out in the absence of butadiene. Whilst this assumption is clearly a source of potential error, it is more accurate than attempting to calculate the ratio of styrene : DPE from the aliphatic region particularly when the

Table 2.8: Compositions of poly(butadiene-*co*-styrene-*co*-DPE) copolymers synthesized in benzene using styrene : DPE ratios determined from the previous copolymerizations of styrene and DPE.

Sample	Sty : DPE : Bd feed ratio	Temp/ °C	Sty : DPE : Bd in copolymer	% 1,4-PBd
PBdSD-1d	1.00 : 0.67 : 5.37	RT to 50	1.00 : 0.50 : 5.42	90
PBdSD-2c	1.00 : 0.58 : 3.28	50	1.00 : 0.50 : 3.34	89
PBdSD-3e	1.00 : 1.55 : 1.99	RT	1.00 : 0.83 : 1.92	87
PBdSD-4d	1.00 : 1.55 : 2.71	RT	1.00 : 0.83 : 2.94	90
PBdSD-5	1.00 : 1.54 : 10.96	25	1.00 : 0.83 : 12.60	90
PBdSD-6	1.00 : 1.55 : 10.99	25	1.00 : 0.83 : 13.13	90
PBdSD-7	1.00 : 1.60 : 10.04	25	1.00 : 0.83 : 13.63	90
PBdSD-8	1.00 : 1.50 : 7.69	25	1.00 : 0.83 : 9.32	90

Table 2.9: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE) copolymers synthesized in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-1d	36,900	39,100	1.06
PBdSD-2c	11,100	11,800	1.06
PBdSD-3e	4,900	5,400	1.09
PBdSD-4d	58,500	62,700	1.07
PBdSD-5	111,900	119,600	1.07
PBdSD-6	50,700	53,100	1.05
PBdSD-7	96,900	99,500	1.03
PBdSD-8	117,100	122,500	1.05

butadiene content is high. A justification for this assumption will be provided later. The data in Table 2.7 shows that the final composition is in good agreement with the molar feed ratio of the monomers. The data for PBdSD-5 to 8 have a slightly higher ratio of butadiene relative to styrene than the feed ratio, however, this could be due to either an underestimation of the styrene content (i.e. the DPE incorporation is lower than

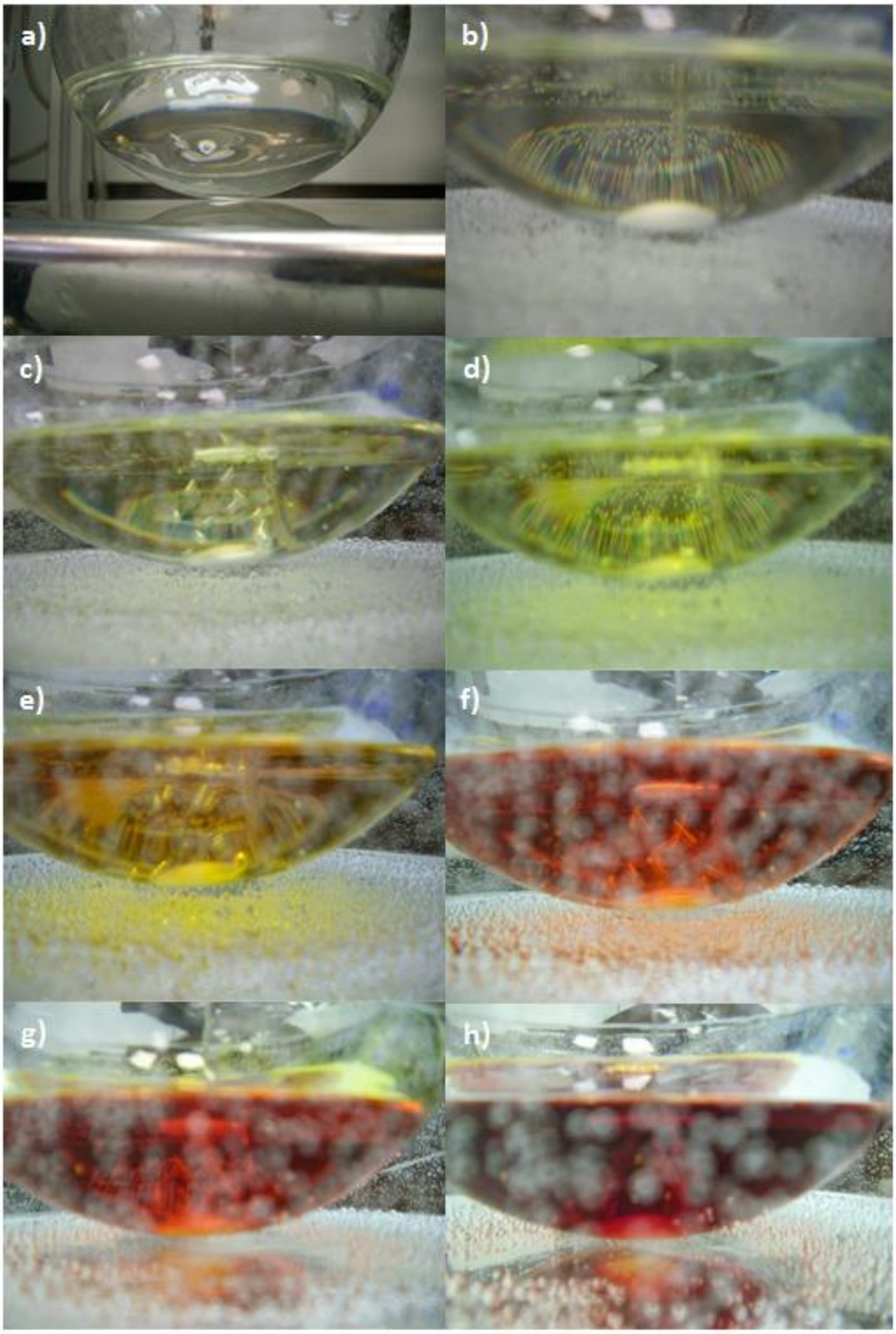

Figure 2.44: Photographs of the copolymerization of butadiene, styrene and DPE after (a) PBdSD-1a; 7.8 hours (b) PBdSD-1b; 25 hours at room temperature (c) 25 hours at room temperature and 10 minutes at 50 °C (d) 25 hours at room temperature and 20 minutes at 50 °C (e) 25 hours at room temperature and 25 minutes at 50 °C (f) 25 hours at room temperature and 32 minutes at 50 °C (g) PBdSD-1c; 25 hours at room temperature and 45 minutes at 50 °C (h) 25 hours at room temperature and 65 minutes at 50 °C.

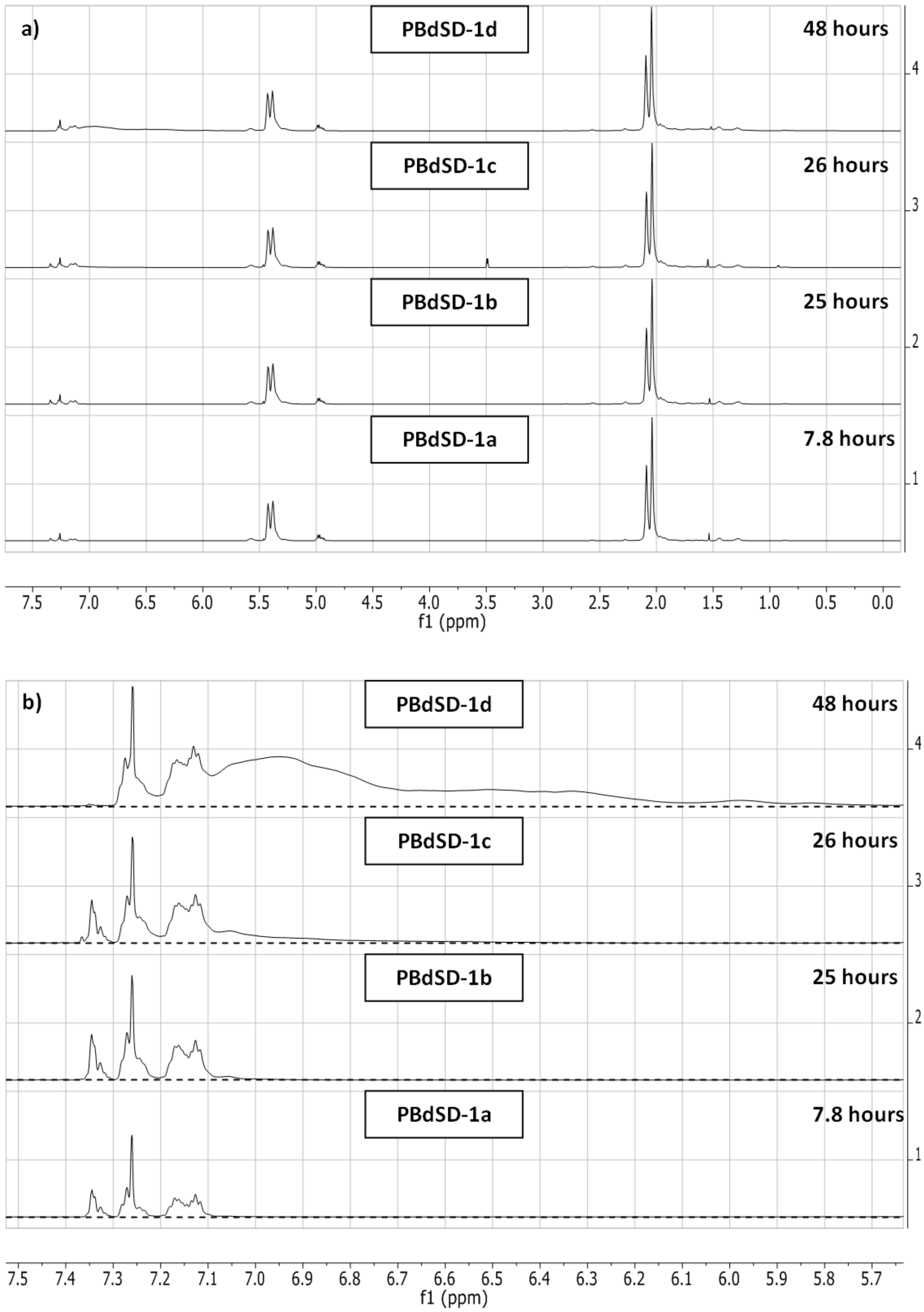

Figure 2.45: (a) ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-1a-d, synthesized in benzene with a molar feed ratio of 1.00 : 0.67 : 5.37 styrene : DPE : butadiene and (b) expansion of the aromatic region (5.7 – 7.5 ppm) with the baseline indicated by a dotted line.

would be expected from previous reactions) or errors associated with weighing the butadiene monomer. In the initial experiment, PBdSD-1, upon addition of *sec*-butyllithium to a solution of benzene, styrene, DPE and butadiene, a pale yellow colour was observed (Figure 2.30a). This pale yellow colour is indicative of polybutadienyllithium end-groups which supports the hypothesis that butadiene will homopolymerize first. After 25 hours at room temperature the reaction was still pale yellow, at which point the temperature was increased to 50 °C. Within 10 – 20 minutes of increasing the temperature the colour of the reaction mixture had become dark yellow (Figures 2.30c-d). After 45 – 65 minutes the colour was red suggesting a mixture of diphenylethyl and styryl carbanions (Figure 2.30g). This red colour remained until the reaction was terminated 22.4 hours later. The reaction was sampled after 7.8 hours (PSD-1a – Figure 2.30a) and 25 hours (PSD-1b – Figure 2.30b) of stirring at room temperature when the reaction mixture was still pale yellow. After heating at 50 °C for 45 minutes when the reaction mixture was red (Figure 2.30g) another sample was extracted (PSD-1c). These samples were analysed by ^{1}H NMR spectroscopy and SEC. The stacked ^{1}H NMR spectra for the intermediate samples and the final copolymer of reaction PBdSD-1 (PSD-1d) are shown in Figure 2.31.

The ^{1}H NMR data in Figure 2.31 shows that the first two samples, PBdSD-1a and PBdSD-1b, contain very little styrene or DPE (indicated by the small integral in the aromatic region). The peak at 7.30 – 7.37 ppm arise from the DPE monomer, the sharp peak at 7.26 ppm arises from $CHCl_3$ present in the NMR solvent and the peaks at 7.09 – 7.30 ppm are likely to arise from some incorporation of styrene or DPE into the initial butadiene-rich block. In the third sample styrene and DPE are slightly more prevalent, and styrene and DPE are strongly incorporated in the final copolymer. The ratios of styrene : DPE : butadiene can be determined from the integrals, for example the ^{1}H NMR spectrum of the first sample, PBdSD-1a, is shown in Figure 2.32. The integral of the aromatic region leads to the following equation:

$$5x + 10y = 0.36 \qquad [2.11]$$

after the integrals from the residual DPE monomer (7.30 – 7.40 ppm) and $CHCl_3$ have been subtracted. The integrals of the alkene region lead to the following equations:

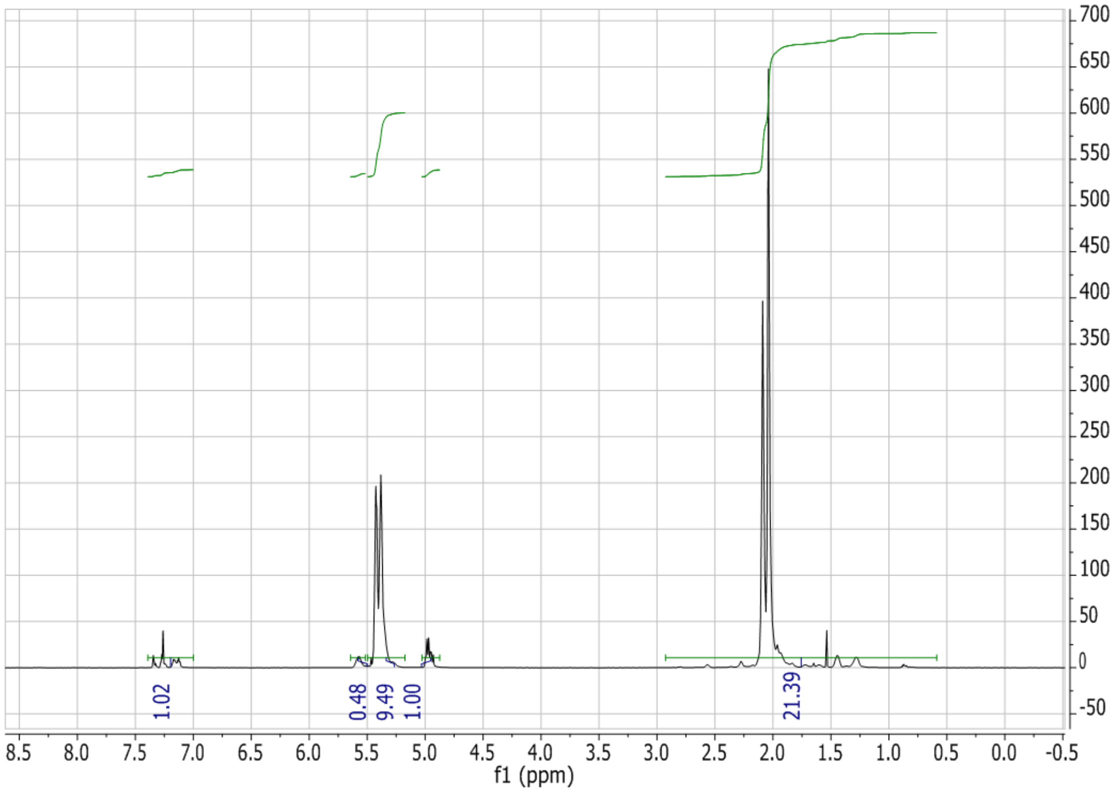

Figure 2.46: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-1a, synthesized in benzene with a molar feed ratio of 1.00 : 0.67 : 5.37 styrene : DPE : butadiene.

$$z_{1,2} = \frac{\frac{1.00}{2} + 0.48}{2} = 0.49 \qquad [2.12]$$

and:

$$z_{1,4} = \frac{9.41}{2} = 4.71 \qquad [2.13]$$

after subtracting the integral of the residual DPE monomer (5.47 ppm). Whilst the final equation arises from the aliphatic region:

$$2y + 3x + 3z_{1,2} + 4z_{1,4} = 21.14 \qquad [2.14]$$

after subtracting the integral of H_2O. The integrals of styrene and DPE (as expected) are too small compared to butadiene to use equation 2.14 to calculate the ratio of styrene : DPE (i.e. this method is too inaccurate and there are no possible solutions of the simultaneous equations). If the ratio of styrene : DPE in the copolymer is assumed to be equal to that of PSD-1 (styrene : DPE = 2.00 : 1.00) which was prepared with the same molar feed ratio of styrene : DPE, then this gives rise to the equation:

$$x = 2.0y \qquad [2.15]$$

Solving these equations gives x = 0.036; y = 0.018 and z = 5.20, from which the ratio of styrene : DPE : butadiene = 1.00 : 0.50 : 144.4, and a 1,4-polybutadiene content of 91 % is calculated. Whilst the error on this calculation is unlikely to be insignificant, this clearly shows that at this point there is little or no styrene/DPE and the sample is almost pure polybutadiene. The composition of the other samples is calculated by the same method and the results are summarised in Table 2.9. The molecular weight data of the samples and final copolymer is reported in Table 2.10. The molecular weight of the final copolymer was 39,100 g mol^{-1} (using the *dn*/*dc* value for polystyrene) higher than the target molecular weight of 18,000 g mol^{-1} indicating that some of the initiator may have been deactivated by impurities. However, the Đ was 1.06 indicating that termination was not an issue during the polymerization. The resulting composition indicates that styrene and butadiene had been fully incorporated. The yield was 78 %, and taking into account that not all the DPE monomer had reacted, this suggests that the reaction had gone to completion.

For the final copolymer, PBdSD-1d, the integrals corresponding to the styrene and DPE in the aliphatic region are large enough to obtain an estimate of the ratio of styrene : DPE (the ^{1}H NMR spectrum is shown in Figure 2.33). Using the integrals from the aromatic, alkene and aliphatic regions gives a styrene : DPE : butadiene ratio = 1:00 : 0.53 : 5.59 (90 % 1,4-polybutadiene) which is consistent with the styrene : DPE ratio in

Table 2.10: Compositions of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-1 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in benzene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 0.67 : 5.37.

Sample	Temp/ °C	Reaction Time/hours	Sty : DPE : Bd in copolymer	% 1,4-PBd
PBdSD-1a	RT	7.8	1.00 : 0.50 : 144.44	91
PBdSD-1b	RT	24.9	1.00 : 0.50 : 41.94	91
PBdSD-1c	RT to 50	25.7	1.00 : 0.50 : 24.76	91
PBdSD-1d	RT to 50	48.1	1.00 : 0.50 : 5.42	90

Table 2.11: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-1 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-1a	13,800	14,600	1.06
PBdSD-1b	19,300	20,400	1.06
PBdSD-1c	22,600	23,800	1.05
PBdSD-1d	36,900	39,100	1.06

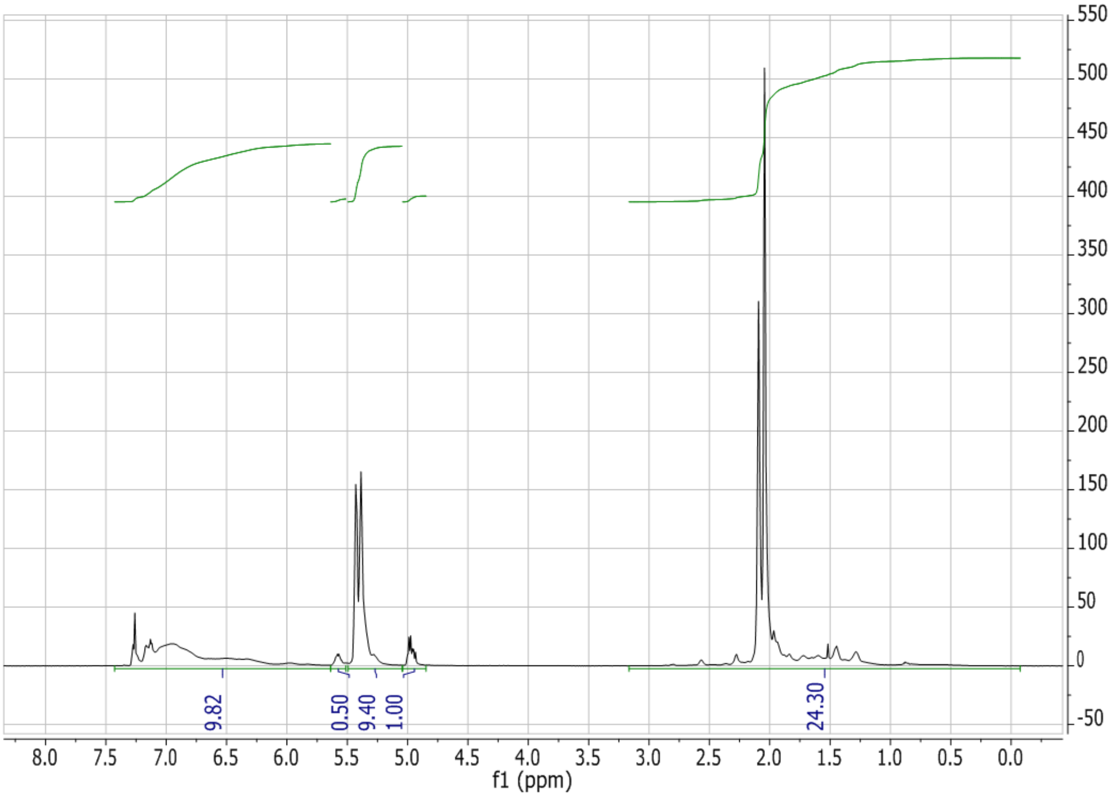

Figure 2.47: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-1d, synthesized in benzene with a molar feed ratio of 1.00 : 0.67 : 5.37 styrene : DPE : butadiene.

the copolymer PSD-1 and the molar feed ratio of styrene : butadiene. Whilst the aliphatic region can be used to predict the ratio of styrene : DPE for PBdSD-1d, it is still likely to be highly inaccurate due to the large integrals from butadiene units dominating the aliphatic region. Furthermore the reactions PBdSD-2 and PBdSD-3 are too low molecular weight and therefore the end-groups will also contribute significantly to the aliphatic region, and reactions PBdSD-5 to 8 have a higher incorporation of butadiene and so the composition of the copolymers prepared in these reactions can only be calculated by using styrene : DPE ratios from previous analogous reactions.

Whilst using a styrene : DPE ratio based on previous experiments is clearly a source of potential error, the previous reactions had an identical molar feed ratio of styrene : DPE and it is therefore likely to be a reasonable assumption that the resulting terpolymers will have an equivalent ratio of styrene : DPE. Furthermore the aliphatic region in the ^{1}H NMR spectra of the terpolymers is dominated by butadiene peaks and calculating the styrene : DPE ratio using the aliphatic region will be highly inaccurate even in cases when the butadiene content is relatively low and the molecular weight is high. Therefore the values used in the analysis, and listed in Table 2.7 and 2.9, are calculated from styrene : DPE ratios obtained from analogous copolymers.

In this preliminary experiment (PBdSD-1; described above), the reaction mixture was initially performed at room temperature, but after 25 hours the reaction mixture was heated to 50 °C in order to increase the rate or propagation whereupon the colour of the reaction mixture became red and ^{1}H NMR analysis revealed that styrene and DPE became incorporated. The reaction was repeated, PBdSD-2, (molar feed ratio = 1.00 : 0.58 : 3.28 styrene : DPE : butadiene) but this time the reaction was heated to 50 °C from the start to investigate the impact of temperature upon the reaction rate. This time the colour of the reaction mixture changed from pale yellow to dark yellow after

Table 2.12: Compositions of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-2a-c, synthesized by the copolymerization in benzene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 0.58 : 3.28 (assuming a 1.00:0.50 ratio of styrene : DPE in the final copolymer).

Sample	Temp/ °C	Reaction Time/hours	M_n/g mol^{-1}	Sty : DPE : Bd in copolymer	% 1,4-PBd
PBdSD-2a	50	1.6	5,100	1.00 : 0.50 : 16.84	89
PBdSD-2b	50	2.0	6,400	1.00 : 0.50 : 8.61	90
PBdSD-2c	50	22.9	11,100	1.00 : 0.50 : 3.34	89

Table 2.13: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-2 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-2a	5,100	5,300	1.04
PBdSD-2b	6,400	7,000	1.09
PBdSD-2c	11,100	11,800	1.06

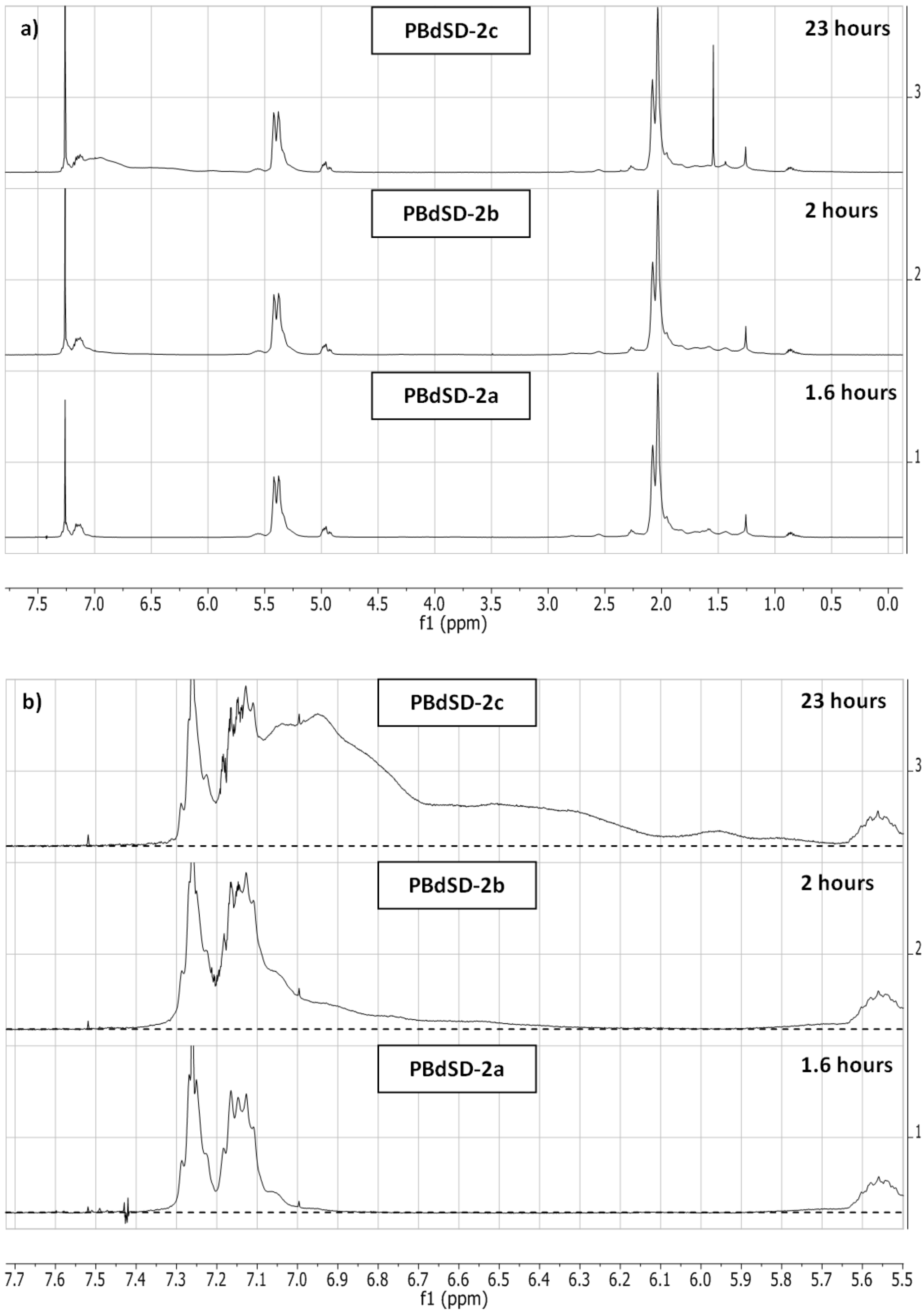

Figure 2.48: (a) ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-2a-c, synthesized in benzene with a molar feed ratio of 1.00 : 0.58 : 3.28 styrene : DPE : butadiene and (b) expansion of the aromatic region (5.6 – 7.8 ppm) with the baseline indicated by a dotted line.

1.6 hours at which point a sample (PBdSD-2a) was extracted. Another sample was extracted after a further 30 minutes (PBdSD-2b) when the colour of the reaction mixture had become red. The reaction was stirred at 50 °C for a further 21 hours before termination. The stacked ^{1}H NMR spectra for the intermediate samples (PBdSD-2a and 2b) and the final copolymer of reaction PBdSD-2 (PBdSD-2c) are shown in Figure 2.34, the resulting terpolymer composition (styrene : DPE : butadiene ratio) is shown in Table 2.11 assuming the ratio of styrene : DPE is equal to that of PSD-1 (styrene : DPE = 2.00 : 1.00) and the molecular weight data is shown in Table 2.12. The ^{1}H NMR data and the calculated compositions again indicate that butadiene is preferentially consumed first prior to the incorporation of styrene and DPE. The yield of the final copolymer, PBdSD-2c, was 76 %, the composition of the final copolymer which is in good agreement with the molar feed ratio and the molecular weight of the final copolymer is 11,800 g mol^{-1} (using the *dn*/*dc* value of polystyrene) all of which indicate that the reaction was complete by 23 hours. Therefore the data for this reaction is consistent with the previous reaction, PBdSD-1, but this time the reaction was complete by 23 hours, showing that the rate of reaction is much faster at 50 °C but the resulting sequence is not significantly affected.

A low molecular weight polymer was prepared by simultaneous terpolymerization specifically for analysis by ^{1}H NMR spectroscopy and MALDI-ToF MS. In previous experiments the impact of end-groups on the aliphatic region of the ^{1}H NMR spectrum prohibited the possibility of calculating the ratio of styrene : DPE. However, in this case it is not the aliphatic region which is of interest as this region is already dominated by signals of polybutadiene. This reaction (PBdSD-3) was carried out at room temperature and sampled throughout. Upon initiation the reaction darkened to an intense yellow colour (Figure 2.35b), however, within seconds the colour faded to pale yellow (Figures 2.35c and 2.35d). A sample was extracted after 35 minutes (PBdSD-3a – Figure 2.35e); 1.3 hours (PBdSD-3b – Figure 2.35f); 7.5 hours (PBdSD-3c – Figure 2.35g) and 11.5 hours (PBdSD-3d – Figure 2.35i). The results of the ^{1}H NMR analysis of PBdSD-3 are shown in Figure 2.36. Due to the low conversion it was not possible to obtain any meaningful analysis on the first sample, PBdSD-3a. As in the previous experiments,

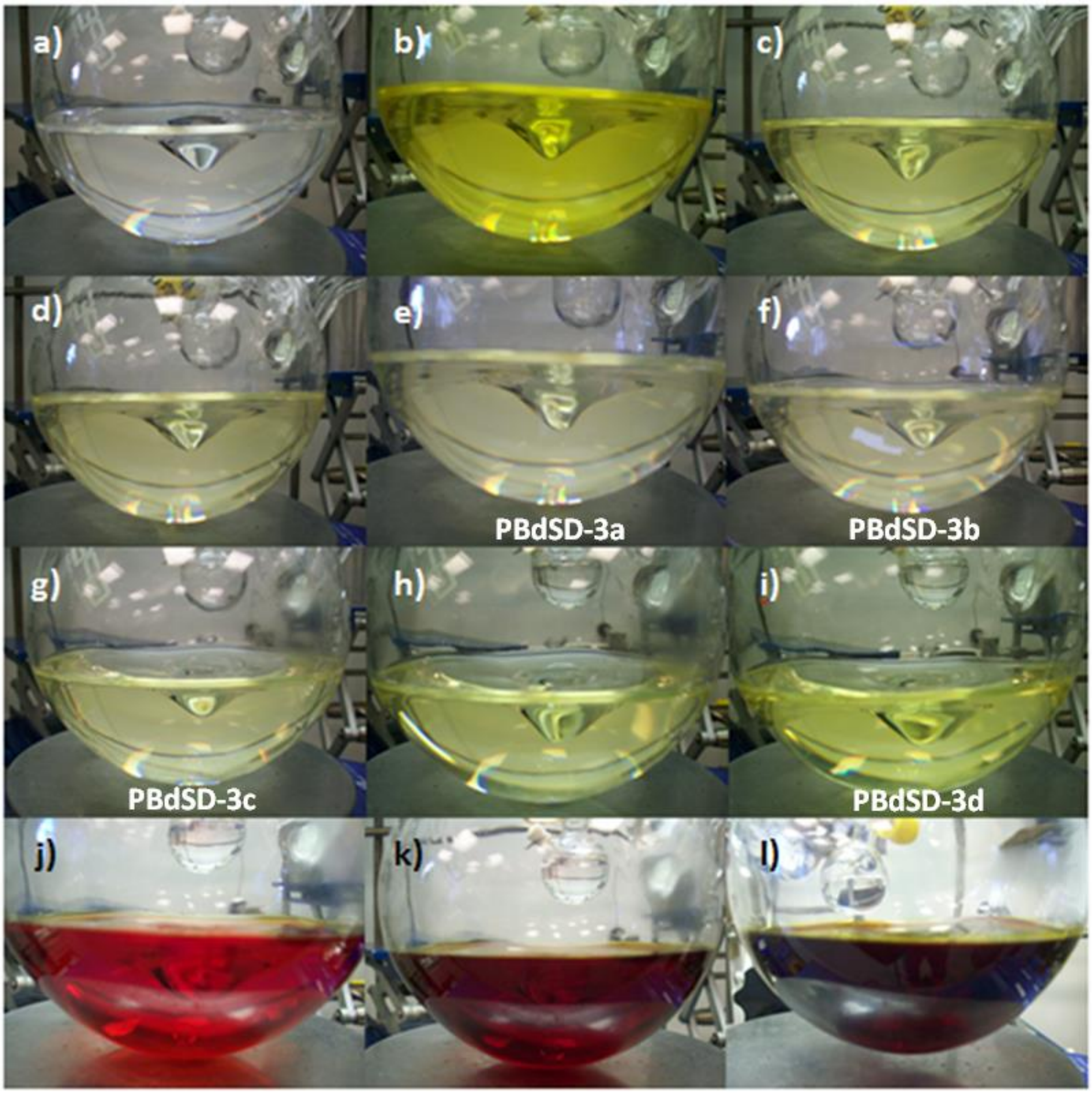

Figure 2.49: Photographs of the copolymerization of styrene, DPE and butadiene (a) before initiation (b) immediately after initiation and after (c) 12 seconds (d) 28 seconds (e) PBdSD-3a; 35 minutes (f) PBdSD-3b; 1.3 hours (g) PBdSD-3c; 7.5 hours (h) 9.6 hours (i) PBdSD-3d; 11.5 hours (j) 16.3 hours (k) 17.5 hours and (l) 21.8 hours at room temperature.

styrene and DPE initially remain almost entirely excluded from the reaction. The styrene : DPE : butadiene ratios as a function of time are shown in Table 2.13 assuming the ratio of styrene : DPE = 1.00 : 0.83 (obtained by the average composition in samples PSD-3 and PSD-4 which were prepared with the same molar feed ratio of styrene : DPE) and the molecular weight data is shown in Table 2.14. The composition of the final copolymer is in good agreement with the molar feed ratio and the molecular weight of the final sample is 4,900 g mol^{-1} (calculated using a *dn*/*dc* value for polystyrene) which is reasonably close to the target molecular weight of 5,500 g mol^{-1},

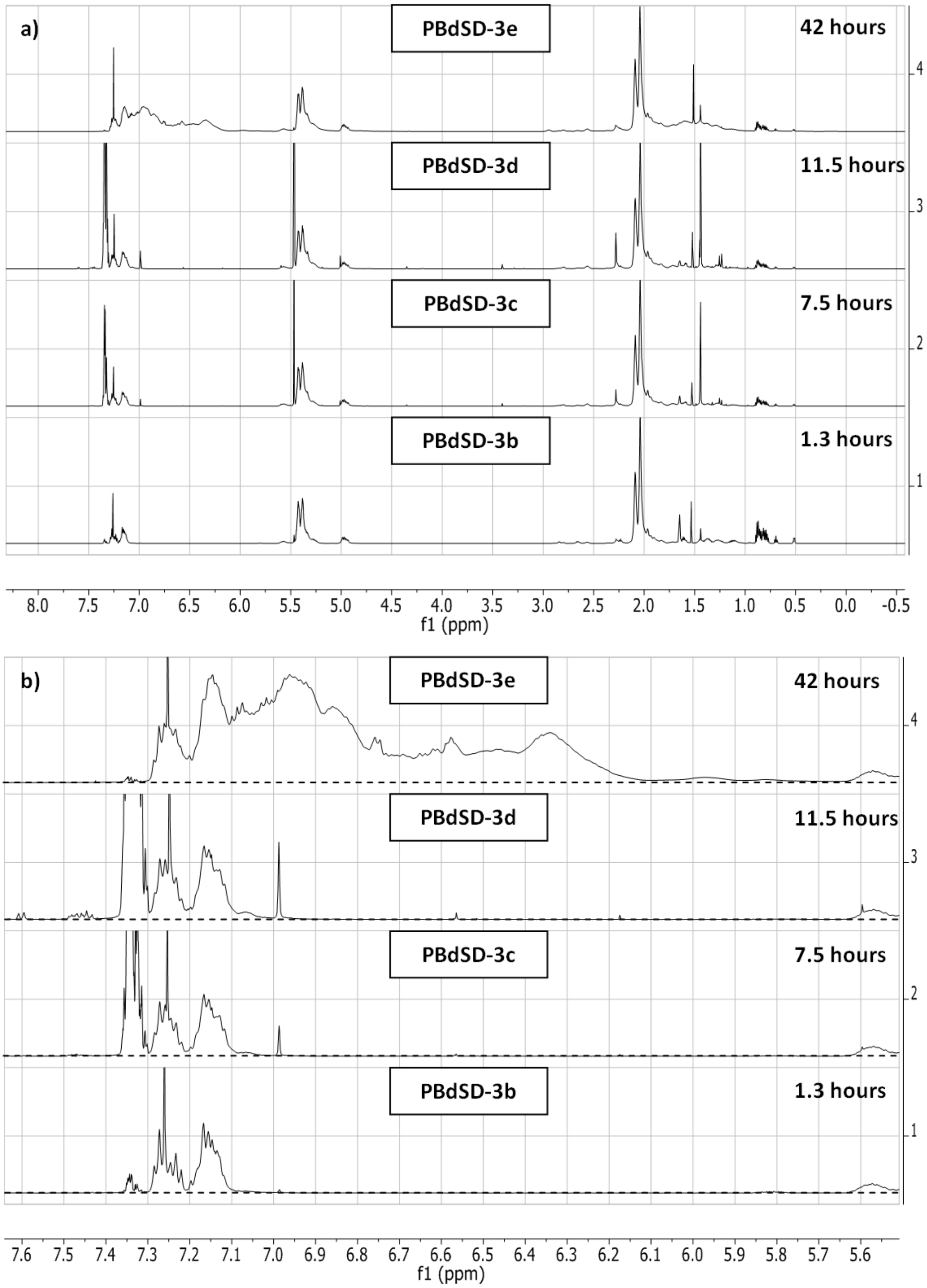

Figure 2.50: (a) ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-3b-e, synthesized in benzene with a molar feed ratio of 1.00 : 1.55 : 1.99 styrene : DPE : butadiene and (b) expansion of the aromatic region (5.6 – 7.6 ppm) with the baseline indicated by a dotted line.

Table 2.14: Compositions of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-3b-e, synthesized by the copolymerization in benzene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99 (assuming a 1.00 : 0.83 ratio of styrene : DPE in the final copolymer).

Sample	Temp/ °C	Reaction Time/hours	Sty : DPE : Bd in copolymer	% 1,4-PBd
PBdSD-3b	RT	1.3	1.00 : 0.83 : 21.96	90
PBdSD-3c	RT	7.5	1.00 : 0.83 : 18.58	89
PBdSD-3d	RT	11.5	1.00 : 0.83 : 15.02	89
PBdSD-3e	RT	42.0	1.00 : 0.83 : 1.92	87

Table 2.15: Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-2 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-3c	1,300	1,400	1.09
PBdSD-3d	1,500	1,500	1.12
PBdSD-3e	4,900	5,400	1.09

indeed the difference between the molecular weight and the target molecular weight may be due to using the *dn/dc* value of polystyrene to calculate the molecular weight. The molecular weight calculated by SEC is also in good agreement with the MALDI-ToF spectrometry for samples PBdSD-3c and 3d.

The MALDI-ToF mass spectrum of the second sample, PBdSD-3b, which was collected after 1.3 hours is shown in Figure 2.37. It should be pointed out the mass difference between two butadiene units and one unit of styrene is only 4.03 g mol^{-1}, however, as the peaks in this case are extremely well resolved and different isotopes can be distinguished (Figure 2.38) it is possible to differentiate between chains comprising different numbers of butadiene and styrene units. Figure 2.38 shows the splitting pattern of the peak at approximately 650 g mol^{-1}; the peaks are split due to the isotopes of silver (^{107}Ag and^{109}Ag) and also due to the difference of four protons between one styrene unit and two butadiene units. The smaller peaks are 1 g mol^{-1} higher than each of the more intense peaks and arise from an isotope of either ^{2}H or ^{13}C present in the copolymer, as ^{13}C has a natural abundance of 1.1 % whilst ^{2}H has only a 0.02 % natural abundance, it is ^{13}C that will contribute most significantly to

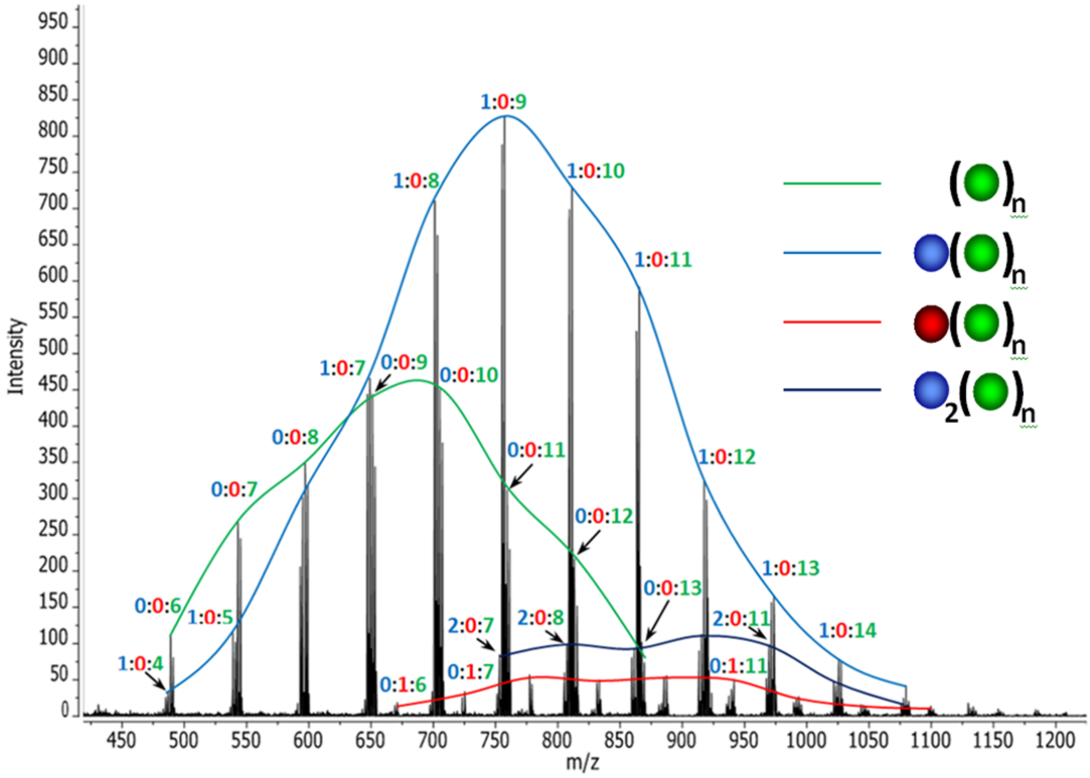

Figure 2.51: MALDI-ToF mass spectrum for the copolymer PBdSD-3b prepared by the anionic copolymerization (in benzene) of styrene, DPE and butadiene (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99) after 1.3 hours. The mole ratio of styrene : DPE : butadiene for any given chain is labelled with styrene in blue, DPE in red and butadiene in green.

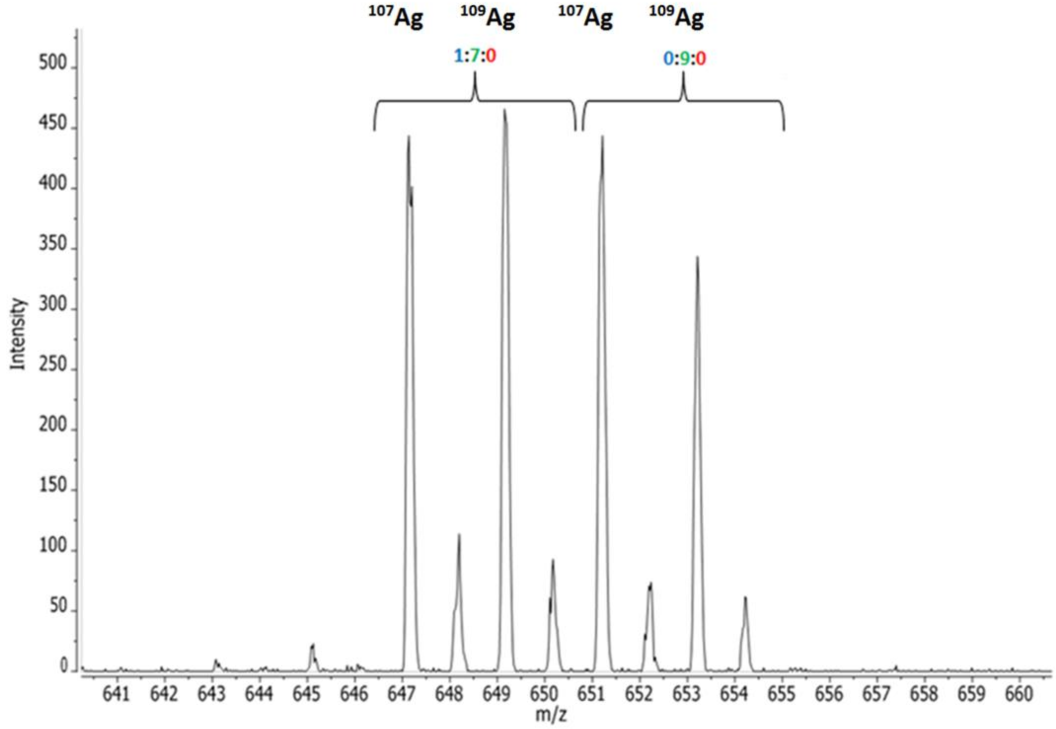

Figure 2.52: Expansion of MALDI-ToF mass spectrum (over the range m/z = 641 – 660) for the copolymer PBdSD-3b prepared by the anionic copolymerization (in benzene) of styrene, DPE and butadiene (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99) after 1.3 hours. The mole ratio of styrene : DPE : butadiene for any given chain is labelled with styrene in blue, DPE in red and butadiene in green.

these peaks. All the sequences in the MALDI-ToF mass spectrum represent chains of predominantly butadiene with zero, one or two units of styrene or DPE. This shows that in the first 1.3 hours of the reaction when this sample, PBdSD-3b, was taken, butadiene has indeed shown a strong preference for self-propagation rather than to undergo cross-propagation to either styrene or DPE. Furthermore there are two main distributions, one distribution of chains containing only butadiene (collectively represented by the green line in Figure 2.37), and a second distribution represented by the most intense signals which arise from chains containing butadiene with only one unit of styrene (grouped by the blue line). It is known that butyllithium preferentially reacts with styrene in preference to butadiene despite butadiene being the more reactive monomer during the copolymerization.[3] Hence this single unit of styrene is likely to have arisen as a result of the initiation step. There are also weaker signals corresponding to chains of butadiene with two units of styrene (represented by the dark blue line), and some chains of butadiene with one unit of DPE (represented by the red line). There also appears to be some signals corresponding to chains containing butadiene, one unit of DPE and one unit of styrene but these signals are very weak. The MALDI-ToF mass spectra for PBdSD-3c and PBdSD-3d were very weak (Figures 2.39 and 2.40) and the final copolymer, PBdSD-3e could not be analysed by MALDI-ToF MS, possibly due to the higher molecular weight of this sample. The peaks in Figure 2.39 for the MALDI-ToF mass spectrum of PBdSD-3c have been assigned as a series of chains of polybutadiene containing one unit of styrene; however, due to the poor resolution these peaks could also contain chains with zero or two units of styrene. There are also some peaks which are likely to correspond to chains containing one unit of DPE but these are not distinguishable from baseline noise. Similarly whilst it is not possible to determine whether there are zero, one or two units of styrene in the majority of peaks in the MALDI-ToF mass spectrum of PBdSD-3d (Figure 2.40), it is still clear that the predominant monomer present in the copolymer is butadiene, and apart from the few chains containing a single unit of styrene which were presumably incorporated due to the reaction with *sec*-butyllithium (as indicated by the initial deep yellow colour in Figure 2.35b) both styrene and DPE have been excluded from the reaction. Both the ^{1}H NMR data and the MALDI-ToF mass spectra of samples

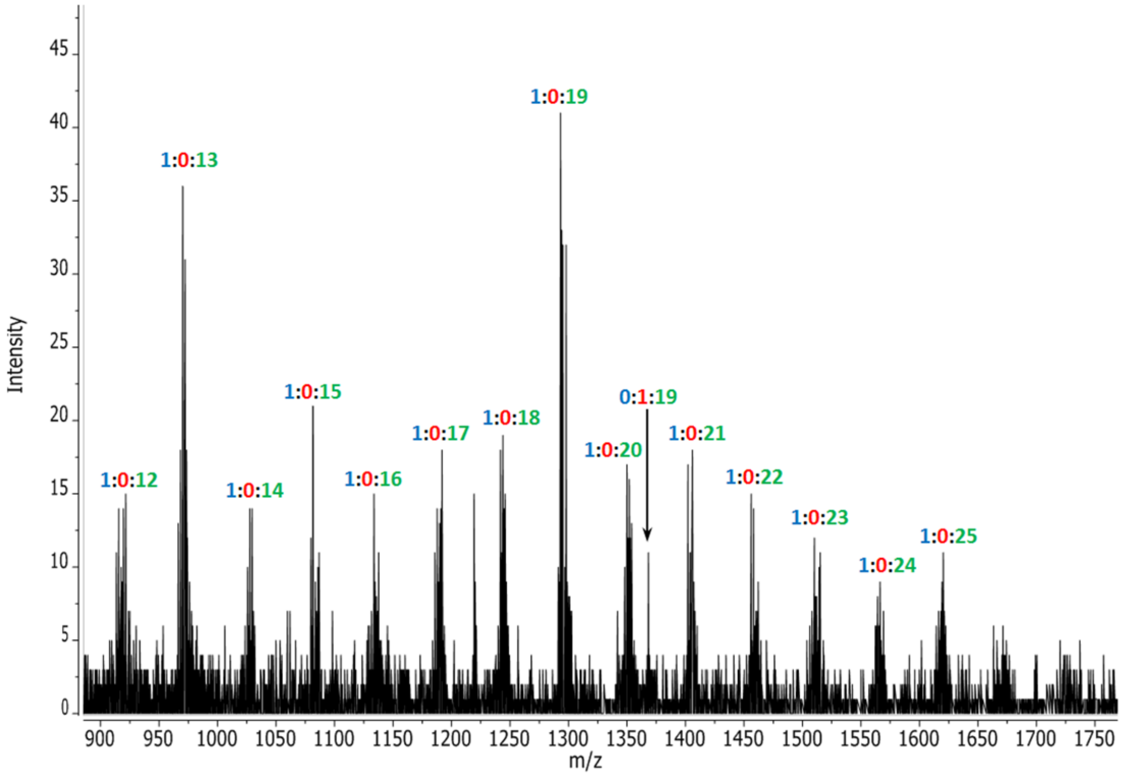

Figure 2.53: MALDI-ToF mass spectrum for the copolymer PBdSD-3c prepared by the anionic copolymerization (in benzene) of styrene, DPE and butadiene (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99) after 7.5 hours. The mole ratio of styrene : DPE : butadiene for any given chain is labelled with styrene in blue, DPE in red and butadiene in green.

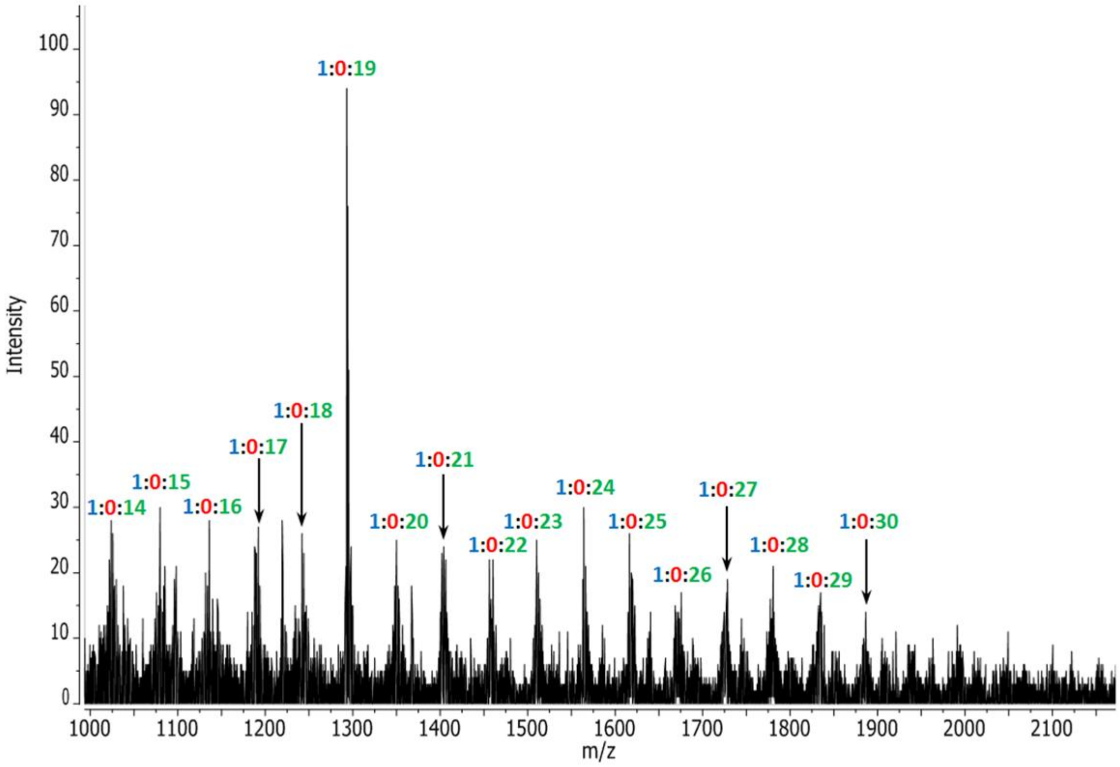

Figure 2.54: MALDI-ToF mass spectrum for the copolymer PBdSD-3d prepared by the anionic copolymerization (in benzene) of styrene, DPE and butadiene (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99) after 11.5 hours. The mole ratio of styrene : DPE : butadiene for any given chain is labelled with styrene in blue, DPE in red and butadiene in green.

PBdSD-3b-d clearly show that butadiene is preferentially consumed before the incorporation of styrene and DPE.

A high molecular weight terpolymer (PBdSD-4) was prepared with samples extracted to explore the T_g (as a function of composition) of the resulting copolymers. The thermal analysis of these samples will be discussed in Chapter 3. All subsequent copolymerizations were allowed to run to completion without sampling and the results were analysed by ^{1}H NMR spectroscopy, these samples were subsequently analysed by TEM for solid state morphology (see next chapter). The copolymer PBdSD-4 was synthesized at room temperature, the reaction was sampled after 4.2 hours and 23 hours at which point the reaction mixture was still pale yellow and after 26 hours when the reaction was dark yellow. The colour of the reaction mixture became red over the next 4 hours. The reaction mixture was stirred at room temperature for a further 3.5 days before termination. The stacked ^{1}H NMR spectra for the intermediate

Table 2.16: Compositions of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-4a-d, synthesized by the copolymerization in benzene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 2.71 (assuming a 1.00 : 0.83 ratio of styrene : DPE in the final copolymer).

Sample	Temp/ °C	Reaction Time/hours	Sty : DPE : Bd in copolymer	% 1,4-PBd
PBdSD-4a	RT	4.2	1.00 : 0.83 : 49.37	90
PBdSD-4b	RT	22.8	1.00 : 0.83 : 25.50	90
PBdSD-4c	RT	26.0	1.00 : 0.83 : 20.55	90
PBdSD-4d	RT	115.0	1.00 : 0.83 : 2.94	90

Table 2.17: Molecular weight data (obtained using triple detection SEC with *dn*/*dc* = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-4 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in benzene.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-4a	8,700	9,300	1.06
PBdSD-4b	22,200	23,000	1.04
PBdSD-4c	23,600	24,400	1.04
PBdSD-4d	58,500	62,700	1.07

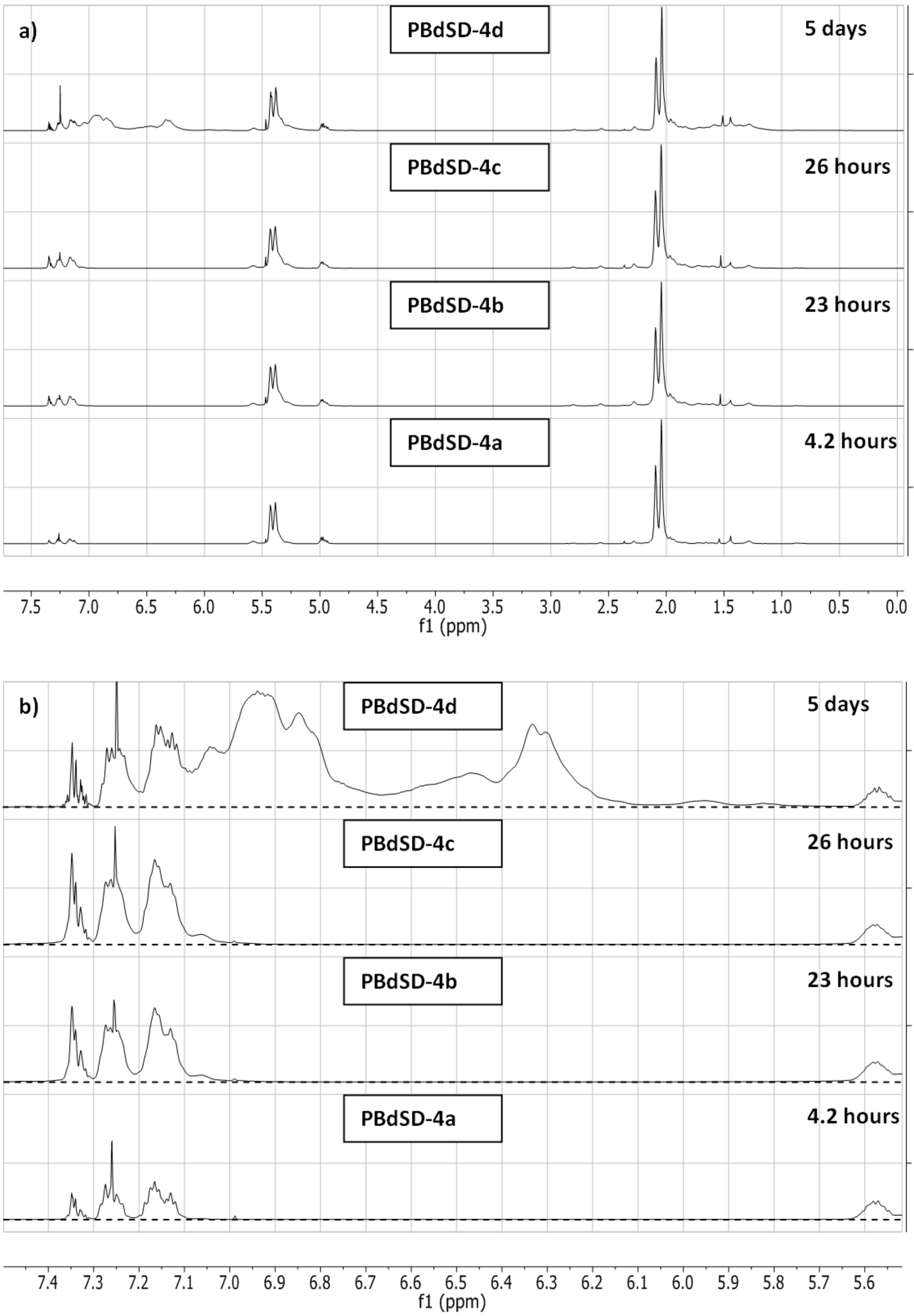

Figure 2.55: (a) ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-4a-d, synthesized in benzene with a molar feed ratio of 1.00 : 1.55 : 2.71 styrene : DPE : butadiene and (b) expansion of the aromatic region (5.6 – 7.4 ppm) with the baseline indicated by a dotted line.

samples (PBdSD-4a-c) and the final copolymer of reaction PBdSD-4 (PBdSD-4d) is shown in Figure 2.41, the terpolymer composition (styrene : DPE : butadiene ratio) is shown in Table 2.15 assuming the ratio of styrene : DPE = 1.20 : 1.00 (obtained by the average composition in samples PSD-3 and PSD-4 which were prepared with the same molar feed ratio of styrene : DPE) and the molecular weight data is shown in Table 2.16. The ^{1}H NMR data is consistent with previous reactions and shows that butadiene was preferentially consumed in the early stages of the reaction. As will be discussed in Chapter 3, the thermal properties are not independent of the molecular weight and hence a suitably high molecular weight was required. Hence, the target molecular weight was 55,000 g mol^{-1}, the molecular weight of the final copolymer was 58,500 g mol^{-1} (calculated using a *dn*/*dc* value of polystyrene) in good agreement with the target molecular weight. The thermal analysis of this copolymer will be discussed in Chapter 3.

The compositions and molecular weight data of the other copolymers (PBdSD-5 to 8) are listed in Table 2.5 and 2.6 and are entirely consistent with the data discussed above, namely that the colour of the reaction mixture was initially pale yellow and darkened to red during the polymerization indicating that butadiene was preferentially consumed in the early stages of the reaction. The time taken for the reaction mixture to change colour from pale yellow to deep red surprisingly varied for each reaction despite the fact that the reactions were all carried out at 25 °C. In reaction PBdSD-5 the colour changed between 2 and 3.5 days; PBdSD-6 changed colour between 1 and 1.5 days; PBdSD-7 changed colour between 2 and 3 days and PBdSD-8 changed colour between 1 and 1.5 days. The final composition of these copolymers is in reasonable agreement with the molar feed ratio of the monomers, although there is a larger amount of butadiene than would be expected from the feed ratio. This could either be due to an overestimation of the DPE incorporation or errors associated with weighing the butadiene monomer and are likely to be a consequence of these reactions using a larger molar feed ratio of butadiene to styrene and DPE than the previous reactions.

When block copolymers of poly(styrene-*co*-DPE)-*block*-polybutadiene were synthesized by the sequential addition of butadiene, some chains of poly(styrene-*co*-

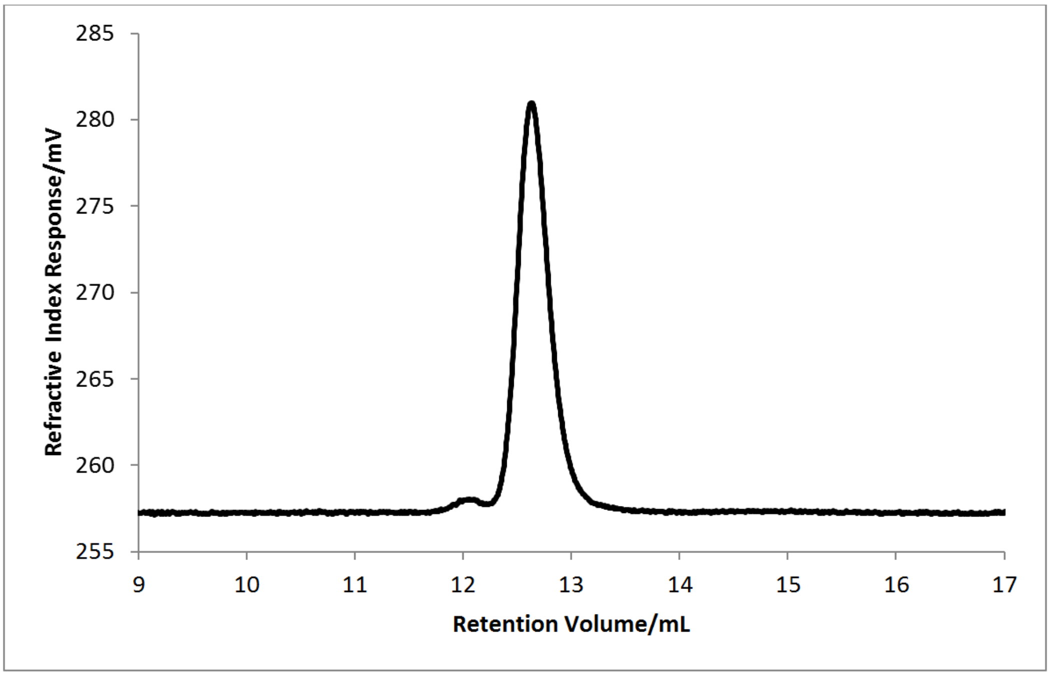

Figure 2.56: SEC chromatogram (refractive index) for poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-6.

DPE) were inadvertently terminated by the introduction of environmental impurities with the butadiene monomer. Using this alternative methodology of simultaneously copolymerizing all three monomers removes the likelihood of introducing environmental impurities during the polymerization and as indicated by the SEC chromatogram (Figure 2.42), there is now no evidence of premature termination which is a clear advantage of this 'fire and forget' approach compared to the sequential addition of monomers.

2.4.3. Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in Toluene

Toluene is also a non-polar solvent and as such the copolymerization of styrene, butadiene and DPE in toluene would be expected to form a similarly tapered copolymer to that formed in benzene. Furthermore, as described in Section 2.1.1, styrene and DPE may form a copolymer with a higher degree of alternation in toluene and hence an excess of DPE may not be required. This would be particularly advantageous in an industrial setting, as there would be less residual DPE monomer,

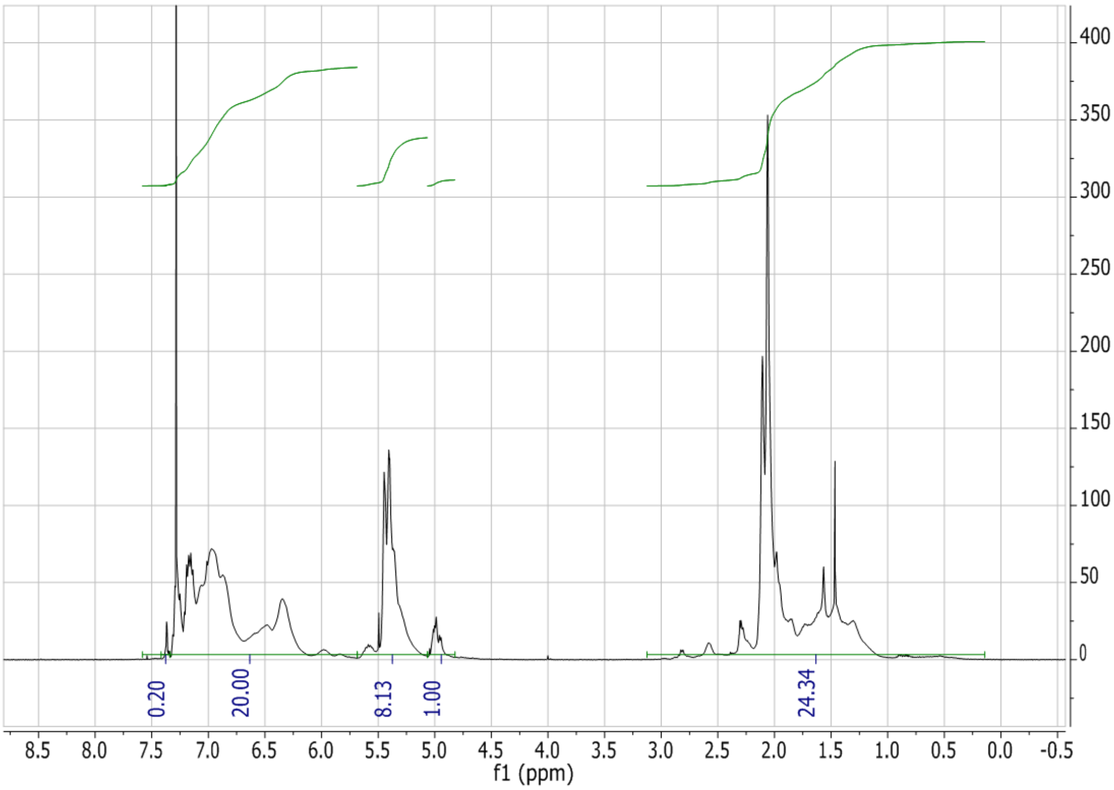

Figure 2.57: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-9, synthesized in toluene with a molar feed ratio of 1.00 : 1.06 : 1.70 styrene : DPE : butadiene.

less wastage of the monomer and no purification required to remove the DPE monomer from the product. The reactivity ratios for the copolymerization of styrene and butadiene in toluene are similar to that in benzene but may even favour a more ordered block copolymer with a shorter tapered section. The reactivity ratio, r_1, (assuming butadiene is M_1 and styrene is M_2) was reported to be 11.3 – 12.9 at 20 °C (compared to that of 10.8 in benzene at 25 °C) and the reactivity ratio, r_2, was found to be 0.004 – 0.04 at 20 °C (compared to 0.04 in benzene at 25 °C).[3] To investigate the hypothesis that a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE) would be formed in toluene, styrene, DPE and butadiene were copolymerized in toluene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.06 : 1.70 (PBdSD-9). As in the case of benzene, the initial reaction colour in toluene was a pale yellow and became red between 14 – 25 hours which suggests that again butadiene is preferentially consumed as expected. The ^{1}H NMR spectrum of the final copolymer is shown in Figure 2.43.

Using the integrals of the aromatic, alkene and aliphatic region of the ^{1}H NMR spectrum, a styrene : DPE : butadiene ratio of 1.00 : 0.57 : 2.40 and a 1,4-polybutadiene content of 88 % was calculated. Alternatively if it is assumed that the styrene : DPE ratio in the terpolymer, PBdSD-9, is equal to that of a poly(styrene-*co*-DPE) copolymer, PSD-7, synthesized with the same molar feed ratio of styrene : DPE then the molar ratio in the resulting terpolymer can be calculated as 1.00 : 0.81 : 2.93. There is a slight discrepancy between the butadiene content in the copolymer and the molar feed ratio, in common with previous reactions. Regardless, the results indicate that when using toluene as the polymerization solvent the results are similar to those obtained when using benzene; namely that butadiene is initially preferentially consumed to form a predominantly polybutadiene section with the styrene and DPE monomers only incorporated when most of the butadiene has been consumed to yield a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE). Furthermore the styrene-*co*-DPE block appears to have a higher degree of alternation than when copolymerized with an equimolar feed ratio in benzene.

2.4.4. Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in THF

As THF is a polar solvent, it was anticipated that an entirely different outcome would occur for the copolymerization of styrene, DPE and butadiene in THF. When butadiene (M_1) and styrene (M_2) are copolymerized in non-polar solvents, butadiene is preferentially consumed over styrene ($r_1 > r_2$), whereas in THF the reactivity ratios switch ($r_2 > r_1$) and styrene is now preferentially consumed over butadiene. According to the literature, in THF at 0 °C the reactivity ratios are $r_1 = 0.2$ and $r_2 = 5.3$ if butadiene is M_1 and styrene is M_2 and at -78 °C the reported reactivity ratios are $r_1 = 0.04$ and $r_2 = 11.0$.[3] It is also now known (from the results of this project) that both butadiene and styrene will copolymerize with DPE to produce almost perfect alternating copolymers. Hence it was expected that in THF, with a molar feed ratio of 1.00 : 2.00 : 1.00 styrene : DPE : butadiene, a tapered copolymer of poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE) should be formed as shown schematically in Figure 2.44.

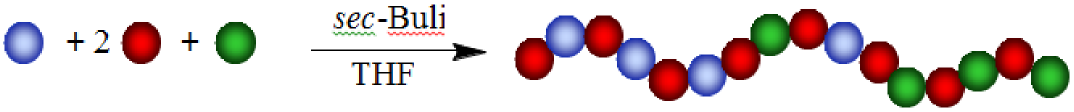

Figure 2.58: Schematic diagram to show the expected copolymer formed when styrene (blue), DPE (red) and butadiene (green) are copolymerized in THF.

Table 2.18: Reactivity ratios for copolymerizations involving butadiene, styrene or DPE in THF.[3]

Monomer 1	Monomer 2	Temperature/°C	r_1	r_2
Butadiene	Styrene	0	0.2	5.3
Butadiene	DPE	0	0.13	0
Styrene	DPE	30	0.13	0

If butadiene is monomer 1, styrene is monomer 2 and DPE is monomer 3, then, as described previously, it can be found from the two component copolymerization reactivity ratios (Table 2.17) that $k_{13} > k_{12} > k_{11}$ (i.e. butadiene preferentially cross-propagates to DPE); $k_{23} > k_{22} > k_{21}$ (i.e. styrene preferentially cross-propagates to DPE) and $k_{32} > k_{31} > k_{33}$ (i.e. DPE preferentially cross-propagates to styrene) assuming $k_{32} > k_{31}$ which is a reasonable assumption as $k_{12} > k_{11}$ and $k_{22} > k_{21}$ (i.e. assuming styrene is a more reactive monomer than butadiene).

It is therefore expected that both butadiene and styrene are most likely to undergo cross-propagation reactions with DPE, although as $\frac{k_{12}}{k_{11}}$ and $\frac{k_{13}}{k_{11}}$ are reasonably similar (5.0 compared to 7.7), butadiene may also react with styrene. As in the previous case when the solvent was benzene, it is not possible to determine whether DPE will preferentially react with styrene or butadiene, but as styrene appears to be the more reactive monomer than butadiene in THF, it is likely that DPE will preferentially react with styrene. A series of copolymerizations of styrene, DPE and butadiene were investigated using THF as the solvent and the reactions were sampled in an attempt to determine the compositional change during the reaction.

Upon initiation of these reactions, the colour of the reaction mixture instantly became red indicating that a proportion of the chain ends were diphenylethyl lithium as expected. As copolymerizations of styrene with DPE in THF, and copolymerizations of butadiene with DPE in THF both result in a red colour, it was expected that the colour of the reaction mixture would remain red throughout. There was a possibility that there may be a slight colour change to a less dark red during the copolymerization signifying butadiene was copolymerizing with DPE instead of styrene copolymerizing with DPE, however, no noticeable colour change was observed and from this visual evidence it was unclear whether styrene or butadiene was preferentially consumed. In the first such copolymerization (PBdSD-10; molar feed ratio = 1.00 : 2.06 : 1.00 styrene : DPE : butadiene) the reaction was sampled after 1 hour (PBdSD-10a); 4 hours (PBdSD-10b); 8 hours (PBdSD-10c) and 22 hours (PBdSD-10d). The final copolymer was terminated after 5 days (PBdSD-10e); however, SEC analysis indicated there was no increase in molecular weight after 22 hours which suggests that the reaction was complete at this point. The stacked ^{1}H NMR spectra for the intermediate samples (PBdSD-10a-c) and the final copolymer of the reaction (PBdSD-10e) are shown in Figure 2.45. The overlaid ^{1}H NMR spectra for PBdSD-10a-e expanded over the alkene region are shown in Figure 2.46. The copolymers (PBdSD-10a-e) were re-precipitated a number of times in order to remove the excess unreacted DPE monomer and to decrease the resulting intense signal at 5.47 ppm corresponding to the alkene protons on the DPE monomer. The signals at 1.86 and 3.75 ppm arise from the THF solvent present in the copolymers. It can be seen from the ^{1}H NMR spectrum (Figures 2.45 and 2.46) that even after 1 hour some butadiene has become incorporated within the copolymer as indicated by the broad peaks in the alkene region (3.3 – 5.7 ppm), although the peaks from 5.0 – 5.7 ppm could arise from a combination of alkene and aromatic signals. As there are no individual peaks that correspond to styrene units it is not possible to quantify the copolymer composition although the alkene peaks do resemble that of poly(butadiene-*co*-DPE) rather than those of polybutadiene. In order to characterize this copolymerization (PBdSD-10) further, it was first necessary to perform another reaction in order to quantify the extent of incorporation of DPE.

To determine the extent of incorporation of DPE in poly(butadiene-*co*-styrene-*co*-DPE) copolymers synthesized in THF, styrene, DPE and butadiene (PBdSD-11; molar feed ratio = 1.0 : 2.0 : 0.9 styrene : DPE : butadiene) were copolymerized without sampling and on a larger scale (total monomer mass = 15.85 g) so that a mass balance/yield

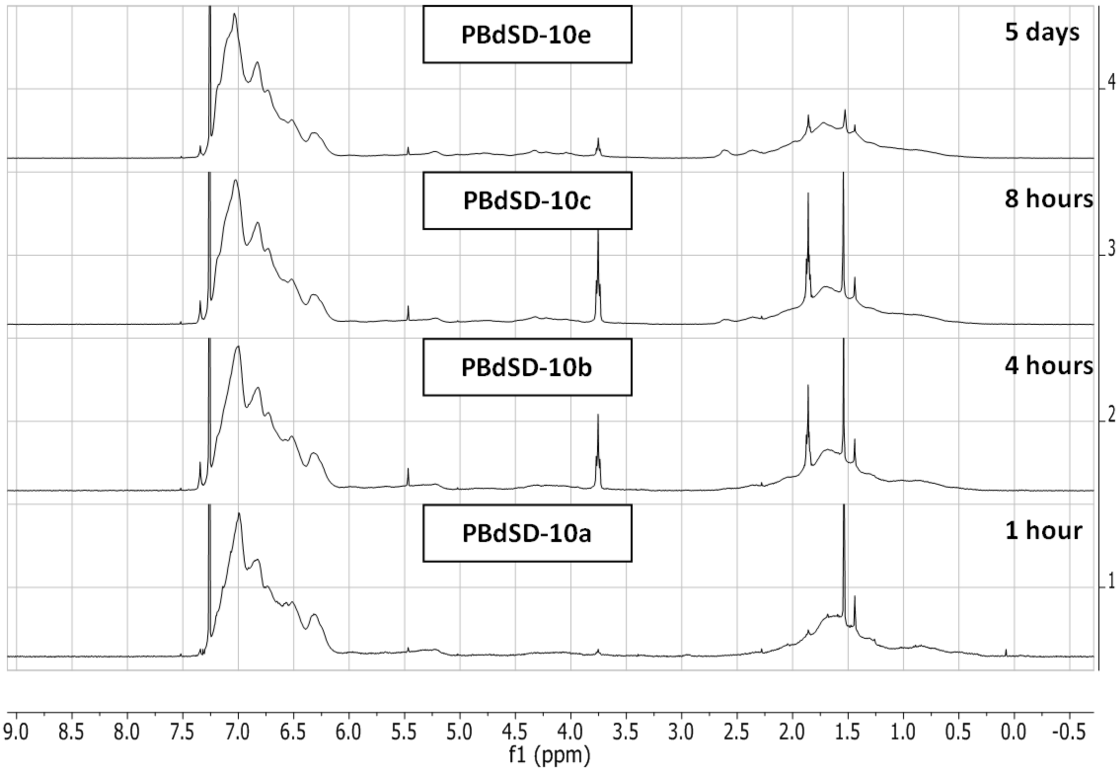

Figure 2.59: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-10a-e, synthesized in THF with a molar feed ratio of 1.00 : 2.06 : 1.00 styrene : DPE : butadiene.

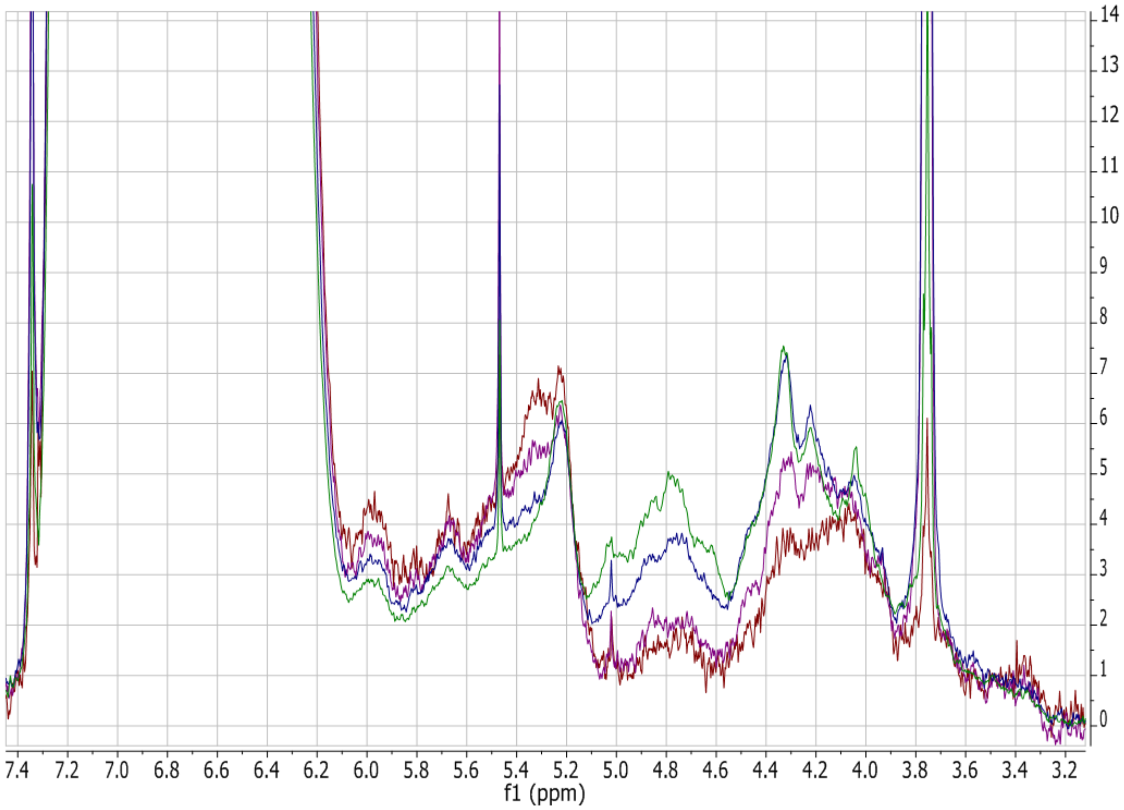

Figure 2.60: Overlay and expansion of the alkene region of the ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-10a-e, synthesized in THF with a molar feed ratio of 1.00 : 2.06 : 1.00 styrene : DPE : butadiene. Red corresponds to PBdSD-10a; purple corresponds to PBdSD-10b; blue corresponds to PBdSD-10c and green corresponds to PBdSD-10e.

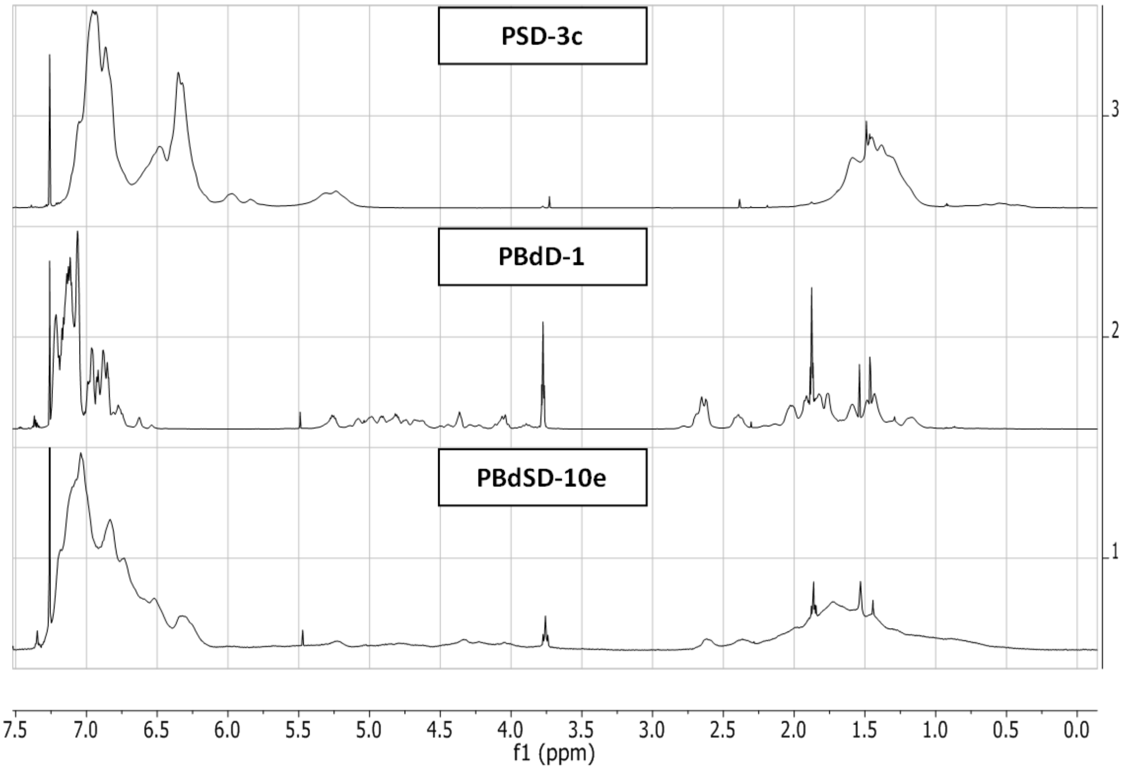

Figure 2.61: ^{1}H NMR spectra (in $CDCl_3$) of poly(styrene-*co*-DPE) synthesized in benzene, PSD-3c; poly(butadiene-*co*-DPE) synthesized in THF, PBdD-1 and poly(butadiene-*co*-DPE-*co*-styrene) synthesized in THF, PSD-10e.

calculation could be accurately used to determine whether all the DPE had been consumed by the polymerization. The reaction was stirred at 0 °C for 3 days before being terminated. After re-precipitation to remove any residual unreacted monomer, the yield was close to quantitative (96 %) suggesting DPE was fully incorporated.

Returning to the copolymers prepared in PBdSD-10 it is now possible to estimate the compositional ratios if it is assumed (a) DPE is fully incorporated, i.e. the moles of DPE in the copolymer = the moles of styrene in the copolymer + the moles of butadiene in the copolymer and (b) that the 1,4-polybutadiene microstructure content is the same as when butadiene is copolymerized with DPE (PBdD-1), i.e. the 1,4-polybutadiene microstructure content is 64 %. Examining the stacked ^{1}H NMR spectra for poly(styrene-*co*-DPE), PSD-3c; poly(butadiene-*co*-DPE), PBdD-1, and poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-10e (Figure 2.47), the peak at 5.0 – 5.5 ppm in the spectrum of the terpolymer (PBdSD-10e) will have contributions from polybutadiene and the aromatic signals from styrene and/or DPE. As the following calculations will only involve the aromatic and aliphatic regions, this peak should not significantly affect the accuracy of the calculations. However, a comparison of the ^{1}H NMR spectra of poly(styrene-*co*-DPE) and poly(butadiene-*co*-DPE) would suggest that aromatic protons contribute predominantly to the intensity of the peak(s) in this region and the integral from this peak was included in the total integral arising from aromatic protons in the following calculations.

In the first sample, PBdSD-10a, from the integral of the aliphatic and aromatic region the following equations can be obtained (after subtracting the integrals from $CHCl_3$ and H_2O):

$$3x + 2y + 3z_{1,2} + 4z_{1,4} = 0.92 \qquad [2.16]$$

and:

$$5x + 10y = 2.38 \qquad [2.17]$$

where $x : y : z$ is the ratio of styrene : DPE : butadiene in the copolymer, $z_{1,2} : z_{1,4}$ is the ratio of 1,2-polybutadiene : 1,4-polybutadiene, and $z = z_{1,2} + z_{1,4}$. It follows from the first assumption (a) that:

$$y = x + z \qquad [2.18]$$

and from the second assumption (b) that:

$$z_{1,2} = 0.36z \qquad [2.19]$$

and:

$$z_{1,4} = 0.64z \qquad [2.20]$$

Hence substituting equation 2.18 into equation 2.17, and equations 2.18, 2.19 and 2.20 into equation 2.16 gives the following equations:

$$15x + 10z = 2.38 \qquad [2.21]$$

and:

$$5x + 5.64z = 0.92 \qquad [2.22]$$

Table 2.19: Compositions of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-10a-e, synthesized by the copolymerization in THF with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 2.06 : 1.00 (assuming full incorporation of DPE in the final copolymer).

Sample	Reaction Time/hours	Sty : DPE : Bd in copolymer
PBdSD-10a	1	1.00 : 1.45 : 0.45
PBdSD-10b	4	1.00 : 1.33 : 0.33
PBdSD-10c	8	1.00 : 1.95 : 0.95
PBdSD-10d	22	1.00 : 2.52 : 1.52
PBdSD-10e	123	1.00 : 2.33 : 1.33

Table 2.20: Molecular weight data (obtained using triple detection SEC with *dn*/*dc* = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-10 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in THF.

Sample	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-10a	14,300	16,400	1.15
PBdSD-10b	44,100	47,000	1.07
PBdSD-10c	60,500	64,800	1.07
PBdSD-10d	67,700	73,400	1.08
PBdSD-10e	67,700	74,000	1.09

Solving equations 2.21 and 2.22 gives a ratio of styrene : butadiene = 2.22 : 1.00, and from equation 2.18, a ratio of styrene : DPE : butadiene = 1.00 : 1.45 : 0.45, indicating that styrene is indeed incorporated preferentially. The composition and molecular weight data for all the intermediate samples (PBdSD-10a-d) and final copolymer of reaction PBdSD-10 (PBdSD-10e) are shown in Table 2.18 and Table 2.19 respectively. It should be noted that this method is subject to potential error arising from using the integral of the aliphatic region and also due to the assumption that the 1,4-polybutadiene microstructure is 64 %. These potential errors could account for the fact that two different compositions are obtained for sample PBdSD-10d and PBdSD-10e despite the fact that SEC indicates that the reaction was complete by 22 hours, and furthermore the final composition does not match the molar feed ratio. Nevertheless, the trend in the data does support the hypothesis that styrene appears to be consumed in preference to butadiene.

To confirm that styrene is incorporated preferentially, a subsequent copolymerization with an almost equimolar ratio of monomers (styrene : DPE : butadiene = 1.00 : 1.07 : 1.02) was performed (PBdSD-12). In this case it was anticipated that in the first instance a nearly alternating copolymer of styrene and DPE would form followed by the formation of a butadiene rich block as the consumption of both styrene and DPE nears completion. As expected, upon initiation the colour of the reaction mixture was red indicating a proportion of the chain ends are living DPE. It was anticipated that styrene and DPE would be preferentially consumed and that the colour of the reaction mixture would become pale yellow in time as the styrene and DPE were consumed, indicative of propagating butadienyllithium. Whilst the aim was to sample the reaction upon this colour change, the red colour persisted and after 24 hours the reaction mixture was sampled. Surprisingly the red colour of the reaction mixture persisted and after 4 days the reaction was terminated.

The red colour is indicative of the presence of diphenylethyllithium and therefore suggests that a proportion of the chain ends are living DPE throughout the reaction. Whilst this is contrary to the expectation that DPE would be preferentially consumed, it may be that the colour of the reaction mixture is dominated by a low concentration of living DPE. The ^{1}H NMR spectrum for PBdSD-12a (Figure 2.48) is identical to the final copolymer, PBdSD-12b, and the SEC indicates that the reaction was complete after 24 hours and hence it is not possible to determine the composition at the early stages of the reaction. The ^{1}H NMR spectrum of PBdSD-12a (Figure 2.48) has signals which resemble those of homopolybutadiene in THF (Figure 2.49) as well as peaks which resemble the copolymer poly(butadiene-*co*-DPE) as shown by the stacked ^{1}H NMR spectra (Figure 2.47). This supports the theory that styrene and DPE are preferentially consumed in the early stages of the polymerization leaving residual butadiene monomer to form a butadiene rich block towards the end of the reaction. This reaction was repeated but with sampling at earlier stages of the reaction to determine the sequence of monomer consumption.

In this repeat reaction (PBdSD-13) the molar feed ratio of styrene : DPE : butadiene was (1.00 : 1.05 : 1.14) and the reaction was sampled after 30 minutes (PBdSD-13a); 45 minutes (PBdSD-13b); 1 hour (PBdSD-13c) and 1.8 hours (PBdSD-13d). The reaction

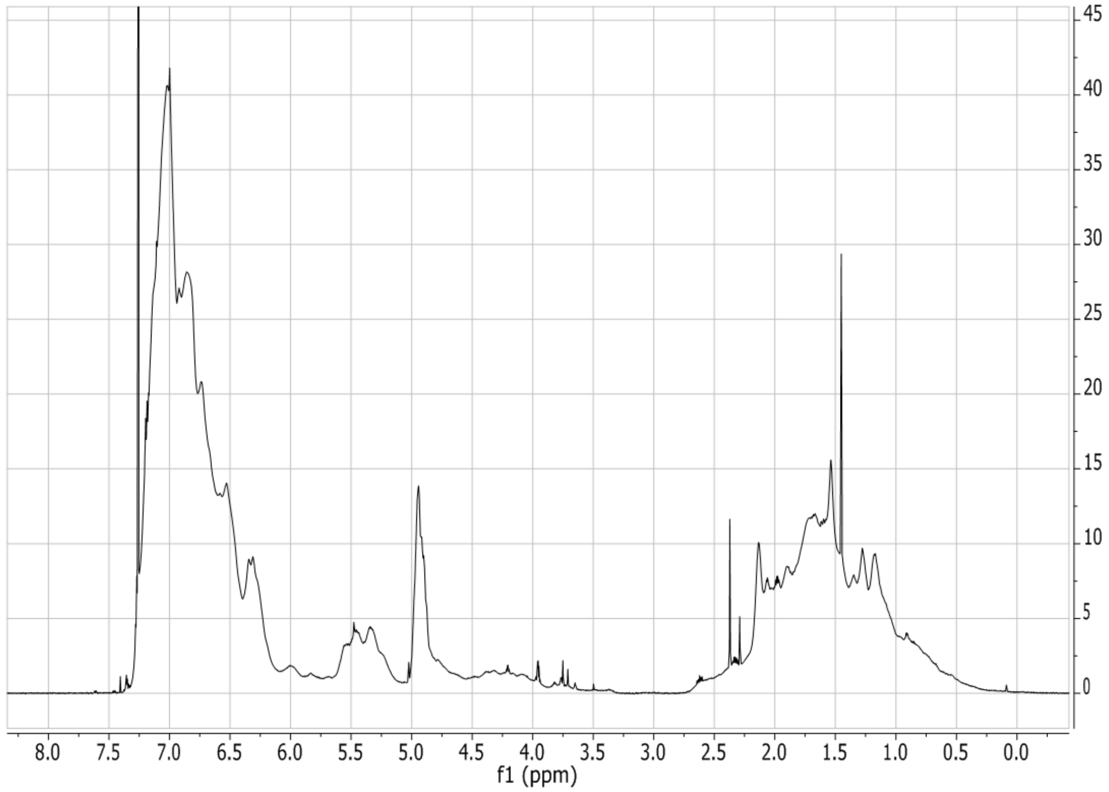

Figure 2.62: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-12a, synthesized in THF with a molar feed ratio of 1.00 : 1.07 : 1.02 styrene : DPE : butadiene.

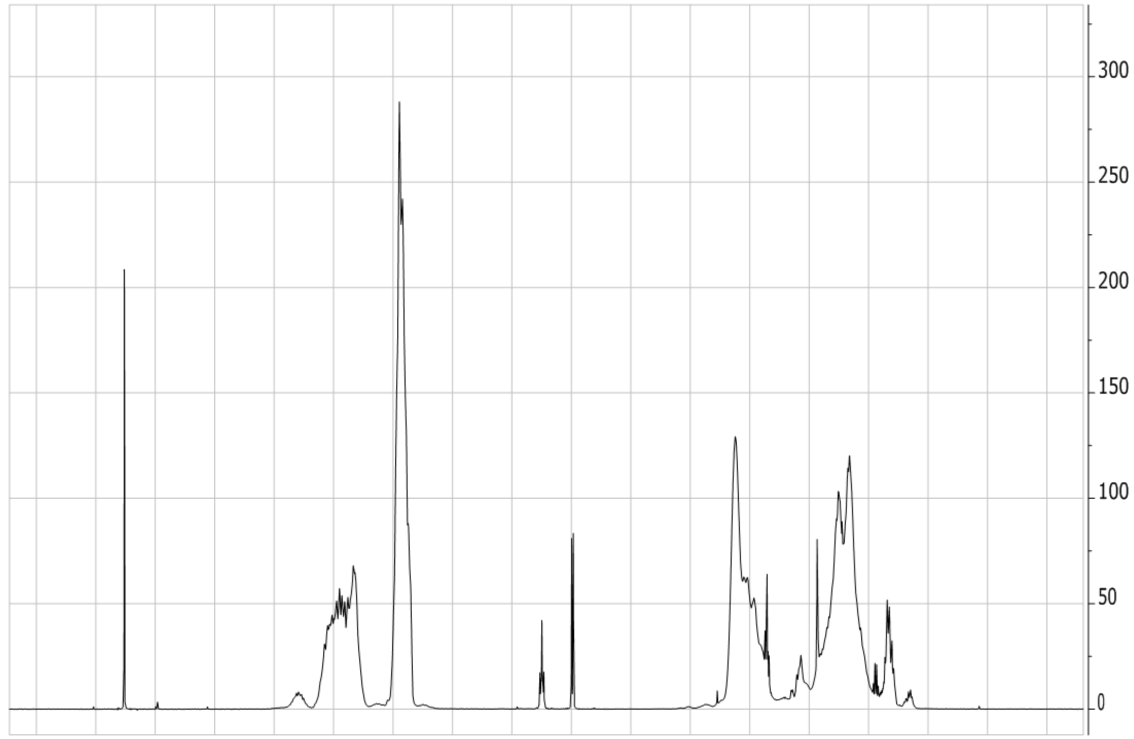

Figure 2.63: ^{1}H NMR spectrum (in $CDCl_3$) of high 1,2-polybutadiene, synthesized in THF (1,2-polybutadiene content = 84 %).

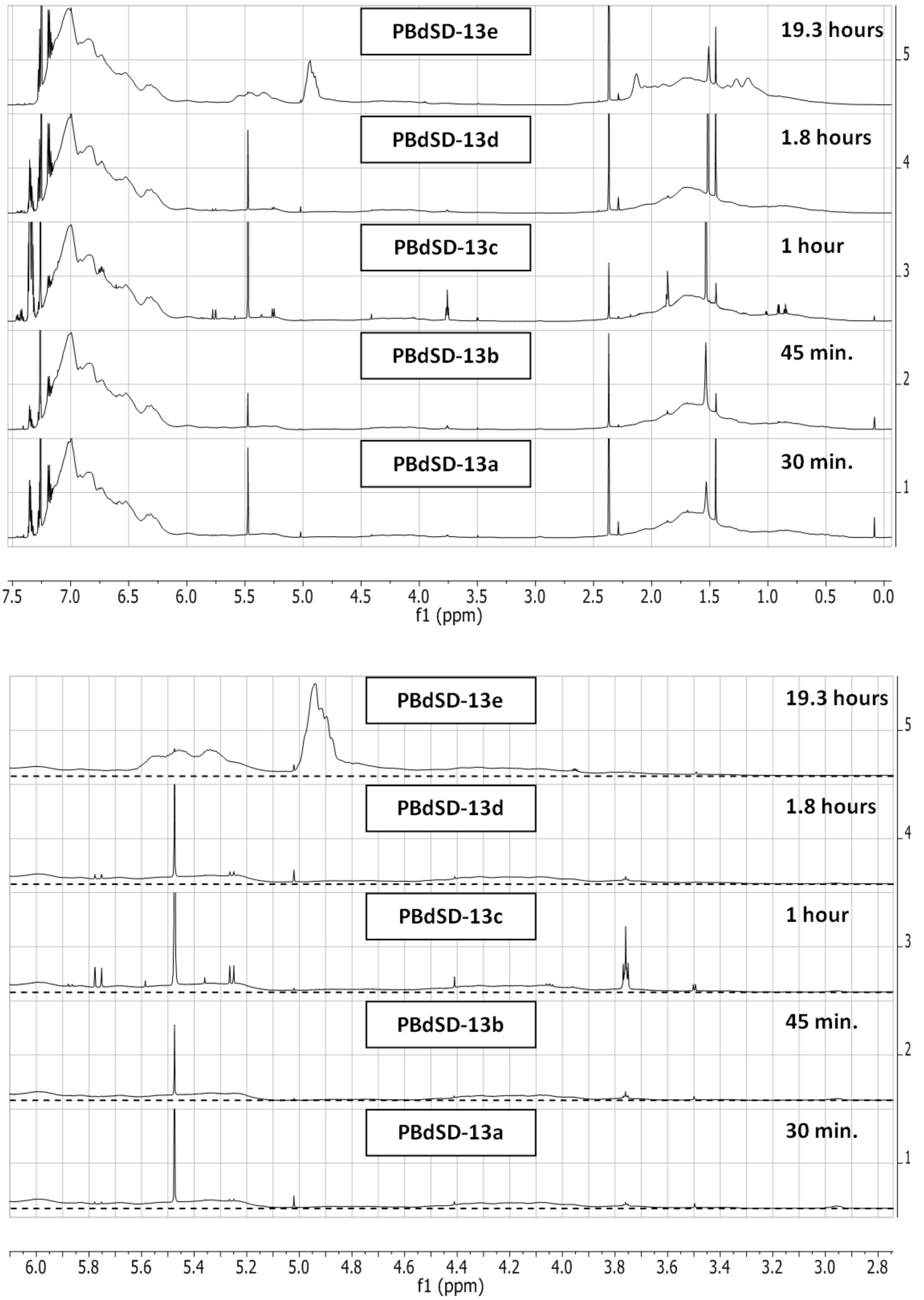

Figure 2.64: (a) ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-13a-e, synthesized in benzene with a molar feed ratio of 1.00 : 1.05 : 1.14 styrene : DPE : butadiene and (b) expansion of the alkene region (2.8 – 6.0 ppm) with the baseline indicated by a dotted line.

Table 2.21: Molecular weight data (obtained using triple detection SEC with *dn*/*dc* = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-13 samples and final copolymer synthesized by the simultaneous copolymerization of butadiene, styrene and DPE in THF with a molar feed ratio of 1.00 : 1.05 : 1.14 styrene : DPE : butadiene

Sample	Reaction Time/hours	M_n/g mol^{-1}	M_w/g mol^{-1}	Đ
PBdSD-13a	0.5	13,800	16,200	1.18
PBdSD-13b	0.75	20,400	23,400	1.15
PBdSD-13c	1.0	25,300	28,500	1.13
PBdSD-13d	1.8	42,000	46,300	1.10
PBdSD-13e	19.3	78,600	90,200	1.15

was terminated after 19.3 hours of stirring at 0 °C. The stacked ^{1}H NMR spectra for the intermediate samples and the final copolymer of the reaction PBdSD-13 (PBdSD-13e) are shown in Figure 2.50 and reveals that the compositions of the four samples (PBdSD-13a to 13d) are practically identical and the peaks corresponding to butadiene units resemble the copolymer poly(butadiene-*co*-DPE) indicating some early incorporation of butadiene. However, the final sample (PBdSD-13e) contains peaks which closely resembles the homopolymer polybutadiene with a high 1,2-polybutadiene content indicating that butadiene is predominantly incorporated in the later stages of the reaction.

SEC data (see Table 2.20) shows that the M_n of the samples increase from 13,800 to 42,000 g mol^{-1} and the final copolymer is 78,600 g mol^{-1} (using a *dn*/*dc* value for polystyrene). This suggests that the copolymer sample PBdSD-13d was extracted when the monomer conversion was approximately 50 %. As ^{1}H NMR spectroscopy reveals that the incorporation of butadiene in PBdSD-13d was low, this clearly shows that the majority of butadiene is consumed in the later stages of the reaction (i.e. after ~ 50 % conversion) and hence styrene is preferentially consumed before butadiene. Therefore when styrene, DPE and butadiene are copolymerized in THF, an alternating tapered copolymer with a gradient of styrene to butadiene, poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE), is formed (shown schematically in Figure 2.51), or if a reduced amount of DPE is used then poly(styrene-*co*-DPE)-*co*-polybutadiene will be formed (shown schematically in Figure 2.52) although it should be noted that there will be a

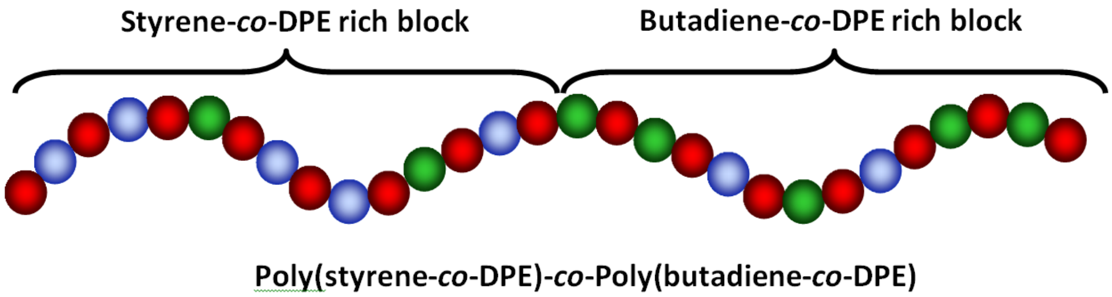

Figure 2.65: Schematic diagram to show the potential structure of a poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE) terpolymer when polymerized in THF with a molar feed ratio of styrene : DPE : butadiene = 1 : 2 : 1 where styrene is represented by blue balls, DPE by red balls and butadiene by green balls.

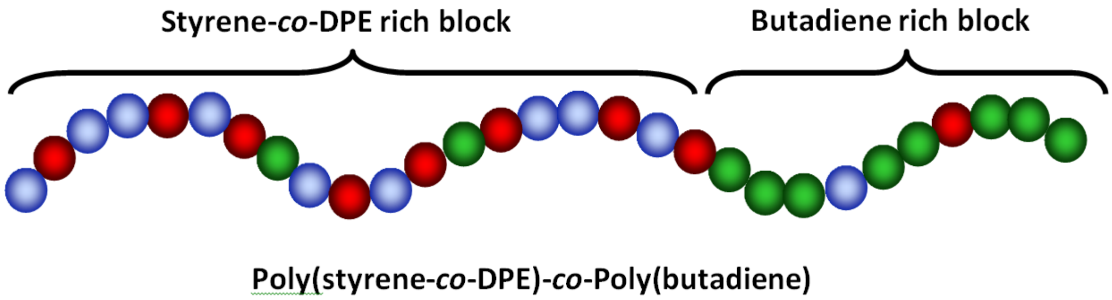

Figure 2.66: Schematic diagram to show the potential structure of a poly(styrene-*co*-DPE)-*co*-poly(butadiene) terpolymer when polymerized in THF with a molar feed ratio of styrene : DPE : butadiene = 1 : 1 : 1 where styrene is represented by blue balls, DPE by red balls and butadiene by green balls.

few imperfections, such as some incorporation of butadiene in the first block and DPE not being fully incorporated in the initial block.

The reaction temperature can also have a strong influence on reactivity ratios as evidenced by the copolymerization of butadiene (M_1) and styrene (M_2) in THF in which the reactivity ratios are $r_1 = 0.04$ and $r_2 = 11.0$ at -78 °C compared to $r_1= 0.2$ and $r_2 = 5.3$ at 0 °C. Hence the copolymerization of styrene, DPE and butadiene in THF should provide a more defined (block-like) tapered copolymer at -78 °C with a shorter tapered middle block. However, the copolymerization of styrene, DPE and butadiene in THF (molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.94 : 0.94) (PBdSD-14) at -78 °C resulted in a monomer conversion below 20 % even after 10 days (the M_n was calculated as 8,200 g mol^{-1} when the target molecular weight was 60,000 g mol^{-1} and the yield was only 17 %). The ^{1}H NMR spectrum is shown in Figure 2.53, which shows very little incorporation of butadiene, however, there is a large amount of DPE

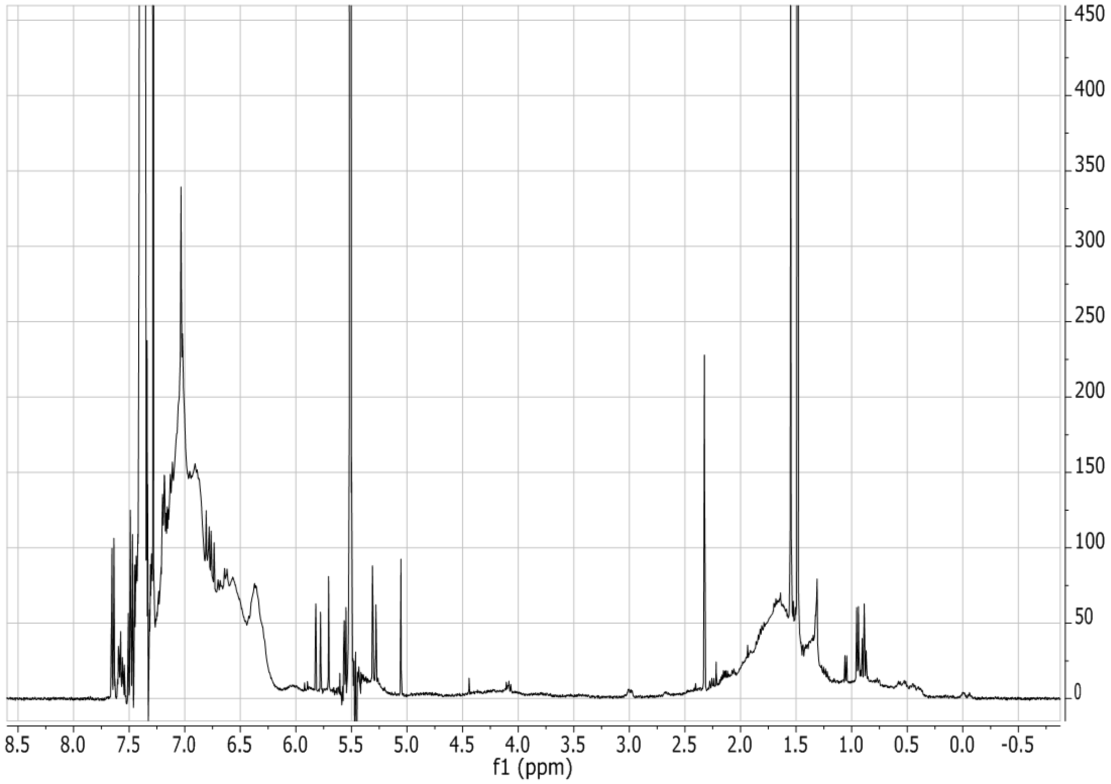

Figure 2.67: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), product of reaction PBdSD-14, synthesized in THF with a molar feed ratio of 1.00 : 1.94 : 0.94 styrene : DPE : butadiene.

monomer (5.5 ppm) and hence the yield which was calculated from the mass is likely to be even less than 17 %. Thus whilst the reactivity ratios may be more favourable at lower temperatures the reaction is retarded to such an extent that it is impractical to prepare sequence controlled copolymers at such a low temperature.

2.4.5. Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in Toluene with TMEDA injection

In previous work with 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene it was found that the rate of end-capping in non-polar solvents was enhanced by the addition of TMEDA,[27-28] hence it seemed that it was a reasonable hypothesis that the incorporation of DPE could be increased when styrene, DPE and butadiene are copolymerized in non-polar solvents if TMEDA, a polar additive was added after the consumption of butadiene. However, it was decided not to add TMEDA from the outset since the presence of TMEDA from the start of the reaction would result in it acting as a randomizer leading to the incorporation of styrene and potentially DPE content in the first block,[3] and moreover, the TMEDA would also alter the butadiene microstructure to increase the 1,2-content. Hence, the aim was to inject TMEDA as soon as the colour of the reaction mixture began to change from a pale yellow to a slightly darker yellow indicating the complete consumption of butadiene and the onset of styrene/DPE consumption.

Prior to carrying out a terpolymerization, and to determine whether TMEDA would increase the incorporation of DPE as described, the copolymerization of styrene and DPE in toluene in the presence of TMEDA was investigated. In a first attempt the copolymerization in toluene of an equimolar feed ratio of styrene and DPE was carried out in the presence of TMEDA (2 mole equivalents with respect to lithium). A target molecular weight of 50,000 g mol^{-1} was chosen specifically to allow accurate analysis by ^{1}H NMR spectroscopy. However, this reaction was unsuccessful and a very low yield of 10 % was obtained. This was believed to be due to the presence of environmental impurities (present prior to the start of the reaction or introduced by the reaction vessel leaking during the polymerization), however, time did not allow for a repeat of this reaction.

A subsequent copolymerization was performed in toluene with a molar feed ratio of styrene : DPE = 1.00 : 1.06 in the presence of TMEDA (2 mole equivalents with respect to lithium) with a target molecular weight of 1,500 g mol^{-1} (PSD-11) specifically to allow analysis by MALDI-ToF MS. The resulting copolymer was obtained in (nearly) quantitative yield (94 %) and the MALDI-ToF mass spectrum of PSD-11 (Figure 2.54) revealed that the copolymer sequence was highly alternating. Indeed almost every signal in the MALDI-ToF mass spectrum corresponds to a perfectly alternating chain. As these results seemed to confirm that the presence of TMEDA does promote the incorporation of DPE in a copolymerization with styrene, subsequent terpolymerizations with styrene, DPE and butadiene with the addition of TMEDA were investigated.

Thus a copolymerization of styrene, DPE, and butadiene in toluene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.02 : 1.82 was then performed with a target molecular weight of 50,000 g mol^{-1} (PBdSD-15). The reaction was stirred at room temperature (~18 °C) for 25.6 hours at which point the pale yellow colour of the

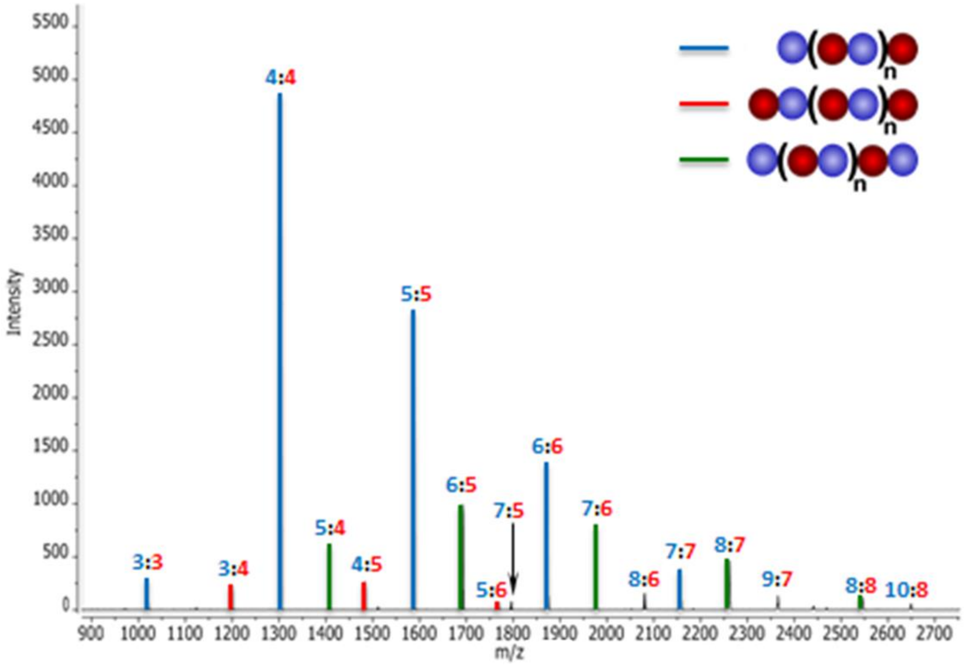

Figure 2.68: MALDI-ToF mass spectrum for the copolymer PSD-11 prepared by the anionic copolymerization (in toluene) of styrene and DPE (monomer feed ratio of styrene : DPE = 1.00 : 1.06) with TMEDA. The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

reaction mixture had only just begun to slightly darken, at which point 48 µL (2 mole equivalents with respect to lithium) of TMEDA was injected. The colour of the reaction mixture instantly changed from pale yellow to red suggesting that the cross-propagation rate of butadiene to styrene and DPE had been significantly increased. The reaction was stirred for a further 2.6 days before being terminated with degassed methanol. Surprisingly only a 34 % yield was obtained, the molecular weight, M_n, was analysed as only 22,700 g mol^{-1} and the ^{1}H NMR spectrum (Figure 2.55) indicated there was relatively low incorporation of styrene and/or DPE (i.e. approximately 28 % of the expected amount relative to the analogous terpolymerization in toluene in the absence of TMEDA). Using the integrals of the aromatic, alkene and aliphatic regions it was possible to obtain an estimate of the styrene : DPE : butadiene ratio = 1.00 : 0.02 : 2.76 suggesting a very low incorporation of DPE. However, as discussed in Section 2.4.2, it is inaccurate to calculate the styrene : DPE ratio using the aliphatic region when the butadiene signals are so intense. Hence whilst this indicates that the DPE has not been incorporated it is not possible in this case to distinguish by ^{1}H NMR spectroscopy whether the incorporation of styrene and/or DPE is low, but given that styrene can homopolymerize and DPE cannot it is more likely that DPE has been excluded.

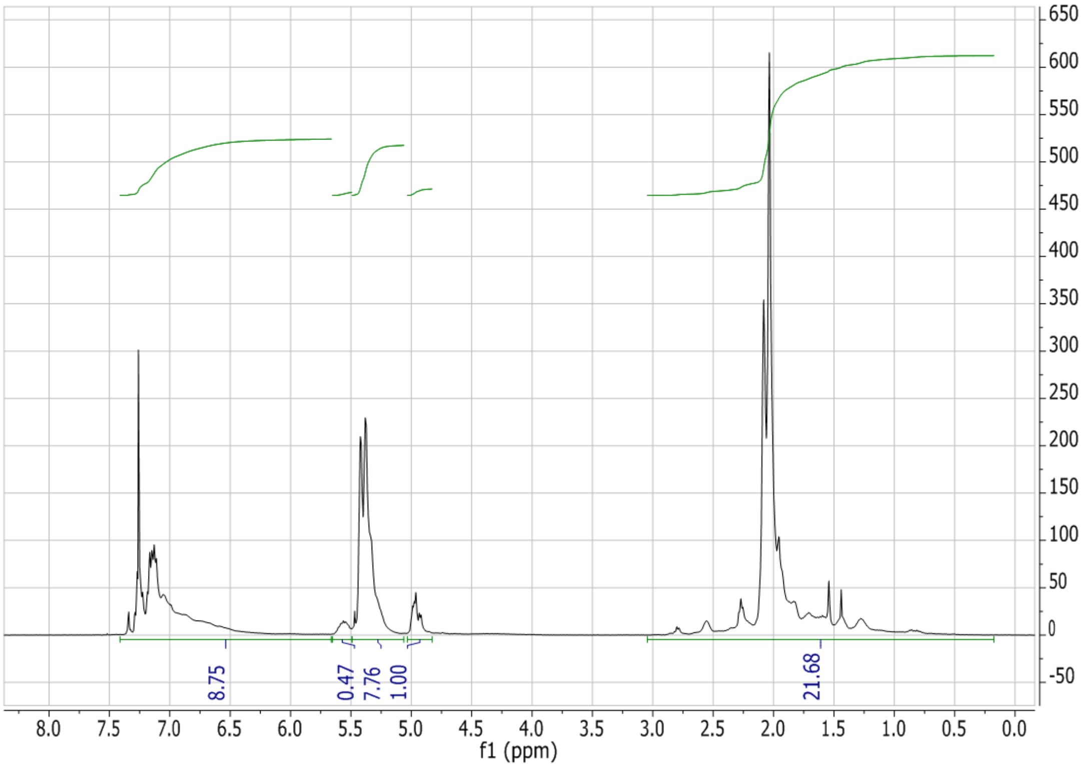

Figure 2.69: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-15, synthesized in toluene with a molar feed ratio of 1.00 : 1.02 : 1.82 styrene : DPE : butadiene with TMEDA injected after 25.6 hours when the reaction had just begun to darken.

The reaction was repeated to clarify these unexpected results. In a similar fashion to the previous reaction, styrene, DPE, and butadiene were copolymerized in toluene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.06 : 1.60 and a target molecular weight of 50,000 g mol^{-1} (PBdSD-16). It was decided that this time TMEDA would be injected when the reaction mixture became dark yellow. It was found in Section 2.4.2. that the time taken for the reaction mixture to change colour is not always consistent, in this case the reaction mixture became dark yellow after the reaction mixture had been stirred at room temperature for 24 hours, at which point 65 μL (2 mole equivalents with respect to lithium) of TMEDA was injected and again the colour of the reaction mixture instantly became red. The reaction was allowed to proceed for 3 days at room temperature before being terminated. Again a low yield (39 %) was obtained, the M_n was calculated to be 19,500 g mol^{-1} and the ^{1}H NMR spectrum indicates a low incorporation of the styrene-*co*-DPE block (Figure 2.56); the styrene : DPE : butadiene ratio in the copolymer was calculated as approximately 1.00 : 0.05 : 2.49.

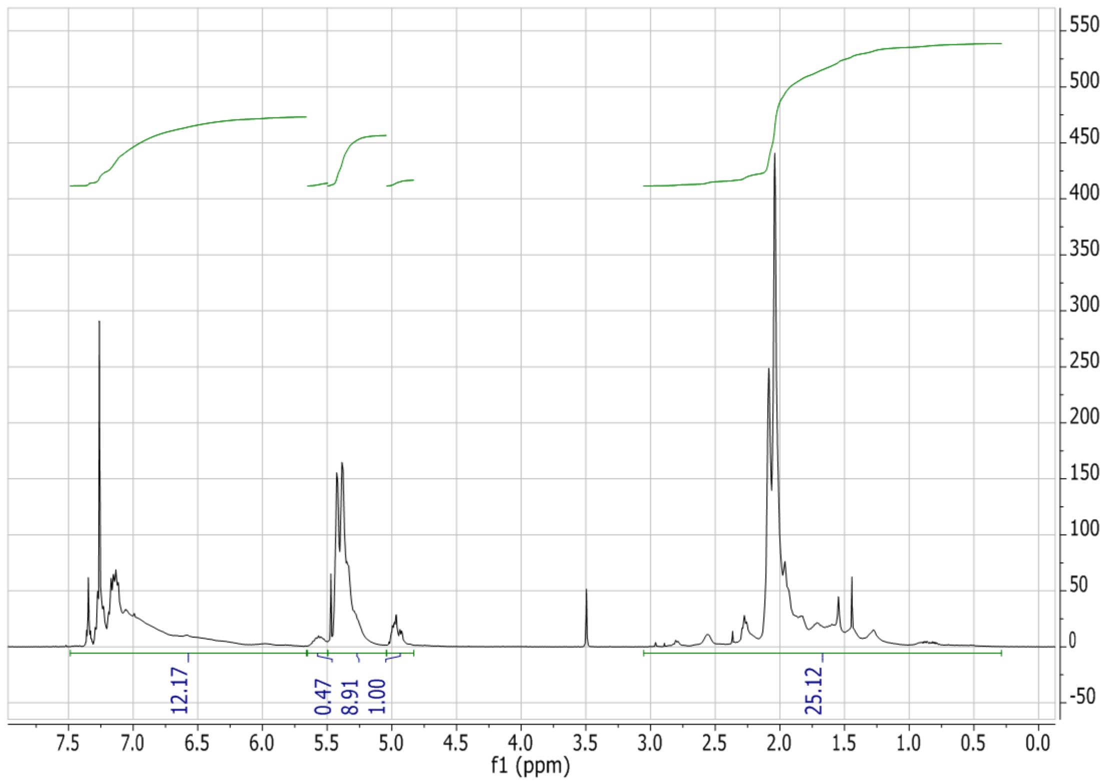

Figure 2.70: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-16, synthesized in toluene with a molar feed ratio of 1.00 : 1.06 : 1.60 styrene : DPE : butadiene with TMEDA injected after 23.8 hours when the reaction was dark yellow.

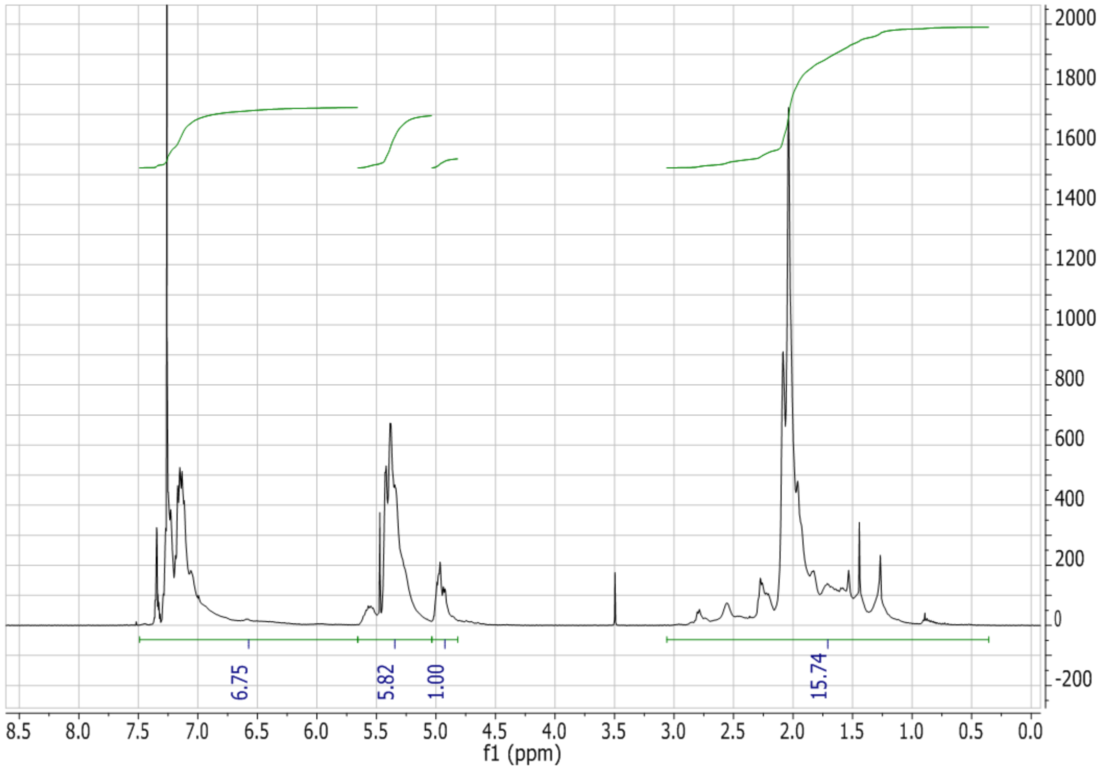

Figure 2.71: ^{1}H NMR spectrum (in $CDCl_3$) of Poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-17, synthesized in toluene with a molar feed ratio of 1.00 : 1.00 : 1.87 styrene : DPE : butadiene with TMEDA injected after 22 hours when the reaction mixture was red.

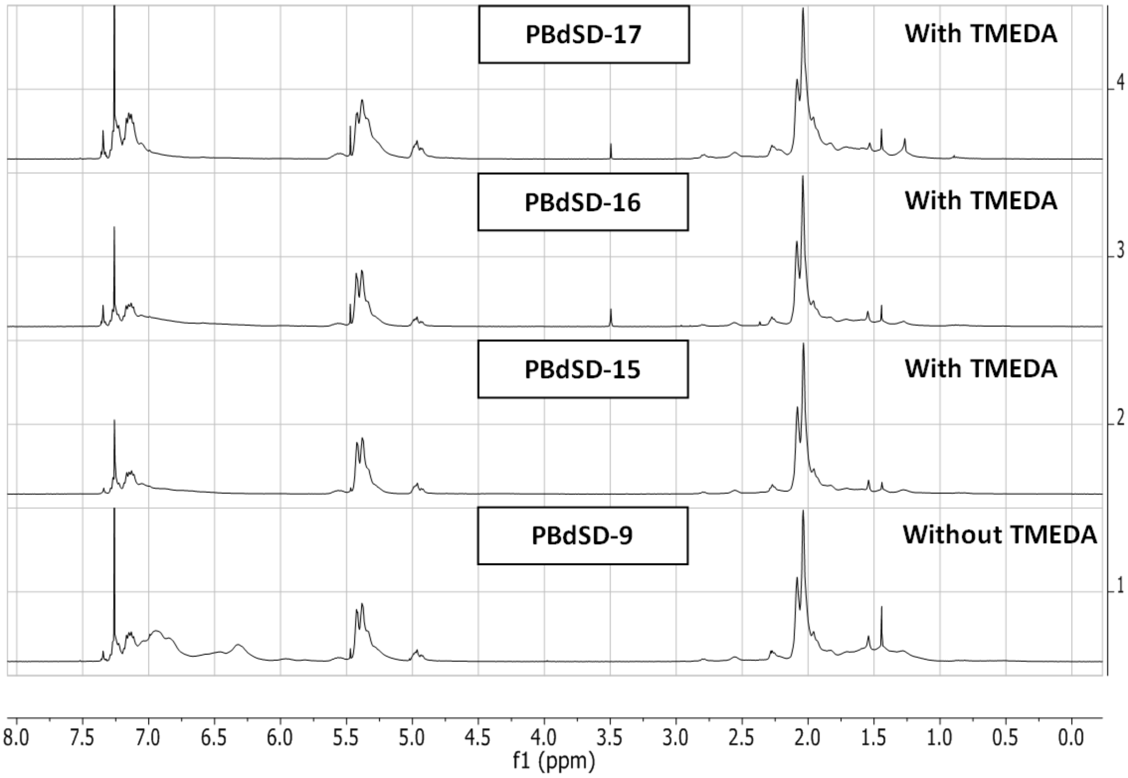

Figure 2.72: ^{1}H NMR spectra (in $CDCl_3$) of poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-9 (without TMEDA); PBdSD-15 (TMEDA injected when the reaction was pale yellow); PBdSD-16 (TMEDA injected when the reaction was dark yellow) and PBdSD-17 (TMEDA injected when the reaction was red).

The reaction was repeated a final time with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.00 : 1.87 and a target molecular weight of 50,000 g mol^{-1} (PBdSD-17). This time the reaction was stirred at room temperature (~20 °C) until the reaction mixture was red before the injection of 44 μL of TMEDA (2 mole equivalents with respect to lithium) which occurred after 22 hours. The reaction was allowed to proceed for a further 4 days at room temperature before being terminated. A yield of 43 % was obtained, the M_n was calculated as 32,900 g mol^{-1} and the ^{1}H NMR spectrum is shown in Figure 2.57. This time the styrene : DPE : butadiene ratio in the copolymer was estimated to be 1.00 : 0.00 : 2.64. For comparison the stacked ^{1}H NMR spectra of all three experiments and the ^{1}H NMR spectrum of PBdSD-9 (molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.06 : 1.70 which was performed in toluene without TMEDA) are shown in Figure 2.58.

The consistency of the incorporation of DPE in these reactions (PBdSD-16 – 18) and the stark difference to when the copolymerization of styrene and DPE in the presence of TMEDA (PSD-11) was surprising and prompted a further investigation of the literature. A paper was found on the copolymerization of styrene and DPE that reported that “the addition of a lewis base such as THF or alkyl potassium compounds…favour the polymerization of styrene, thus resulting in lower DPE incorporation".[21] Considering the results of this article and the copolymerizations PBdSD-16 to 18 it was concluded that TMEDA inhibits the incorporation of DPE and that the copolymer PSD-11 (poly(styrene-*co*-DPE) synthesized in toluene with TMEDA) was therefore an outlier which cannot be easily explained. It is also surprising that the paper[21] reported that when THF is used as an additive, it disfavours the incorporation of DPE. This is surprising because it has been shown herein and by Yuki *et al*.[2] that styrene and DPE form a highly alternating sequence when copolymerized with THF as the solvent. It is possible that the role that THF plays when used as a solvent is different to the role played by THF when used as an additive in a non-polar solvent. In the case of the copolymerization of styrene and DPE in toluene with TMEDA (PSD-11) it is possible that the higher concentration of TMEDA with respect to toluene (0.39 M) meant that TMEDA was no longer acting just as an additive, and the lower incorporation of DPE only occurs when TMEDA is present in a low concentration. For comparison, the concentration of TMEDA in the copolymerizations PBdSD-16 to 18 was between 0.004 and 0.005 M. It should also be noted that these results indicate an increase in the value of k_{11}/k_{12} (if styrene is monomer 1 and DPE is monomer 2) but provide no information on the individual values of k_{11} or k_{12} and hence these results do not contradict the previous examples in literature in which TMEDA is used to enhance k_{12} and promote the end-capping with DPE derivatives.[27]

The low yields obtained for copolymers PBdSD-16 to 18 are largely explained by the low incorporation of DPE, for example if DPE is excluded from the yield calculation then the yields of PBdSD-16, 17 and 18 become 65 %, 78 % and 81 % respectively. The copolymers PBdSD-17 and 18 therefore show a reasonably high yield (assuming no incorporation of DPE), however, that of PBdSD-16 is still quite modest.

It should also be noted that whilst the 1,4-polybutadiene content for PBdSD-15 and PBdSD-16 were 89 % and 90 % respectively, in the last reaction (PBdSD-17) the 1,4-polybutadiene content was 84 %. Whilst this is not a particularly large difference, it is difficult to explain why the 1,4-polybutadiene content would be lower in this reaction, the presence of TMEDA could lower the 1,4-polybutadiene content, but as it was added at a later stage of the reaction than the previous two experiments it seems unlikely that the 1,4-polybutadiene content would be reduced in this experiment but remain close to 90 % in the previous experiments.

2.4.6. Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in Benzene with a Difunctional Initiator

It has been shown above that styrene, DPE and butadiene form a tapered copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE) when copolymerized in benzene using a 'fire and forget' approach. In light of that it was surmised that if a difunctional initiator is used in an analogous 'fire and forget' copolymerization, then the monomers should be consumed in the same fashion. Thus butadiene should polymerize from the initiator before crossing over to styrene and DPE to prepare a tapered "tri-block" copolymer of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) as shown schematically in Figure 2.59. As these copolymers should have an almost ABA "tri-block" structure, they could potentially be useful as thermoplastic elastomers and this 'fire and forget' approach could allow a useful alternative method of synthesizing them.

The addition of *sec*-butyllithium (in the presence of lithium *sec*-butoxide) to 1,3-*bis*(1-phenylvinyl)benzene results in the formation of such a difunctional initiator (Figure 2.60). The addition of lithium *sec*-butoxide is required to ensure an equal rate of initiation from both active sites and hence allows copolymers with a narrow, monomodal molecular weight distribution to be obtained.[29] The initiator precursor, 1,3-*bis*(1-phenylvinylbenzene) was synthesized according to a previously reported method.[30] Upon addition of *sec*-butyllithium to 1,3-*bis*(1-phenylvinylbenzene) a red colour resulting from the dilithium initiator was observed. The reaction was allowed to proceed for 2 hours at 60 °C to ensure complete conversion of the initiator precursor into the dilithium initiator.

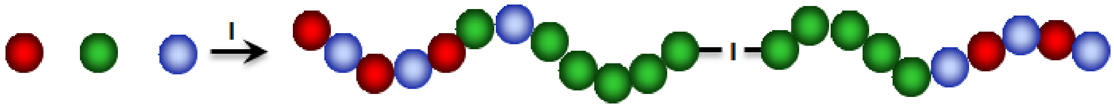

Figure 2.73: Schematic diagram to show the expected copolymer formed when styrene (blue), DPE (red) and butadiene (green) are copolymerized in benzene with a difunctional initiator, I.

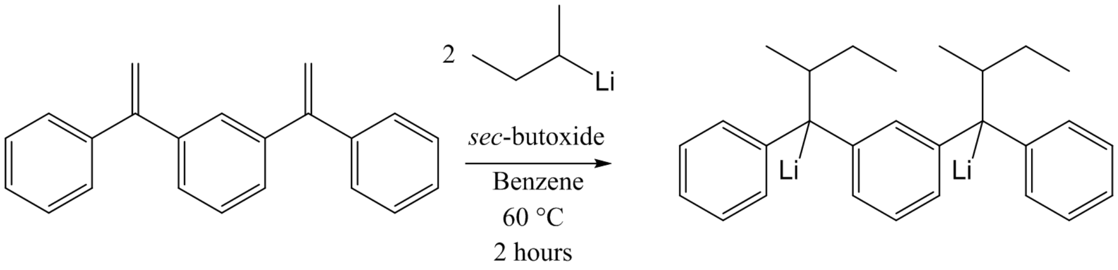

Figure 2.74: Reaction scheme for the formation of the difunctional initiator from 1,3-bis(1-phenylvinylbenzene).

A copolymerization of styrene, DPE and butadiene was carried out in benzene with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.60 : 12.39 and a target molecular weight of 150,000 g mol^{-1} (P(BdSD)$_2$-I). The high molecular weight and the molar feed ratio were chosen in an attempt to obtain a spherical or cylindrical morphology which is required for desirable thermoplastic elastomer properties. Upon addition of the red initiator to the monomer solution, the colour of the reaction mixture initially became red but could be seen to slowly fade to yellow indicative of propagating polybutadiene. The copolymerization was stirred at 40 °C, and the reaction mixture colour changed from yellow to red after 2 – 2.5 days. The reaction was stirred at 40 °C for a further 4 days before being terminated. The resulting copolymer was analysed by both SEC (Figure 2.61) and ^{1}H NMR spectroscopy (Figure 2.62). The molecular weight of the resulting polymer was 316,000 g mol^{-1} (calculated using the *dn/dc* value for polystyrene); almost double the target molecular weight. The higher than expected molecular weight could be due to a weaker concentration of difunctional initiator than expected, or, more likely be due to the introduction of impurities prior to initiation.

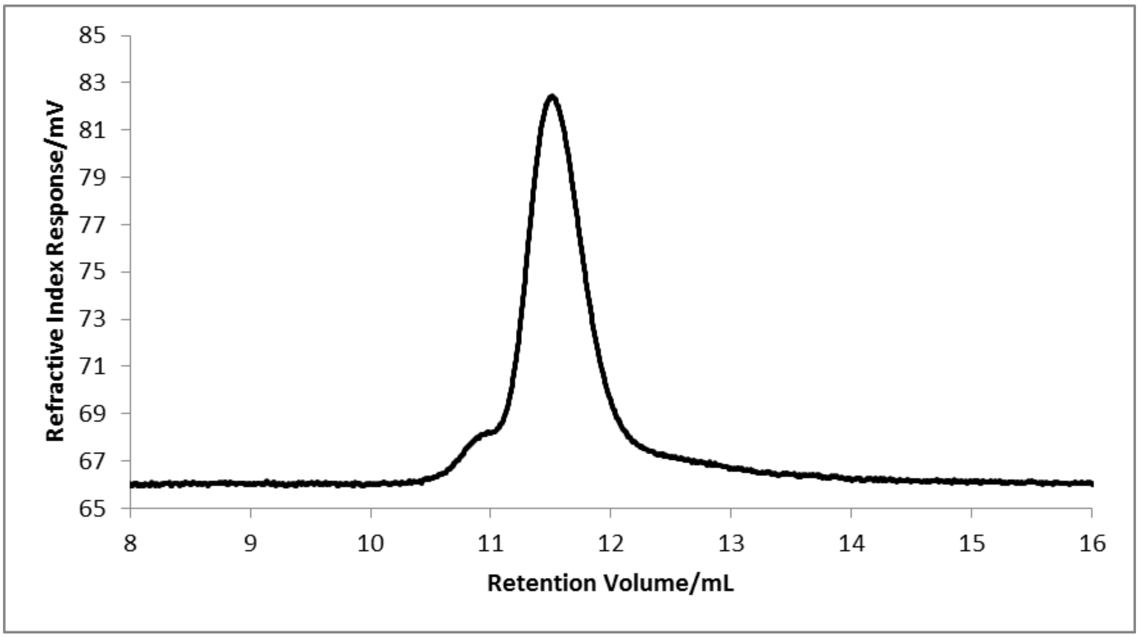

Figure 2.75: SEC chromatogram (refractive index) for the poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer.

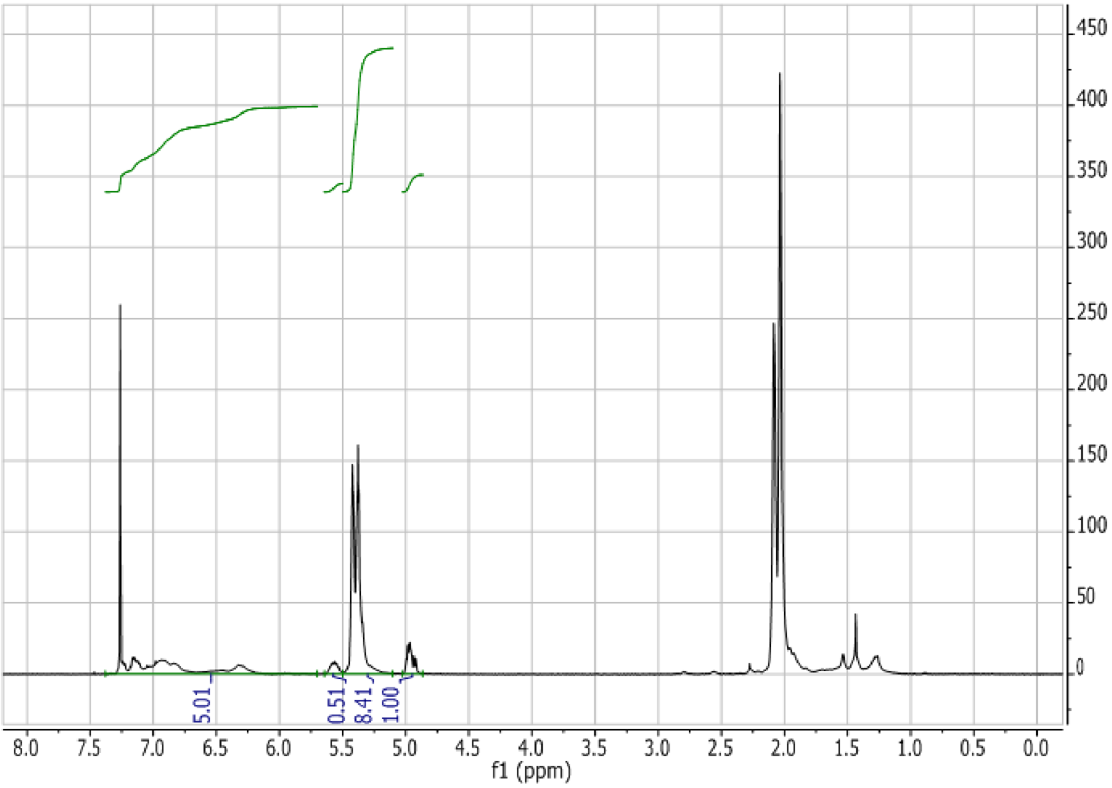

Figure 2.76: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer, $P(BdSD)_2$-I, synthesized in benzene with a molar feed ratio of 1.00 : 1.60 : 12.39 styrene : DPE : butadiene.

The SEC chromatogram (Figure 2.61) of the copolymer P(BdSD)$_2$-I is quite narrow and shows that there are relatively little undesired polymeric products as indicated by the low dispersity, Đ, of 1.07. There is a lower molecular weight tail which could have resulted from inadvertent partial termination due to a slow leak or from a slow rate of cross-propagation from butadiene to styrene and/or DPE upon depletion of butadiene, but the latter would be expected to broaden the dispersity and does not really explain the formation of the low molecular weight tail. There is also a small high molecular weight shoulder resulting from cross-coupling due to the introduction of environmental impurities during termination with methanol.

The target composition of the copolymer was 1.00 : 1.00 : 12.40 styrene : DPE : butadiene and was chosen to produce a copolymer with a polybutadiene content of 70 wt. %. in order to give the desired spherical or cylindrical morphology and will be discussed in the next chapter. The ratio of styrene : DPE : butadiene was found to be 1.00 : 0.83 : 15.62 from the integrals of the aromatic and alkene region in the ^{1}H NMR spectrum (Figure 2.62) assuming the ratio of styrene : DPE = 1.20 : 1.00 (obtained by the average composition in samples PSD-3 and PSD-4 which were prepared with the same molar feed ratio of styrene : DPE). This assumption was used for the same reason as described in Section 2.4.2, namely the suspected poor accuracy if using the aliphatic region of the ^{1}H NMR spectrum to calculate the ratio of styrene : DPE. This then indicates that P(BdSD)$_2$-I has a composition which contains approximately 77 wt. % polybutadiene.

2.4.7. Copolymerization by Sequential Addition of Styrene, Butadiene and 1,1-Diphenylethylene using a Difunctional Initiator in Benzene

In order to compare the impact of the ‘fire and forget’ synthetic methodology upon the physical properties of the resulting “tri-block copolymer”, the synthesis of an analogous ABA tri-block copolymer was attempted by the conventional sequential addition of monomers approach. When poly(styrene-*co*-DPE)-*block*-polybutadiene (PSD-PBd-1 to 8) was synthesized using *sec*-butyllithium (a monofunctional initiator) the styrene-*co*-DPE block was synthesized first. This was because the rate of cross-propagation from butadiene to styrene/DPE is lower than that of styrene/DPE to butadiene and hence the second block will be more disperse if butadiene was polymerized first. However, when synthesizing poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) using a difunctional initiator, butadiene must be polymerized first and styrene and DPE added subsequently in order that polybutadiene be the middle block. In a first attempt to synthesize poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) with a molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.60 : 12.39 and a target molecular weight of 150,000 g mol^{-1} (P(SD)-PBd-P(SD)-1), butadiene was initiated using the difunctional initiator and stirred for 3 days at room temperature and 3 days at 40 °C at which point DPE was added. To overcome the slower cross-over from butadiene to styrene and DPE, TMEDA (purified with *n*-Buli) was added at the same time as the DPE (and prior to the addition of styrene) which increases the rate of cross-propagation of butadiene to styrene and DPE. The reaction mixture was stirred at 40 °C for 25 hours to end-cap the living butadiene with DPE before styrene was added by distillation. The reaction mixture was stirred at 40 °C for a further 6 days before being terminated. Whilst it is now believed that TMEDA inhibits the incorporation of DPE, this reaction was performed based on the previous assumption that TMEDA would increase the incorporation of DPE (as in the case of PSD-11).

The ^{1}H NMR spectrum of P(SD)-PBd-P(SD)-1 (Figure 2.63) revealed that there was practically no incorporation of styrene or DPE. The peaks in the aromatic region are too weak to obtain a ratio of styrene : DPE and, even if it is assumed that DPE has been fully excluded, the styrene : butadiene ratio would be 1 : 79 suggesting only 16 % incorporation of styrene. The molecular weight was calculated as 200,500 g mol^{-1} using the *dn*/*dc* value for polystyrene, however, as the ^{1}H NMR spectrum reveals that the polymer is nearly entirely polybutadiene it is more appropriate to use the *dn*/*dc* value for polybutadiene which would indicate that the molecular weight is actually 300,800 g mol^{-1}, double the target molecular weight. Additionally, a yield of 70 % was obtained, which is consistent with butadiene being fully consumed and very little incorporation of styrene and DPE.

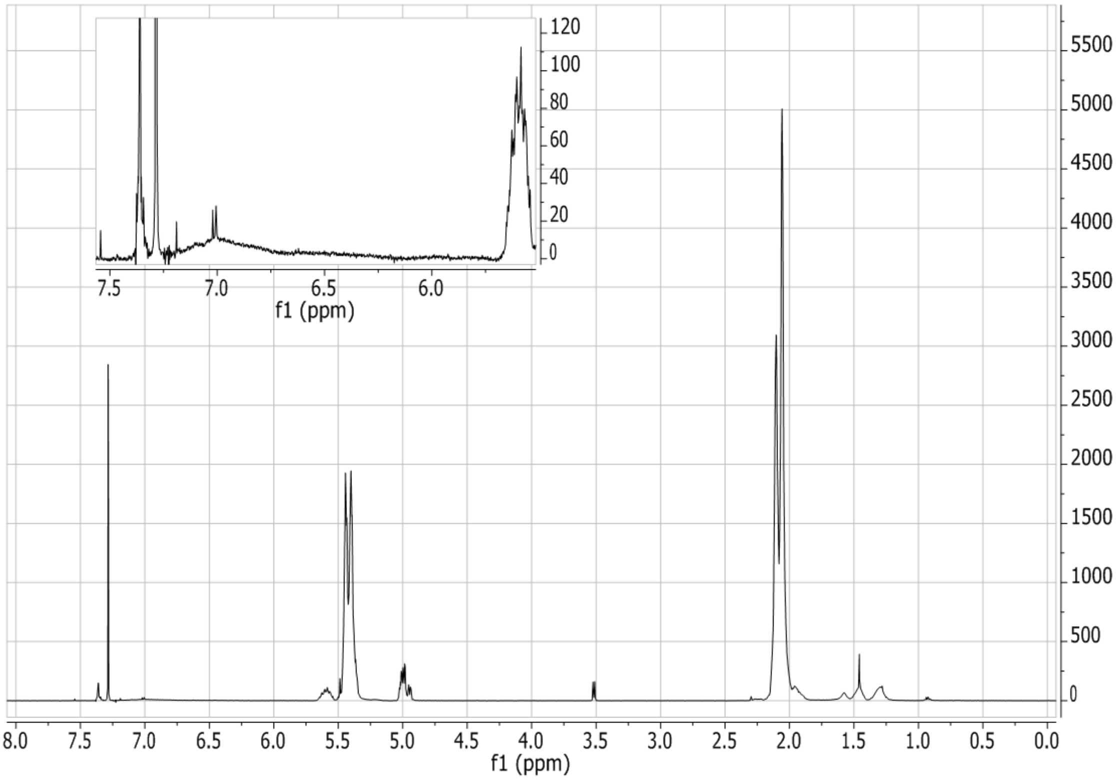

Figure 2.77: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer, P(SD)-PBd-P(SD)-1, synthesized in benzene with a molar feed ratio of 1.00 : 1.76 : 12.74 styrene : DPE : butadiene.

To confirm these results the reaction was repeated (P(SD)-PBd-P(SD)-2). The target molecular weight was again 150,000 g mol^{-1} and in this reaction the styrene : DPE : butadiene molar feed ratio was 1.00 : 1.61 : 12.45. The reaction was then stirred at 40 °C for 2 days before the addition of DPE/TMEDA (purified with *n*-Buli). The reaction was stirred at 40 °C for another day before the addition of styrene. The reaction was stirred at 40 °C for a further 6 days before being terminated by the addition of methanol. SEC analysis showed that the molecular weight was 320,700 g mol^{-1} using the *dn*/*dc* value for polybutadiene. ^{1}H NMR spectroscopy again revealed that there was very little incorporation of styrene and DPE, and assuming no incorporation of DPE, the styrene : butadiene ratio was estimated to be 1 : 64. Although it is now believed that TMEDA inhibits the incorporation of DPE when copolymerized with styrene, this does not explain the low incorporation of styrene.

The reaction was repeated without TMEDA (P(SD)-PBd-P(SD)-3). The target molecular weight was 150,000 g mol^{-1} and the styrene : DPE : butadiene molar feed ratio was 1.00 : 1.60 : 12.39. The reaction was stirred at 40 °C for 4 days before the addition of styrene and DPE. In order to minimise the inadvertent premature termination that typically occurs upon the sequential addition of monomers, styrene and DPE were purified by the drop wise addition of *n*-Buli to a mixture of styrene and DPE. As styrene and DPE would begin to polymerize if an excess of *n*-Buli were added to the styrene/DPE mixture, *n*-Buli was only added until a permanent yellow colour was observed signifying that the styrene/DPE was almost at the point of initiation. At this point the mixture of monomers was decanted in to the reaction flask. Upon addition of the styrene/DPE mixture the colour of the reaction mixture could be seen to slowly turn red over the next 30 minutes. The reaction mixture was then stirred at 40 °C for 6 days before being terminated with degassed methanol. In this case a 96 % yield was obtained and ^{1}H NMR analysis (Figure 2.64) of the final product indicated that this time the styrene and DPE were fully incorporated. However, the SEC chromatogram (Figure 2.65) revealed that the dispersity, Đ, of the resulting copolymer was 1.6 and there was quite a significant amount of cross-coupled polymer present as evidenced by high molecular weight peaks at a retention volume of 10.2 – 11.2 ml and caused by the introduction of environmental impurities (O_2 and CO_2) being inadvertently added during the termination of methanol. The reason the amount of cross-coupling is so high compared to other reactions is likely to be a result of the very high viscosity of these high molecular weight difunctional copolymers, which means the rate of termination by methanol is slow (diffusion limited) allowing competing termination reactions to occur if O_2 or CO_2 are present. The amount of cross-coupled material can be estimated as being 12 % by mass of the total polymer from the area under the curve in the refractive index response of the SEC chromatogram. Additionally, there is a low molecular weight impurity with a peak at a retention time of approximately 14.1 ml. It is likely that this peak arises as a result of polybutadiene chains that were prematurely terminated by the introduction of environmental impurities with DPE and styrene. Irrespective of the cross-coupled material and the low molecular weight material present, the peak is very broad which is likely to be a result of the slow cross-over reaction from butadiene to styrene/DPE in the absence of TMEDA. The molecular weight (of the main peak at a retention volume of 11.7 ml), M_n, is 372,000 g mol^{-1} is also much higher than the target molecular weight. The problems of low incorporation

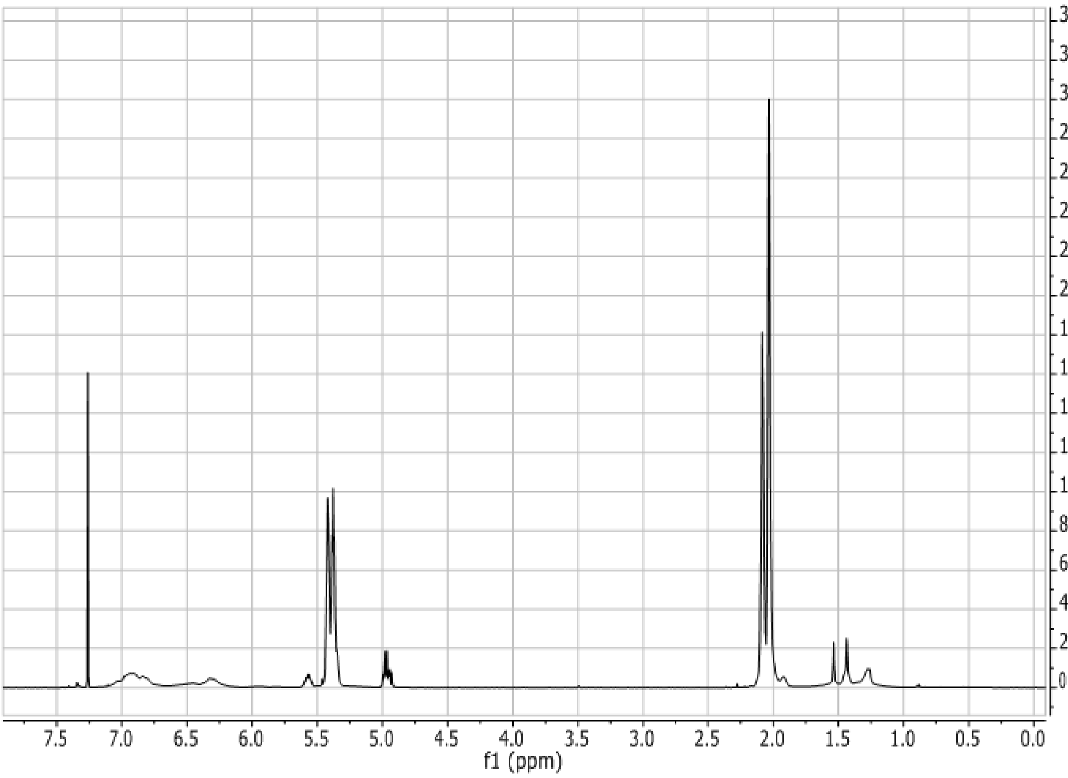

Figure 2.78: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer, P(SD)-PBd-P(SD)-3, synthesized in benzene with a molar feed ratio of 1.00 : 1.60 : 12.39 styrene : DPE : butadiene.

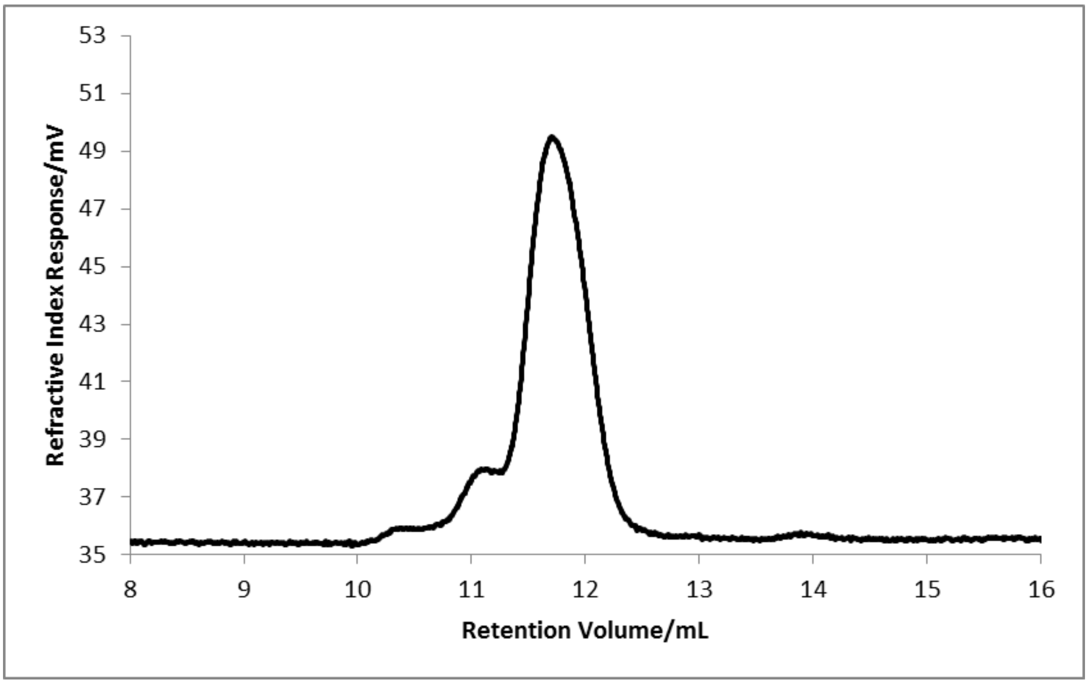

Figure 2.79: SEC chromatogram (refractive index) for the poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer, P(SD)-PBd-P(SD)-3.

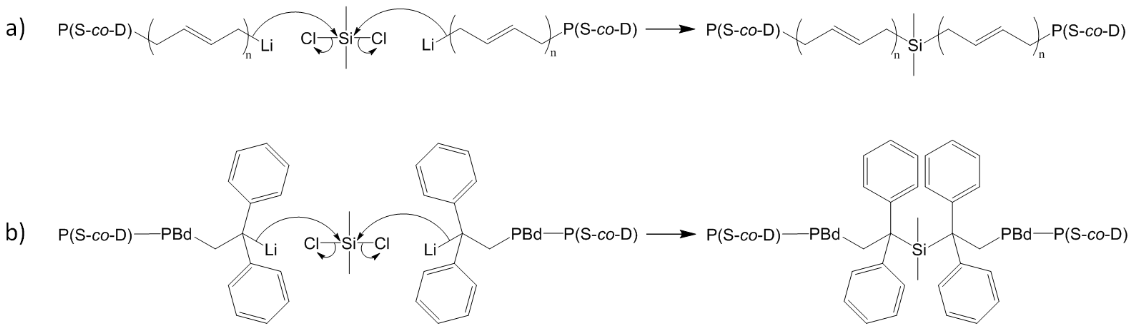

Figure 2.80: Reaction scheme showing the coupling of (a) poly(styrene-*co*-DPE)-*block*-polybutadienyllithium and (b) 1,1-diphenylethyllithium end-capped poly(styrene-*co*-DPE)-*block*-polybutadiene with DCDMS. Note: it is unlikely that the reaction of the two polymeric chains with DCDMS will happen simultaneously as depicted.

of DPE when using TMEDA, and that of high dispersity in the absence of TMEDA highlight the benefits of using a synthetically facile methodology like the 'fire and forget' approach. In light of the problems associated with the use of a difunctional initiator when using a sequential addition methodology, it was decided to attempt an alternative synthetic method which also relies upon sequential addition of monomers. Thus a poly(styrene-*co*-DPE)-*block*-polybutadiene AB di-block copolymer was prepared by sequential addition of monomers as before and coupling of this di-block with dichlorodimethyl silane (DCDMS) was attempted to produce an ABA tri-block. However, as has been reported in Section 2.4.1, during the production of such a di-block copolymer it is possible that unreacted DPE monomer might remain at the end of the reaction and effectively end-cap the polymer chains after consumption of butadiene. Whilst this was not a significant issue when preparing the di-block copolymer, it could be a significant problem for the synthesis of an ABA tri-block by coupling – and this proved to be the case! If the AB di-block chains become end-capped with a terminal DPE unit then the coupling reaction with DCDMS would be sterically challenging as shown in Figure 2.66. Ideally the coupling agent would be injected before this end-capping occurs, but it is not possible to know when all the butadiene has been fully consumed.

In one such reaction, P(SD)-PBd-P(SD)-4, styrene and DPE were copolymerized at 40 °C for 3.5 days at which point a sample was extracted (P(SD)-PBd-P(SD)-4a) before the addition of butadiene by distillation. The styrene : DPE : butadiene molar feed ratio was 1.00 : 1.60 : 12.46. The analogous copolymer prepared by the simultaneous 'fire

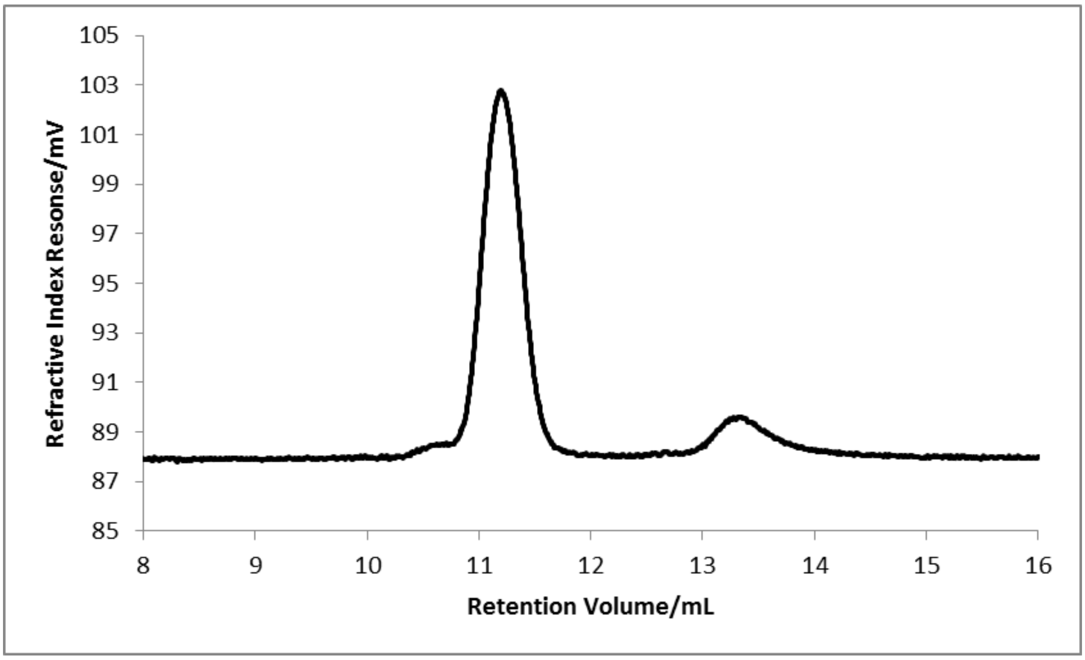

Figure 2.81: SEC chromatogram (refractive index) for the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer prior to the addition of the coupling agent, P(SD)-PBd-P(SD)-4b.

and forget' copolymerization had a molecular weight, M_n, of 320,000 g mol^{-1}, so a comparably high target molecular weight of 400,000 g mol^{-1} was used for the final coupled copolymer. Although the target molecular weight was slightly higher than that obtained by the simultaneous copolymerization, it is worth noting that the morphological (and mechanical) properties are largely molecular weight independent above 100 Kg mol^{-1}.[31] Upon addition of butadiene, the red colour corresponding to living styrene/DPE chain ends could be seen to fade slowly to a pale yellow colour within 1 hour. The reaction was stirred at 40 °C, and sometime (overnight) between 7 and 23 hours, the colour of the reaction mixture reverted back to red – possibly due to end capping by unreacted DPE. The reaction was stirred at 40 °C for a further hour before a sample was extracted for analysis (P(SD)-PBd-P(SD)-4b) and then the coupling agent, DCDMS, was added. The reaction was stirred at 50 °C for a further 24 hours at which point the reaction mixture had faded to a pale orange colour. The reaction was then terminated with methanol. A comparison of the SEC chromatogram of the sample taken before the addition of the coupling agent (P(SD)-PBd-P(SD)-4b) (Figure 2.67) and that of the final copolymer (P(SD)-PBd-P(SD)-4c) (SEC chromatogram shown in Figure 2.68) shows that only a very small amount of polymer had successfully coupled as

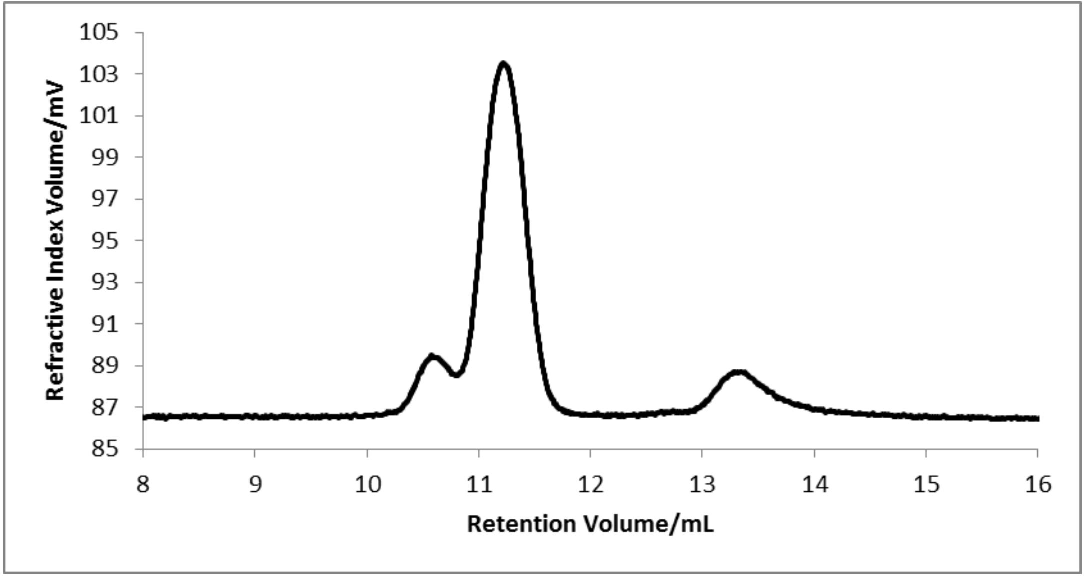

Figure 2.82: SEC chromatogram (refractive index) for the poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer after the addition of the coupling agent, P(SD)-PBd-P(SD)-4c.

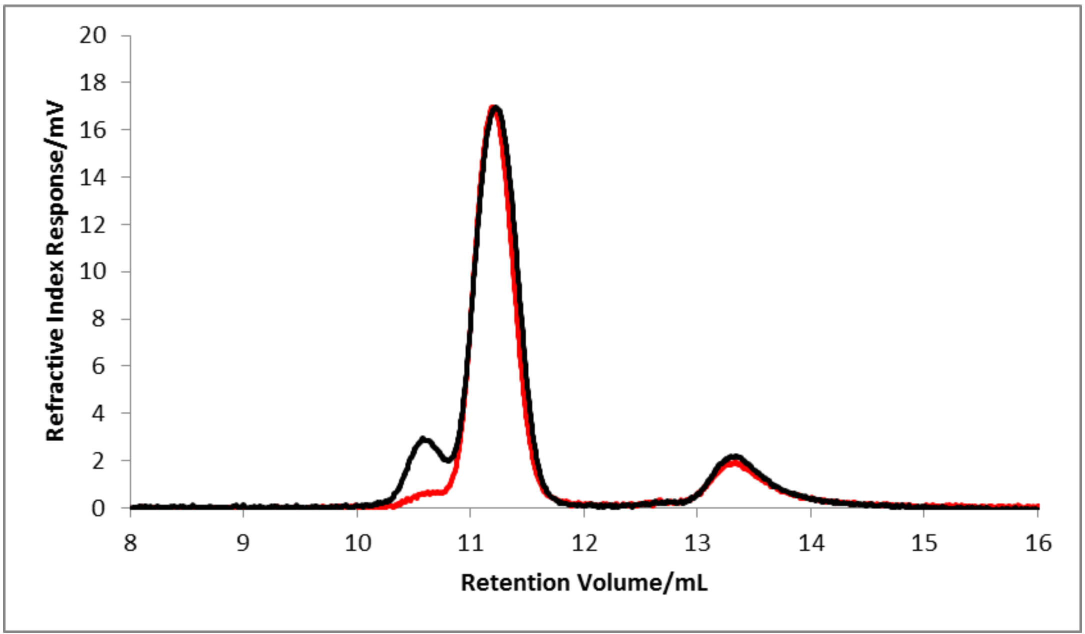

Figure 2.83: SEC chromatogram (refractive index) showing the poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer after the addition of the coupling agent, P(SD)-PBd-P(SD)-4c (black) and poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer prior to the addition of the coupling agent, P(SD)-b-PBd-b-P(SD)-4b (red).

evidenced by the small peak at a retention volume of 10.6 ml, despite the fact it is known from literature that 3 hours is adequate to couple polybutadienyllithium at 50 °C in hydrocarbon solvents.[32] The overlaid chromatograms of both samples are shown in Figure 2.69. This would suggest that the living chains are much less susceptible to coupling if they have begun to end-cap with DPE, and hence this is not a viable route for preparing poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymers. Moreover, the peak at a retention volume of 13.3 ml shows there is a fairly significant amount of undesirable poly(styrene-*co*-DPE) copolymer chains that were inadvertently prematurely terminated by the introduction of environmental impurities either with the butadiene monomer and/or during the sampling of the reaction.

In attempting to prepare an ABA tri-block copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) by the sequential addition of monomers, two approaches have been described. Both approaches have proved challenging. The sequential addition of a mixture of styrene and DPE to a living polybutadiene block initiated with a difunctional initiator could probably be described as the more successful, but the very high viscosity of the living polymer makes clean termination a problem and the introduction of environmental impurities resulted in high molecular weight by-products. The addition of TMEDA resulted in poor conversion due to the exclusion of DPE, but in the absence of a polar modifier the cross-over reaction led to a high dispersity. Moreover, the addition of a second batch of monomer is also accompanied by the deactivation of a small number of chains by impurities. Similar problems were encountered when attempting to make the same polymer by a coupling strategy and the coupling itself was hampered by the possible end-capping of chains by unreacted DPE.

In contrast the simultaneous ‘fire and forget’ copolymerization of all three monomers using a difunctional initiator proved to be experimentally much more facile and successful. It should be noted that the ‘fire and forget’ approach will result in a tapered copolymer rather than a perfect block copolymer, however, the impact of this tapering on the physical properties of the resulting copolymer will be discussed later.

2.5. The Impact of Switching the Polarity during the Copolymerization of Butadiene and 1,1-Diphenylethylene on the Monomer Sequence Distribution

When butadiene and DPE are copolymerized in a non-polar solvent, such as toluene, butadiene has a strong tendency for self-propagation and DPE is almost totally excluded. However, in a polar solvent such as THF, the same pair of monomers will

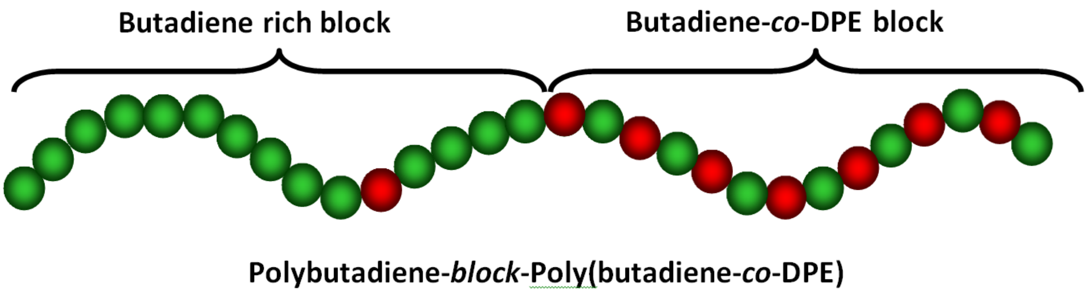

Figure 2.84: Schematic diagram to show the potential structure of a polybutadiene-*block*-poly(butadiene-*co*-DPE) terpolymer when butadiene (green balls) and DPE (red balls) (molar feed ratio of butadiene : DPE = 1 : 1) are initially copolymerized in toluene with THF added before the complete consumption of butadiene.

copolymerize to form an almost perfectly alternating copolymer. Therefore, it was surmised that if the copolymerization of butadiene and DPE was carried out (initially) in a non-polar solvent, and THF were to be added before the complete consumption of butadiene, then the resulting copolymer would have a sequence comprising of an initial block of polybutadiene followed by a block of nearly alternating butadiene and DPE and thus a block copolymer of polybutadiene-*block*-poly(butadiene-*co*-DPE) would be formed (as shown by the schematically in Figure 2.70).

In a first attempt to test this hypothesis butadiene and DPE with a molar ratio of DPE : butadiene = 1.00 : 1.05 and a target molecular weight of 58,400 g mol^{-1} was initiated in 20 ml of toluene (PBdD-4). The reaction was stirred at room temperature for 2.5 hours at which point a sample was removed (PBdD-4a) for analysis. The remaining reaction mixture was then cooled to 0 °C and 20 ml of THF added. Upon addition of the THF the reaction mixture became pale orange and was left for a further 16 hours (overnight) by which time the reaction mixture had faded to a pale yellow, and then was colourless after a further 24 hours indicating the unintended termination of the living solution. Whilst it is possible that the reaction was terminated by reacting with THF,[3] previous reactions with THF at 0 °C had shown no indication of inadvertent termination and it is more likely that environmental impurities were introduced with the THF. The sample (PBdD-4a) contained no polymer, however, the ^{1}H NMR spectrum of the final product (PBdD-4b) (Figure 2.71) showed peaks that were characteristic of poly(butadiene-*co*-DPE) and using the integrals of the aromatic, alkene and aliphatic region the

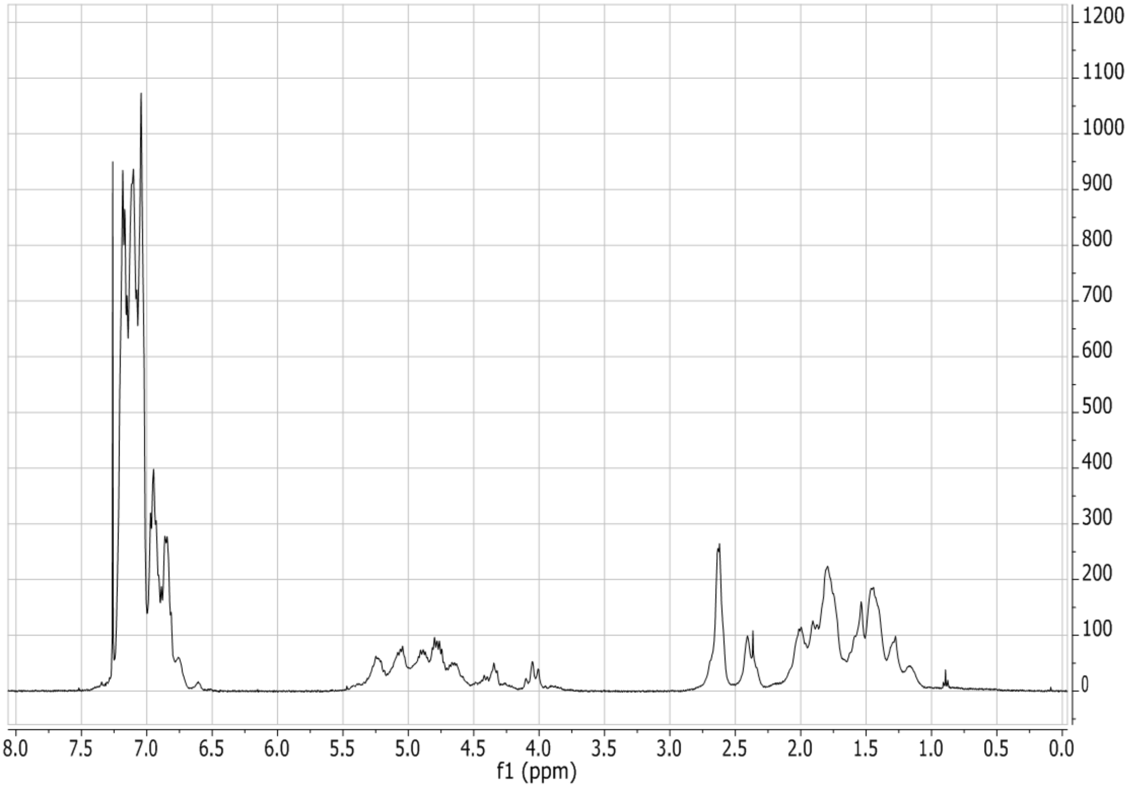

Figure 2.85: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-4b, synthesized in toluene with THF added after 2.5 hours at room temperature and with a molar feed ratio of 1.00 : 1.05 DPE : butadiene.

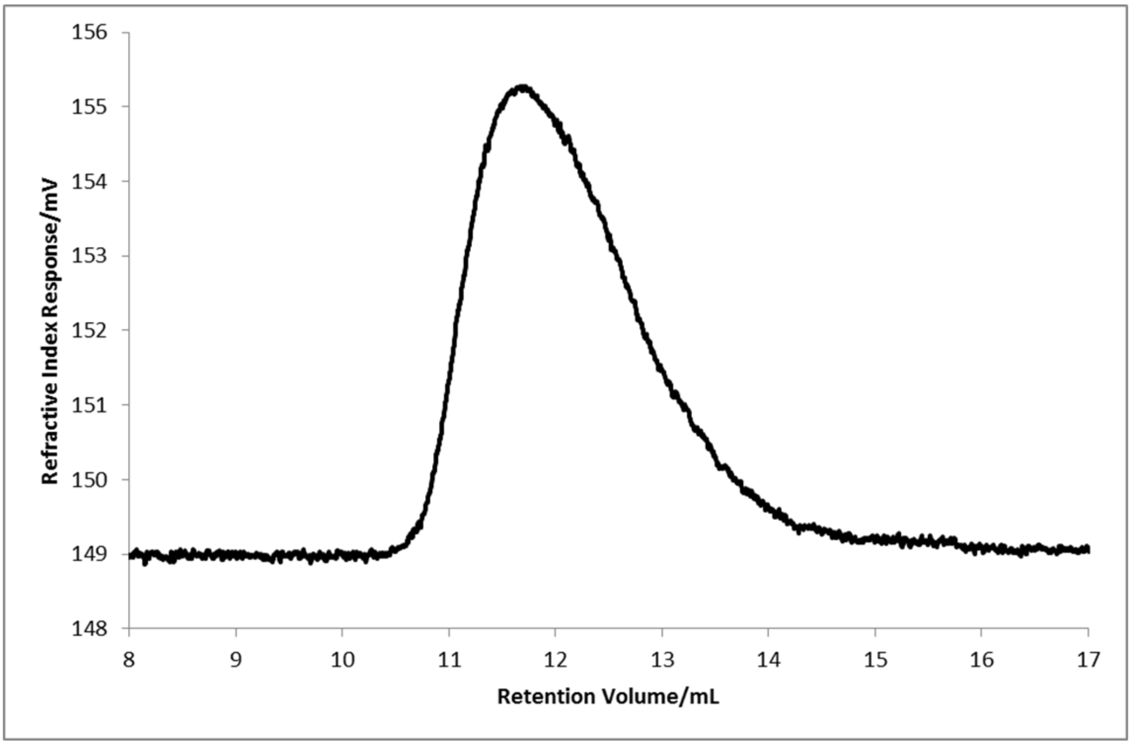

Figure 2.86: SEC chromatogram (refractive index) for the poly(butadiene-*co*-DPE) copolymer, PBdD-4b.

butadiene : DPE ratio was calculated as 1.12 : 1.00. The target molecular weight was 58,400 g mol^{-1}, assuming full incorporation of DPE; however, if DPE was totally excluded from the reaction then the molecular weight would be expected to be 14,000 g mol^{-1}. The molecular weight, M_n, was found to be 103,000 g mol^{-1}, with a very high dispersity (Đ = 2.67). Moreover, the SEC trace (Figure 2.72) contained a low molecular weight tail indicating slow termination may have occurred, hence a slow leak of environmental impurities could explain both the high dispersity and the high molecular weight. The yield of the final copolymer PBdD-4b was found to be 16 %. The yield is also dependent on the incorporation of DPE, however, in this case, as there appears to be a very high incorporation of DPE, the low yield is likely a consequence of inadvertent termination.

This reaction was then repeated (PBdD-5) with a molar feed ratio of DPE : butadiene = 1.00 : 0.96 initially in 46 ml of toluene with a target molecular weight of 89,200 g mol^{-1}. This time the reaction was stirred at 40 °C for 3.3 hours before the reaction was sampled (PBdD-5a), cooled to 0 °C, and 40 ml of THF added to give an approximately 50 : 50 by volume mixed solvent. The reaction darkened to an orange/red colour upon addition of THF but again the colour faded such that by 16 hours (overnight) the reaction had faded to a pale orange colour which was paler still after a further 24 hours – again suggesting termination. The reason for the termination is again likely to be due to a slow leak or environmental impurities being introduced during the addition of THF. However, in this case, the ^{1}H NMR spectra of both the sample (PBdD-5a) and final copolymer (PBdD-5b) (Figures 2.73 and 2.74) indicated that butadiene underwent preferential self-propagation and only a small amount of DPE had been incorporated. The ^{1}H NMR spectra of both PBdD-5a and PBdD-5b appear similar, however, the ratio of butadiene : DPE was calculated as 23.4 : 1.0 for PBdD-5a and 15.2 : 1.0 for PBdD-5b. This indicates that there was an increase in the incorporation of DPE upon the addition of THF. The reason there was not a larger incorporation of DPE is either due to most of the butadiene monomer reacting prior to the addition of THF or due to termination caused by the introduction of impurities. The yield was found to 22 %, however, as the ^{1}H NMR spectrum indicates there is a low incorporation of DPE, if DPE is excluded from

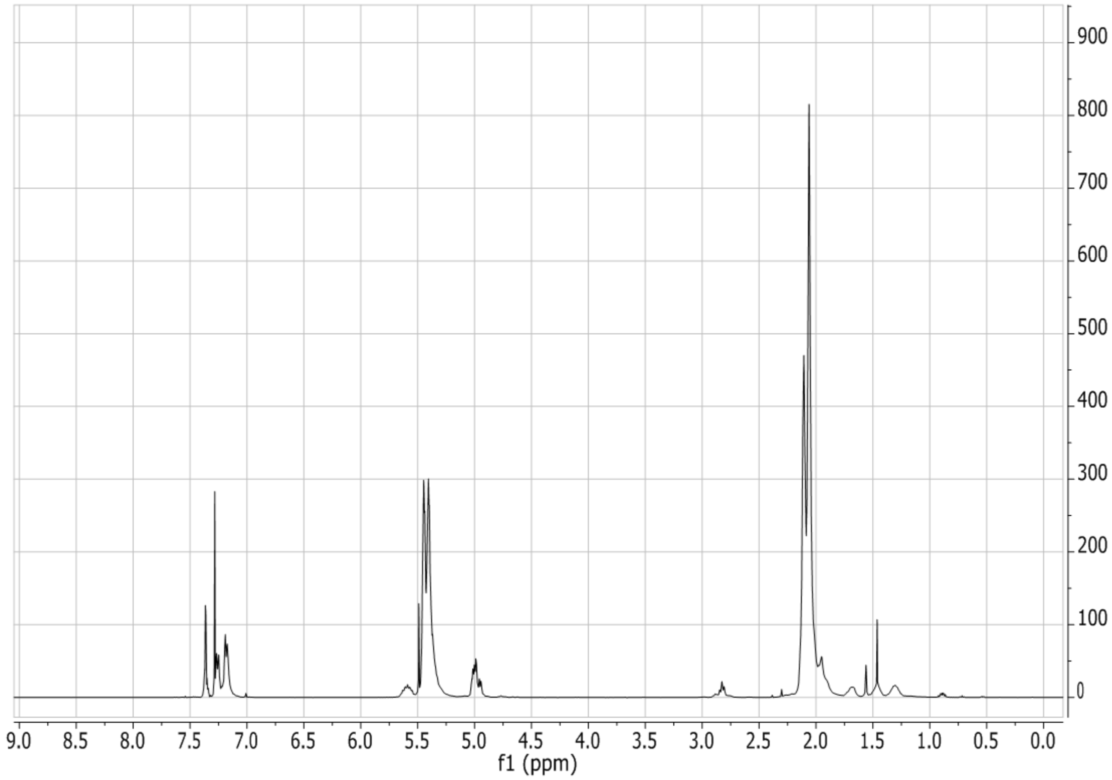

Figure 2.87: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-5a, synthesized in toluene with a molar feed ratio of 1.00 : 0.96 DPE : butadiene.

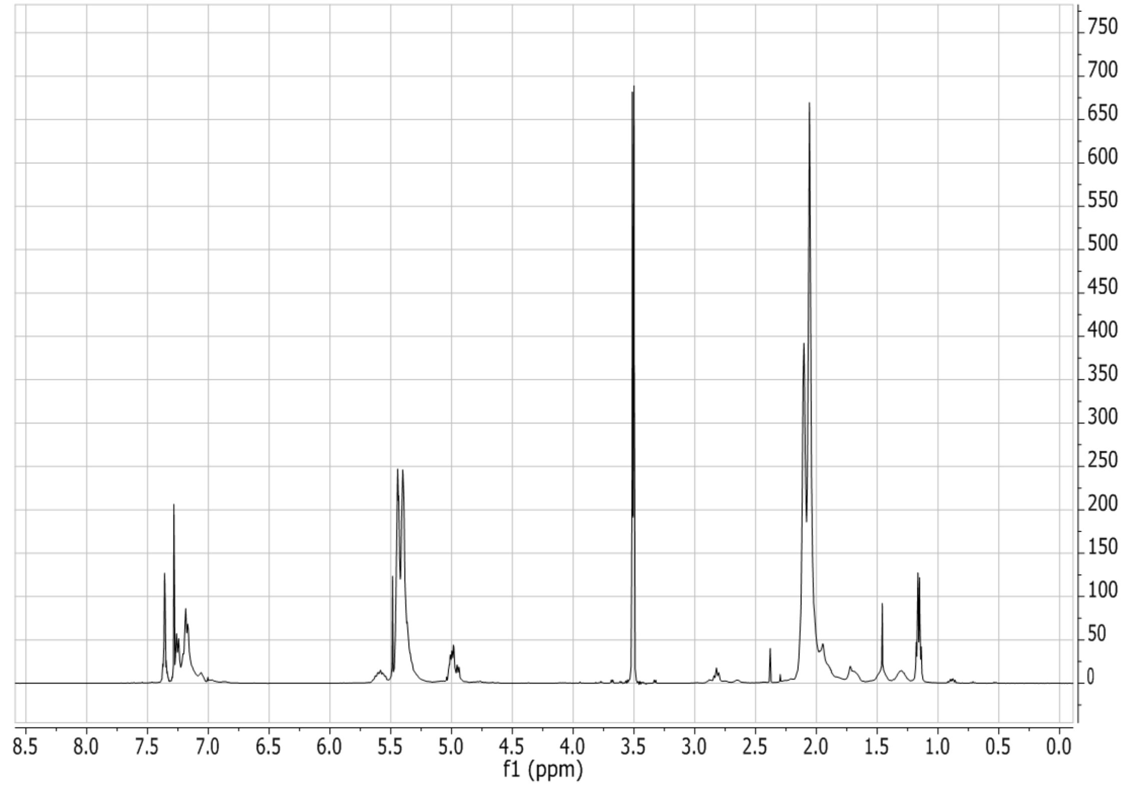

Figure 2.88: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-5b, synthesized in toluene with THF added after 3.3 hours at 40 °C and with a molar feed ratio of 1.00 : 0.96 DPE : butadiene.

the yield calculation a nearly quantitative yield is obtained and hence it is likely that the consumption of butadiene was almost complete upon the addition of THF. These results are consistent with the molecular weights obtained by SEC. If DPE was totally excluded from the reaction the expected molecular weight, M_n, would be 20,000 g mol^{-1}. The M_n calculated by SEC for sample PBdD-5a was found to be 14,300 g mol^{-1}, whereas that found for the final copolymer PBdD-5b was 17,200 g mol^{-1}. It should be noted that these values were obtained using a *dn*/*dc* for polystyrene, however, if the *dn*/*dc* for polybutadiene is used the M_n values are 21,300 g mol^{-1} and 25,600 g mol^{-1} for PBdD-5a and PBdD-5b. These results are consistent with the assumption that butadiene had been almost entirely consumed before the addition of THF.

In a further attempt to optimise this reaction, molar feed ratio of DPE : butadiene = 1.00 : 0.96 was added to 52 ml of toluene (PBdD-6). As the previous reaction indicated almost complete consumption of butadiene after 3.3 hours at 40 °C, in this reaction a sample was collected after 1 hour of stirring at 40 °C (PBdD-6a), at which point the reaction was cooled to 0 °C and 50 ml of THF added in. This time the reaction mixture became red upon addition of the THF and remained so until termination with methanol 48 hours later to yield PBdD-6b. In this case it is likely that considerably less environmental impurities were introduced with the THF and the majority of the chains were therefore not inadvertently terminated, however, there were a few chains that were inadvertently terminated as shown by the overlaid SEC chromatograms of PBdD-6a and PBd-6b (Figure 2.75). The ^{1}H NMR spectrum of the sample (PBdD-6a) and the final copolymer (PBdD-6b) are shown in Figures 2.76 and 2.77. The spectrum of PBdD-6a clearly shows that the sample collected after about 1 hour is predominantly butadiene indicating the strong preference for butadiene to self-propagate in non-polar solvents (as expected) and the butadiene : DPE ratio was calculated as 34.8 : 1.0 from the integrals of the ^{1}H NMR. However, upon the addition of THF, and a change in solvent polarity, butadiene has a stronger tendency to copolymerize with DPE as indicated by the data in Figure 2.77 and the ratio of butadiene : DPE, calculated as 1.6 : 1.0. The yield was found to 48 %, however, as mentioned before the yield is dependent upon the incorporation of DPE. SEC analysis (Figure 2.75) also indicates a large increase in the molecular weight after the addition of THF, PBdD-6a was found to have an M_n

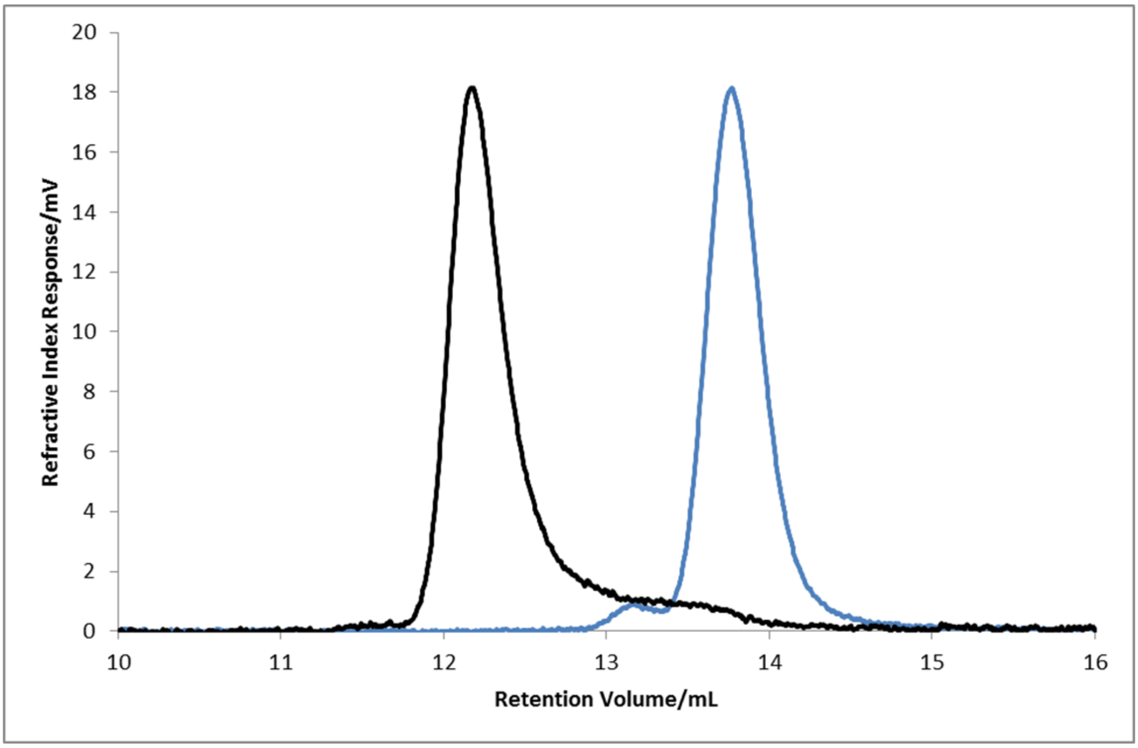

Figure 2.89: Overlay of the SEC chromatograms (refractive index) for the poly(butadiene-*co*-DPE) copolymers, PBdD-6a (blue) and PBdD-6b (black).

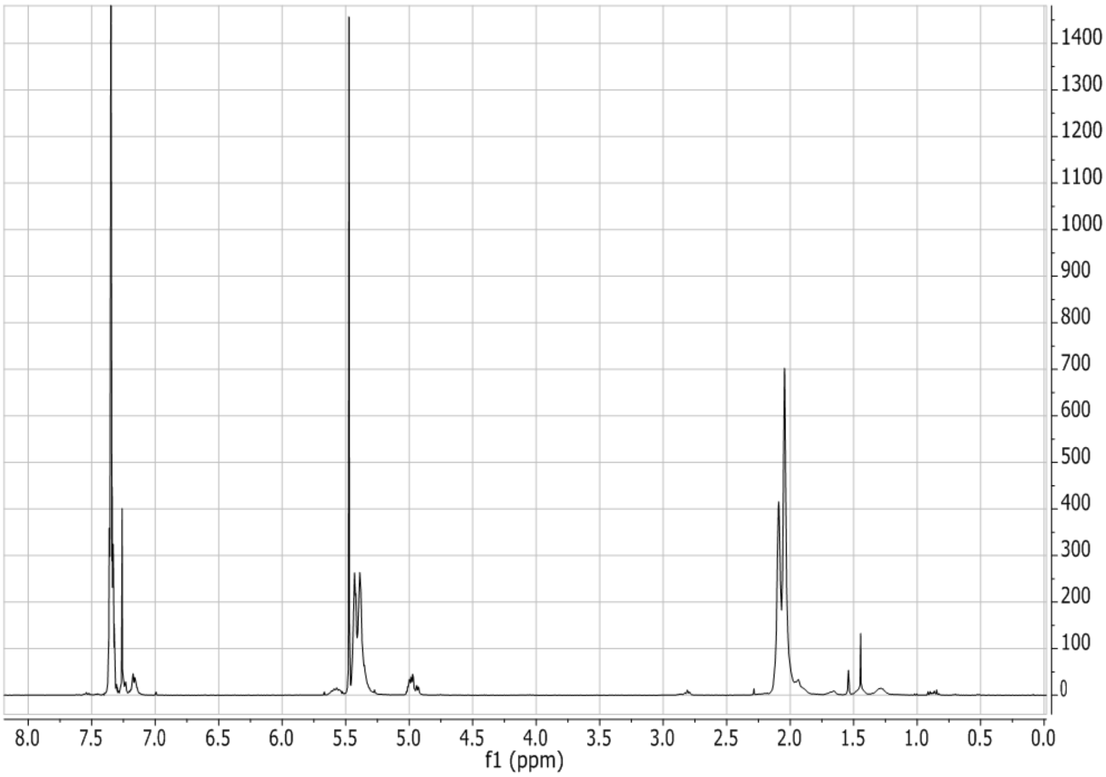

Figure 2.90: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-6a, synthesized in toluene with a molar feed ratio of 1.00 : 0.96 DPE : butadiene.

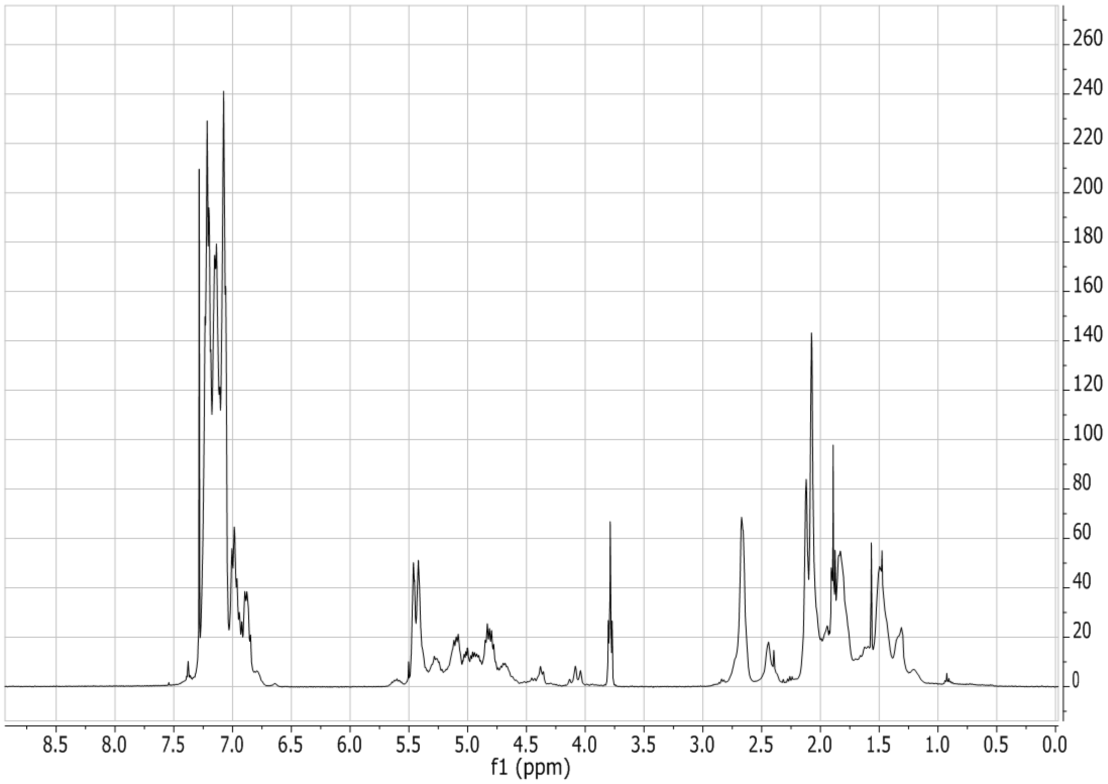

Figure 2.91: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-6b, synthesized in toluene with THF added after 57 minutes at 40 °C and with a molar feed ratio of 1.00 : 0.96 DPE : butadiene.

value of 10,600 g mol^{-1} whereas PBdD-6b was found to be 130,600 g mol^{-1}. Whilst the target molecular weight was approximately 90,000 g mol^{-1} as some chains were inadvertently terminated upon the addition of THF (Figure 2.75) this could give rise to the higher molecular weight. This final reaction supports the hypothesis that switching the polarity of the solvent during the copolymerization of butadiene and DPE results in a dramatic change in reactivity ratios and results in the formation of a block copolymer of polybutadiene-*block*-poly(butadiene-*co*-DPE). Furthermore, since as the switch in polarity will be almost instantaneous upon the addition of THF, the transition from one 'block' to the other should be fairly rapid and there should be no tapering.

2.6. Copolymerization of Butadiene and 1,1-Diphenylethylene in THF with a 3 : 1 Mole Ratio of Butadiene : DPE

An additional way to influence control the monomer sequence distribution in such copolymerization reactions is by controlling the monomer feed ratio. Whilst an equimolar feed ratio of butadiene and DPE will form an almost perfectly alternating copolymer (in THF), the copolymerization of a mixture of the same pair of monomers

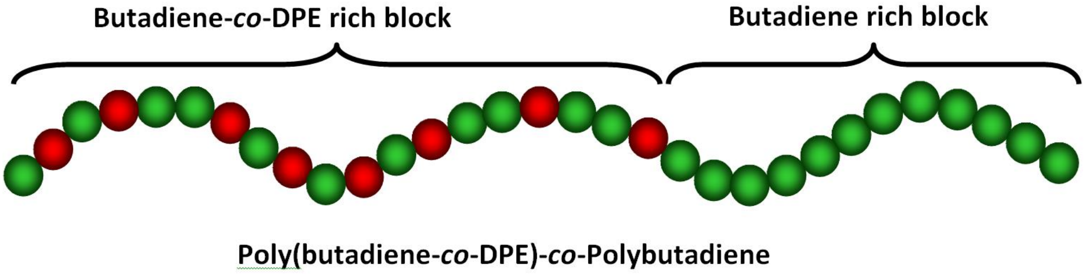

Figure 2.92: Schematic diagram to show the potential structure of a poly(butadiene-*co*-DPE)-*co*-polybutadiene terpolymer when butadiene (green balls) and DPE (red balls) are copolymerized in THF with a molar feed ratio of butadiene : DPE = 3 : 1.

in which butadiene is present in excess will result in a different outcome. Thus given the tendency for butadiene and DPE to copolymerize in THF, one might expect a butadiene-*co*-DPE tapered copolymer to form initially, and then when all the DPE has been consumed the remaining butadiene would form a 'block' of polybutadiene as shown schematically in Figure 2.78.

To test this hypothesis a copolymerization of butadiene and DPE was carried out in THF with a molar feed ratio of 1.00 : 2.85 DPE : butadiene and with a target molecular weight of 50,700 g mol^{-1} (PBdD-7). Upon initiation the colour of the reaction mixture became red and after stirring for 1.5 hours at 0 °C the reaction was sampled (PBdD-7a). The reaction was allowed to proceed at 0 °C for a further 1 hour by which time the colour of the reaction mixture had become purple. This colour change was thought to be due to chain termination caused by the introduction of an impurity during the sampling, however, a subsequent reaction proved this was not the case. The reaction was stirred at 0 °C for a further 21 hours before termination with methanol. SEC analysis of the initial sample (PBdD-7a) and the final copolymer (PBdD-7b) are shown in Figure 2.79. These data reveal that a small proportion of the polymer had been terminated whilst sampling, however, the majority remained active and went on to produce a copolymer in 93 % yield with a molecular weight, M_n, of 83,300 g mol^{-1}. The ^{1}H NMR spectra of sample PBdD-7a and the final copolymer PBdD-7b are shown in Figures 2.80 and 2.81 respectively. The ^{1}H NMR spectrum of the sample PBdD-7a shows that despite the reduced feed ratio of DPE, there is still a very strong initial incorporation of DPE. Furthermore, from the integrals of the ^{1}H NMR spectrum in the

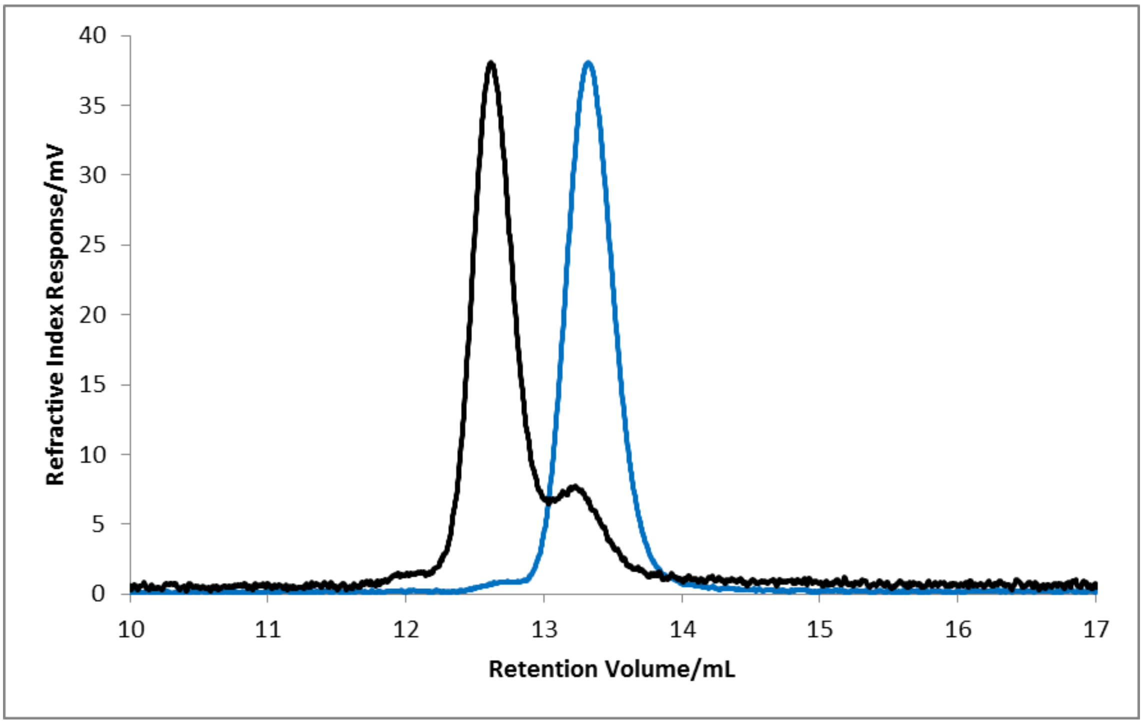

Figure 2.93: Overlay of the SEC chromatograms (refractive index) for the poly(butadiene-*co*-DPE) copolymers, PBdD-7a (blue) and PBdD-7b (black).

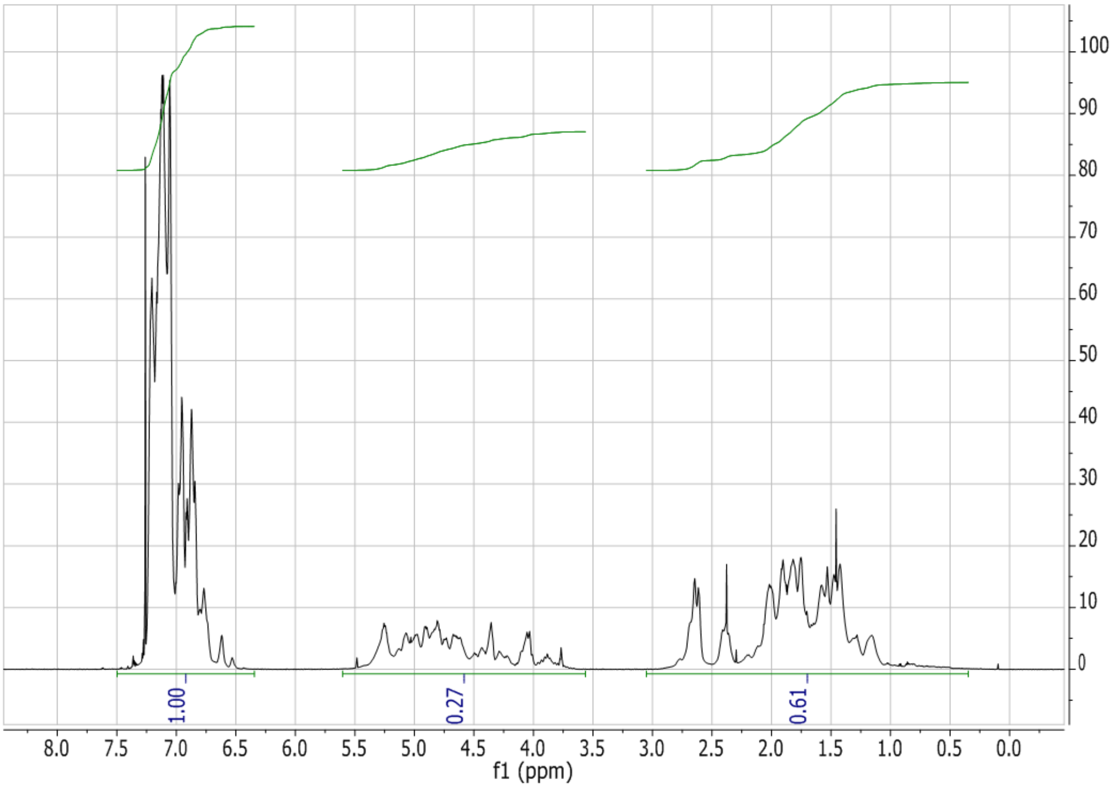

Figure 2.94: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-7a, synthesized in THF with a molar feed ratio of 1.00 : 2.85 DPE : butadiene and terminated after 1.5 hours at 0 °C.

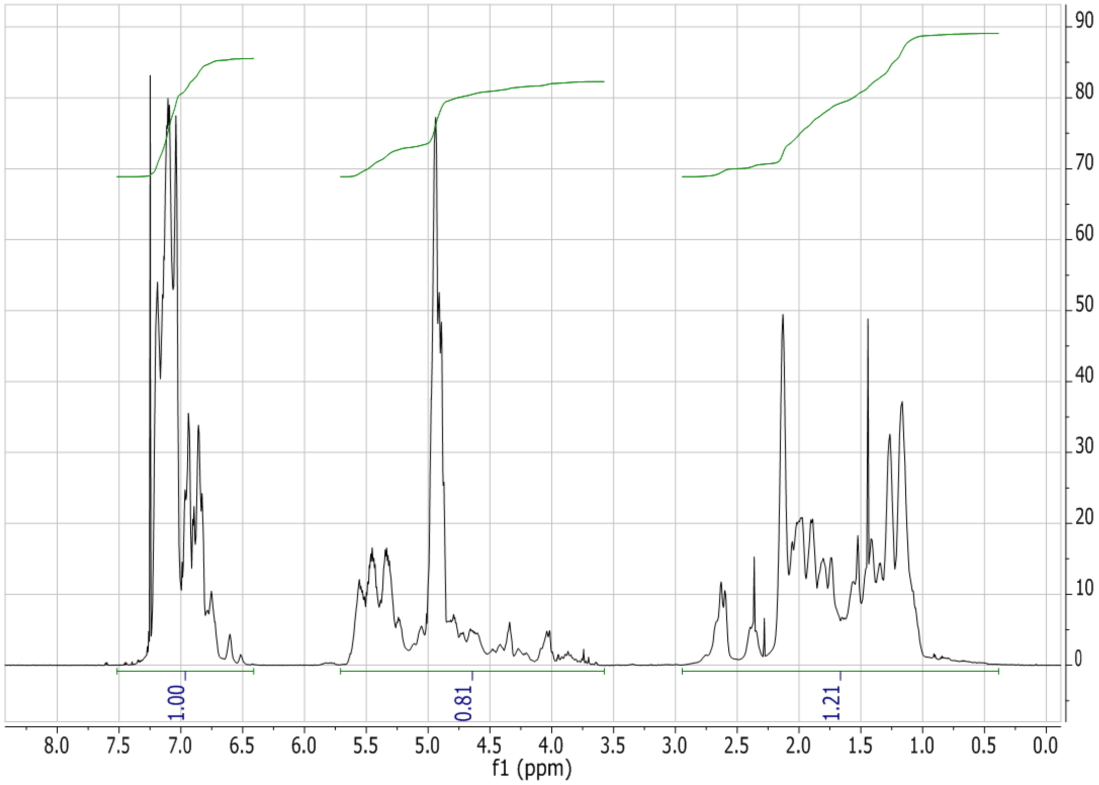

Figure 2.95: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-7b, synthesized in THF with a molar feed ratio of 1.00 : 2.85 DPE : butadiene and terminated after 22.8 hours at 0 °C.

aromatic, alkene and aliphatic regions, the composition of DPE : butadiene for sample PBdD-7a is calculated as 1.00 : 1.15 and a 1,4-polybutadiene content of 62.5 % which is entirely consistent with the 1,4-polybutadiene content found for the copolymer PBdD-1 where butadiene and DPE were copolymerized in THF with an equimolar feed ratio. Whilst partial termination occurred when the reaction was sampled, this should not affect the relative rate of incorporation of the monomers and hence will not affect the ^{1}H NMR spectrum of PBdD-7b. There will however be some chains with a higher DPE content which were terminated prior to the complete consumption of DPE, and some chains with a higher molecular weight ‘block’ of polybutadiene than the target molecular weight. The integrals from the ^{1}H NMR spectrum of the final copolymer (PBdD-7b) were used to calculate a ratio of 1.00 : 3.12 DPE : butadiene in the resulting copolymer – very close to the initial feed ratio – and a 1,4-polybutadiene content of 33.7 %. This lower 1,4 enchainment indicates that the second ‘block’ of polybutadiene has a high 1,2 microstructure, which is consistent for butadiene when polymerized in THF. These combined results support the hypothesis that a near-alternating copolymer

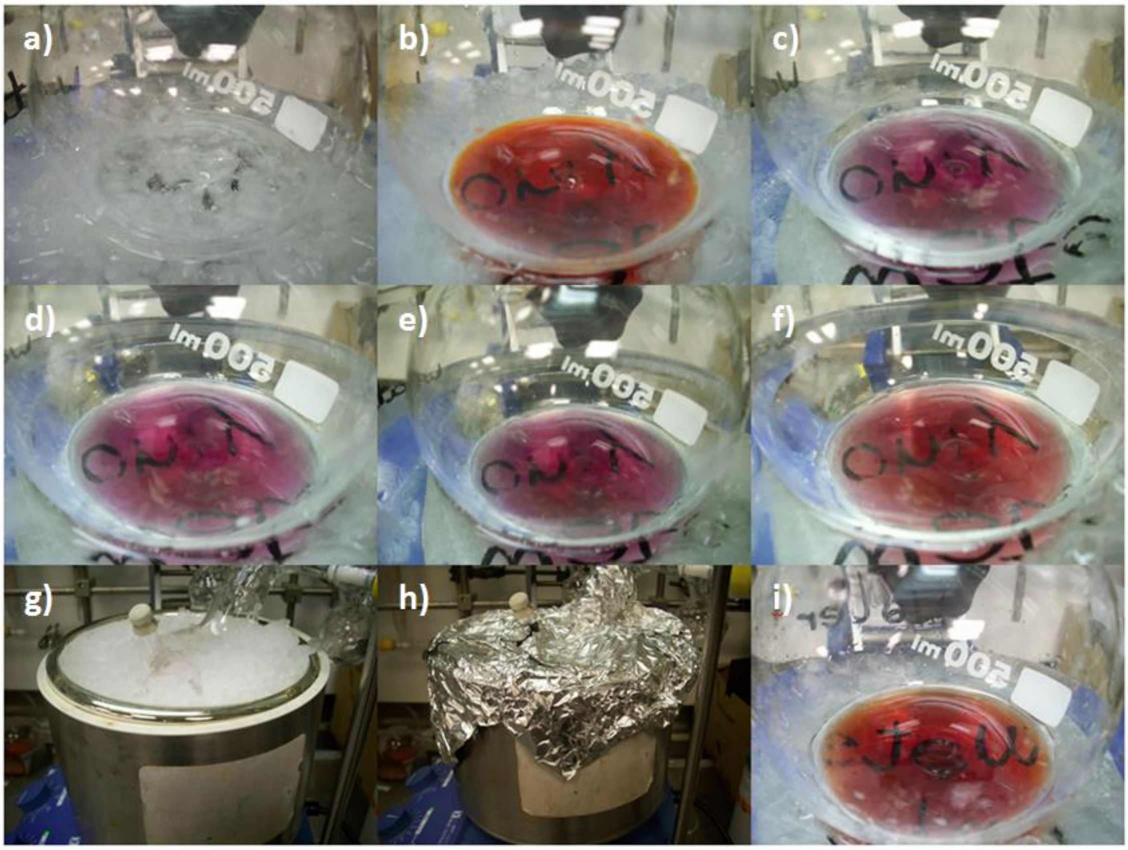

Figure 2.96: Photographs of the copolymerization of DPE and butadiene (PBdD-8) (a) before initiation (b) immediately after initiation and after (c) 1.1 hours (d) 1.7 hours (e) 2 hours (f) 2.7 hours (g) 2.8 hours (h) 2.9 – 14.7 hours (overnight) (i) 14.7 hours at 0 °C.

of poly(butadiene-*co*-DPE) is formed initially until the DPE is consumed upon which polybutadiene 'block' is formed by consumption of the remaining butadiene.

To obtain a copolymer of poly(butadiene-*co*-DPE)-*co*-polybutadiene without any partially terminated material, the reaction was repeated without sampling. The reaction was repeated with a molar feed ratio of DPE : butadiene = 1.00 : 2.85 and a target molecular weight of 51,500 g mol^{-1} (PBdD-8). The reaction mixture was stirred at 0 °C for 15.2 hours before being terminated with degassed methanol. Again the reaction mixture changed colour from red to purple after 1.1 hours of stirring at 0 °C (Figures 2.82a-i) which reverted back to red after a further 1.5 hours. The initial red colour of the reaction mixture and the high incorporation of DPE in sample PBdD-7a confirms that initially butadiene and DPE copolymerize with a high incorporation of DPE.

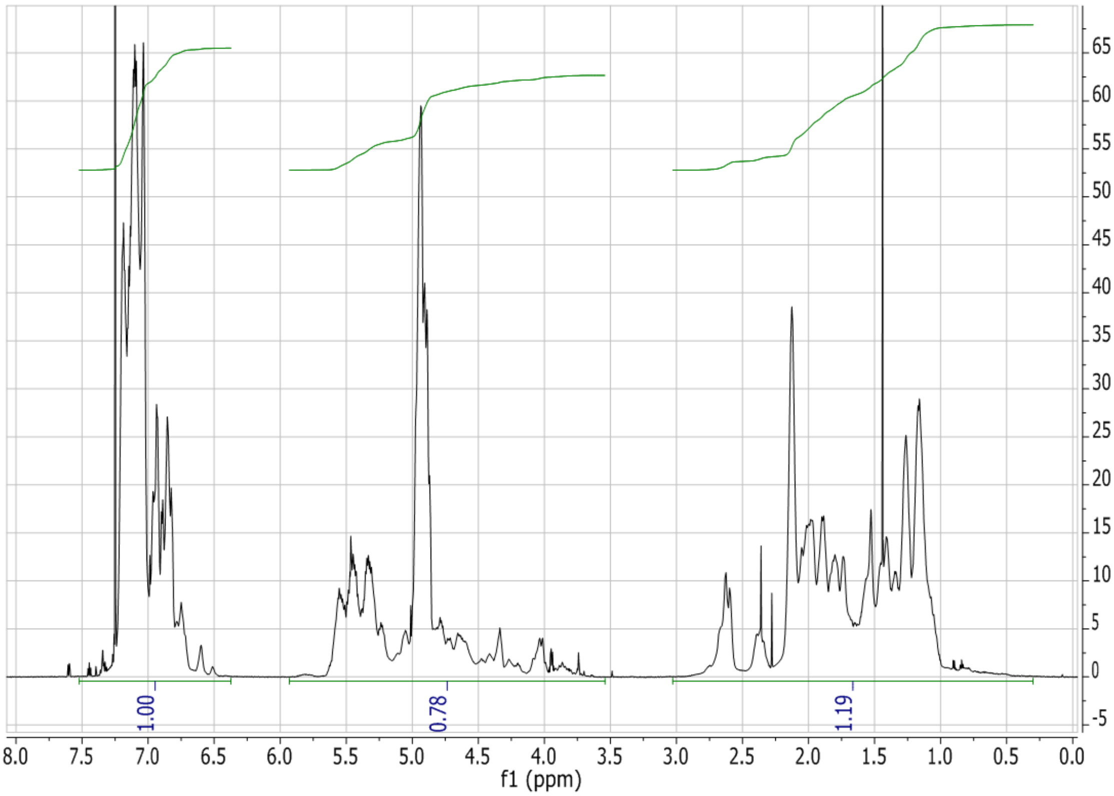

Figure 2.97: ^{1}H NMR spectrum (in $CDCl_3$) for the poly(butadiene-*co*-DPE), PBdD-8, synthesized in THF with a molar feed ratio of 1.00 : 2.85 DPE : butadiene and terminated after 15.2 hours at 0 °C.

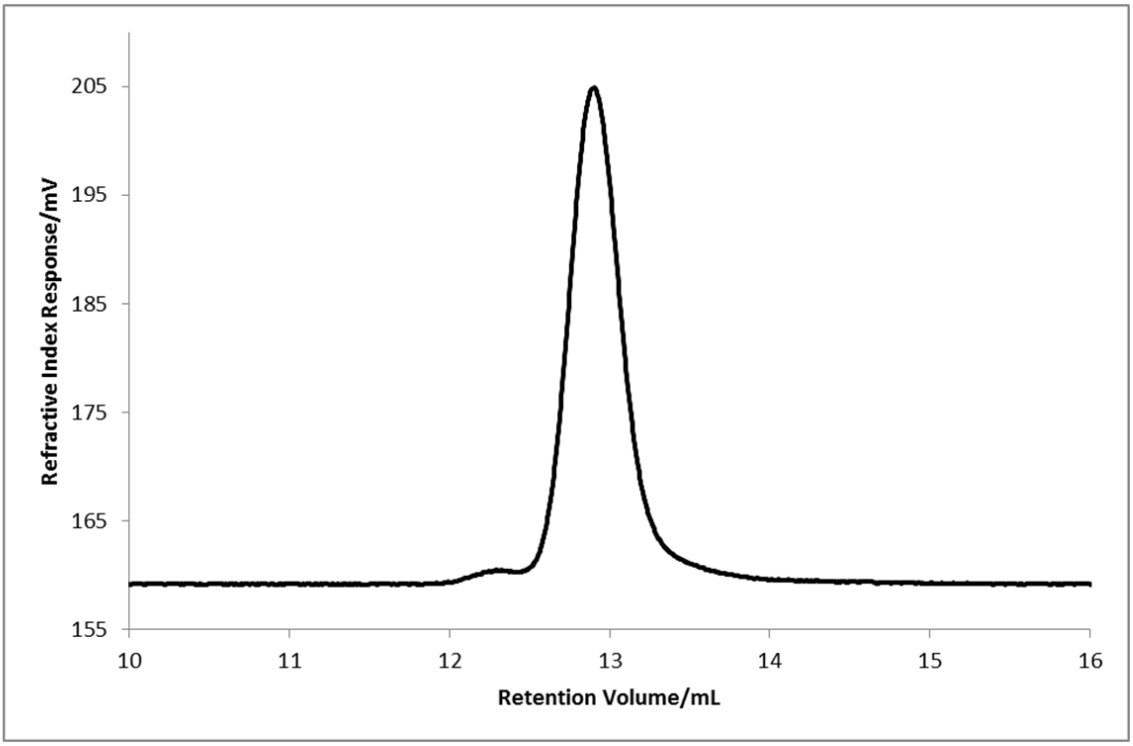

Figure 2.98: SEC chromatogram (refractive index) for the poly(butadiene-*co*-DPE) copolymer, PBdD-8.

Whilst the colour change to purple is surprising, the ^{1}H NMR of both PBdD-7b (Figure 2.81) and PBdD-8 (Figure 2.83) both indicate that in the later stages of the reaction butadiene undergoes self-propagation. It is possible that as the DPE content diminshes the incorporation of DPE becomes reduced and butadiene predominantly undergoes self-propagation leaving some unreacted DPE (i.e. the rate of self-propagation of butadiene becomes greater than the rate of cross-propagation to DPE as the concentration of DPE becomes very low but not zero). Then as the concentration of butadiene diminishes, the rate of butadiene self-propagation will also decrease and the rate of cross-propagation again becomes dominant which could explain why the colour of the reaction mixture reverts back to red.

The yield was 96 % indicating complete incorporation of DPE and the molecular weight, M_n, was 71,600 g mol^{-1} (using the *dn*/*dc* value of polystyrene). This value is slightly higher than the target molecular weight of 51,500 g mol^{-1}. SEC analysis (Figure 2.84) shows a narrow distribution with only a very small amount of coupled material as indicated by the peak at a retention volume of 12.3 ml. The dispersity, Đ, was 1.07 and hence this reaction has successfully demonstrated that this method can be used to produce poly(butadiene-*co*-DPE)-*co*-DPE copolymers with a narrow dispersity with no premature termination. The ^{1}H NMR spectrum of the copolymer (PBdD-8) is shown in Figure 2.83 and from the integrals the ratio of DPE : butadiene is calculated as 1.00 : 3.00 and the 1,4-polybutadiene content is calculated as 34.4 %, which is consistent with the monomer molar feed ratio and the 1,4-polybutadiene content found for the previous reaction. Furthermore the ^{1}H NMR spectrum clearly shows alkene peaks that are characteristic of poly(butadiene-*co*-DPE) and also alkene peaks which are characteristic of the homopolymer of polybutadiene. In conclusion when butadiene and DPE are copolymerized with a larger feed ratio of butadiene with respect to DPE, a copolymer of poly(butadiene-*co*-DPE)-*co*-polybutadiene is formed, and due to the strong preference of butadiene to cross-propagate to DPE the initial block appears to be near-alternating despite the reduced molar feed ratio of DPE.

2.7. References

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CHAPTER 3

Thermal and Morphological Analysis of Sequence Controlled Copolymers

3. Thermal and Morphological Analysis of Sequence Controlled Copolymers

The thermal properties of copolymers are highly important as they correlate mechanical properties to temperature and therefore the temperature range within which the material possesses desired properties and the temperature required to process the polymer. These factors impact upon potential applications. Typically it is desirable for glassy polymers to have a glass transition temperature (T_g) well above the operating temperature (i.e. the temperature range at which a device operates or a product is used and may be subjected to during the lifetime of the application) and for rubbery polymers to have a T_g well below the operating temperature. For example polystyrene has a T_g of 100 °C and therefore cannot be used for any applications in which it might be exposed to higher temperatures as it would begin to flow and deform.[1] Conversely if a rubbery polymer is exposed to temperatures lower than the T_g it will become hard and brittle, e.g. if rubber tubing is frozen in liquid nitrogen the tubing freezes and is prone to breaking upon impact. Hence T_g has a dramatic effect upon the resulting mechanical properties. In the case of tri-block ABA thermoplastic elastomers, which require a rubbery middle block and two glassy outer blocks, there is both a low and high operating temperature limit. The low operating temperature results from the rubbery block which will no longer possess the desired mechanical properties (i.e. flexibility) below its T_g. The high operating temperature results from the T_g of the glassy block, below its T_g, the glassy block confines the rubbery matrix (i.e. provides reversible cross-links) providing beneficial elastomeric properties.[2] Above the T_g of the glassy block the copolymer will behave as a flexible rubbery polymer without the desirable elastomeric properties. It should be noted that in order to process these copolymers it is necessary to heat the copolymer above the T_g of the glassy block in order to mould the copolymer before cooling below the T_g and allowing the reversible cross-links to reform.

As described in Section 1.3.1, block copolymers tend to phase separate which arises due to the incompatibility of the two (or more) blocks (i.e. enthalpic contribution vs. entropic contribution). The solid state phase separated morphology of a block copolymer will also have an impact upon the resulting mechanical properties. As described in Section 1.3.2, ABA tri-block thermoplastic elastomers require either a spherical or cylindrical morphology in order to create a flexible rubbery matrix constrained by hard domains.[2]

3.1. Thermal Analysis of Poly(Styrene-*co*-1,1-Diphenylethylene)

As well as being a monomer of interest from the perspective of monomer sequence control, DPE is also interesting in so much that it can increase the T_g of the resulting copolymers and allow T_g to be tuned as a function of co-monomer composition.[3-5] DPE is a bulky monomer and results in reduced chain motion and stiffening of the polymer backbone, in turn leading to polymers with higher values of T_g. Previous studies suggest that a perfectly alternating copolymer of styrene and DPE will result in a copolymer with a T_g of approximately 180 °C, substantially higher than polystyrene which has a T_g of about 100 °C.[1] In the present study T_g values (shown in Table 3.1) were obtained by differential scanning calorimetry (DSC) (typical examples are shown in Figures 3.1 – 3.3), which can be correlated with the corresponding composition.[3]

Table 3.22: Copolymer composition and T_g values measured by DSC for the copolymerization of styrene and 1,1-diphenylethylene.

Sample	DPE mole %	DPE wt. %	T_g/°C	M_n/g mol^{-1}
PSD-9	47	61	177	60,000
PSD-3b	46	60	171	21,400
PSD-4	46	59	169	40,100
PSD-3c	45	59	170	91,800
PSD-8	45	59	168	71,600
PSD-7	45	58	170	57,200
PSD-2	42	56	158	10,700
PSD-1	33	46	142	9,000
PSD-6	-	-	98	1,900
PSD-10	-	-	99	1,800

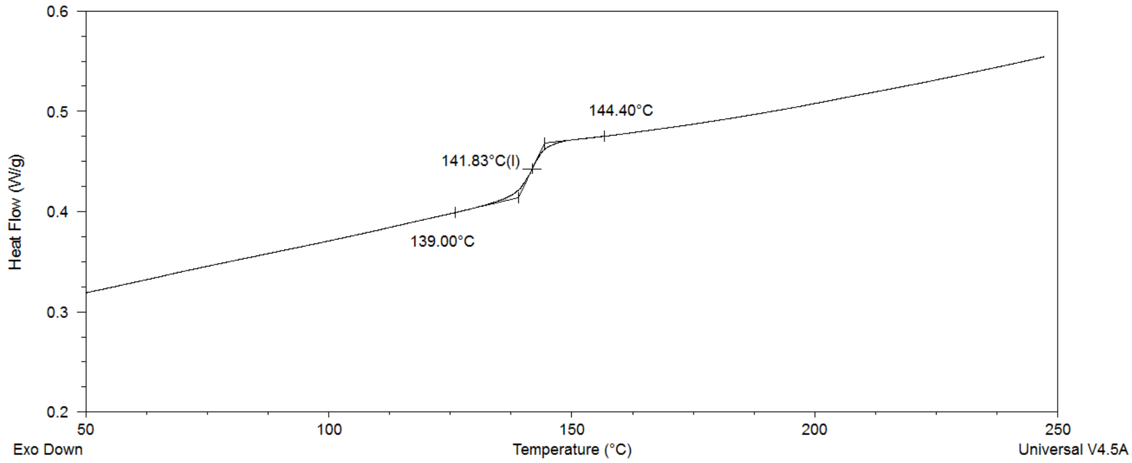

Figure 3.99: DSC thermogram obtained for the poly(styrene-*co*-DPE) copolymer, PSD-1, heated at a rate of 10 °C/min.

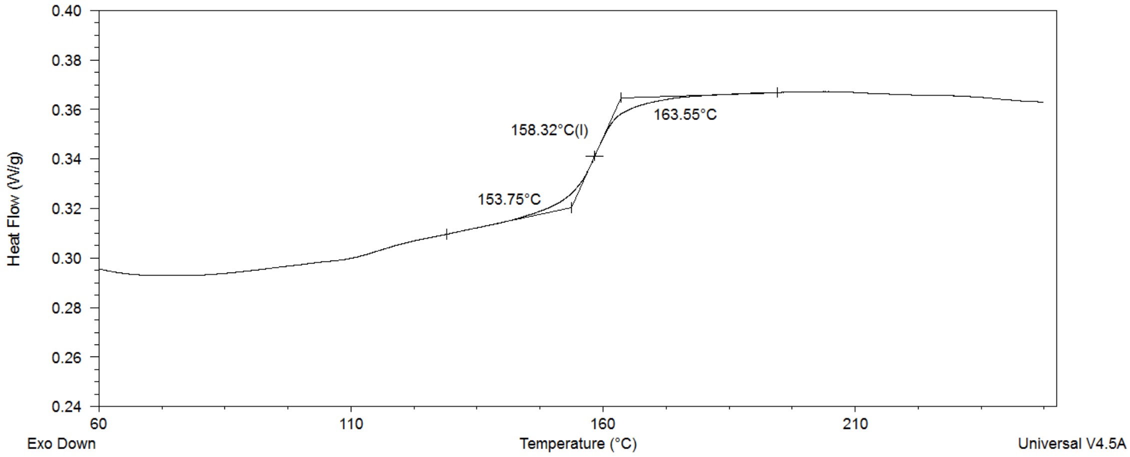

Figure 3.100: DSC thermogram obtained for the poly(styrene-*co*-DPE) copolymer, PSD-2, heated at a rate of 10 °C/min.

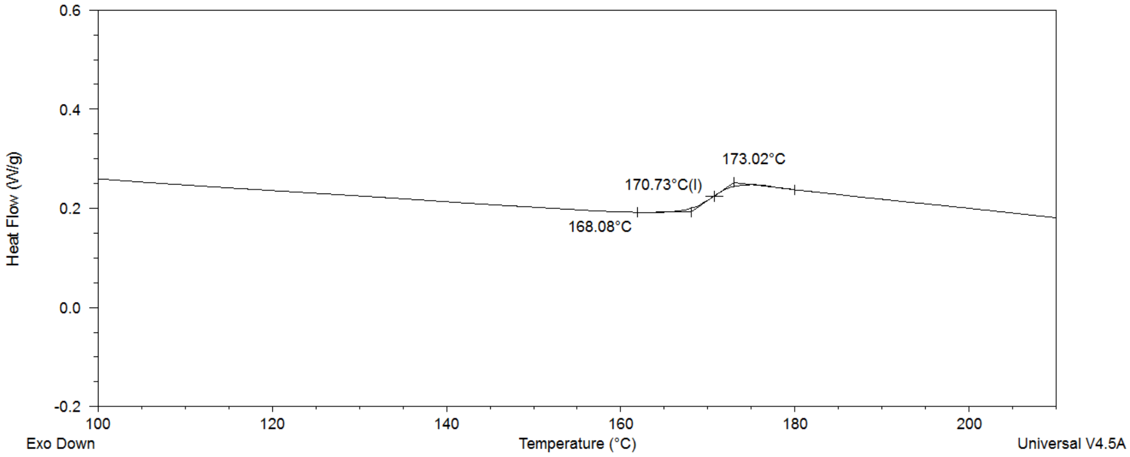

Figure 3.101: DSC thermogram obtained for the poly(styrene-*co*-DPE) copolymer, PSD-3b, heated at a rate of 20 °C/min.

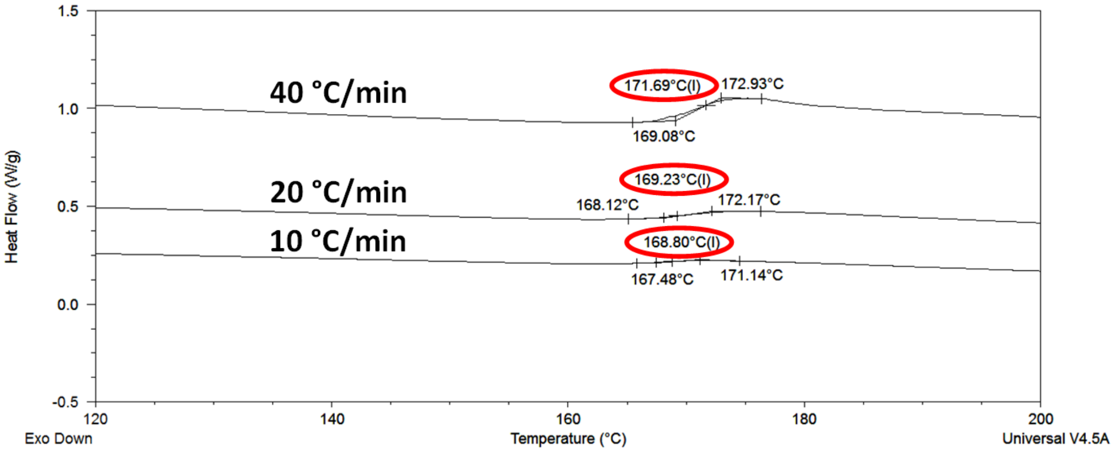

Figure 3.102: DSC thermogram obtained for the poly(styrene-co-DPE) copolymer, PSD-4, using a heating rate of 40 °C/min; 20 °C/min and 10 °C/min with the T_g highlighted by red circles.

The heating rate used to determine T_g was either 10 °C/min, 20 °C/min or 40 °C/min. A lower heating rate provides a more accurate T_g as it minimises any thermal lag. However, in some cases the T_g was too small to be detected with a heating rate of 10 or 20 °C/min, and a higher heating rate was required as this generates a larger change in heat flow at the T_g. This larger change in heat flow is due to a larger amount of heating power being required when passing through the T_g more quickly. To determine the impact of the heating rate on T_g, a number of heating and cooling cycles were performed on copolymer sample, PSD-4, with different heating rates (Figure 3.4). This shows that a change in heating rate between 10 and 40 °C/min results in a change in T_g from 168.8 to 171.7 °C, and hence the heating rate only affects T_g by about 3 °C. As the transition typically occurs over a range of about 8 °C this is therefore not a large source of error.

Xu and Bates have previously reported that the T_g of poly(styrene-*co*-DPE) increases by 1.09 °C/wt. % DPE,[3] however, Knoll *et al.* found T_g increases by 1.26 °C/wt. % DPE.[5] Plotting the experimental values of T_g for copolymers PSD-1 to 4 and PSD-7 to 9 versus wt. % DPE shows that T_g increases linearly by a value of 1.19 °C/wt. % DPE (Figure 3.5). However, T_g is not independent of molecular weight as shown by the Flory-Fox equation:

$$T_g = T_g^{\infty} - \frac{K}{M_n} \qquad [3.1]$$

where T_g^∞ is the T_g of a theoretical polymer of infinite molar mass.[1] K is a constant and

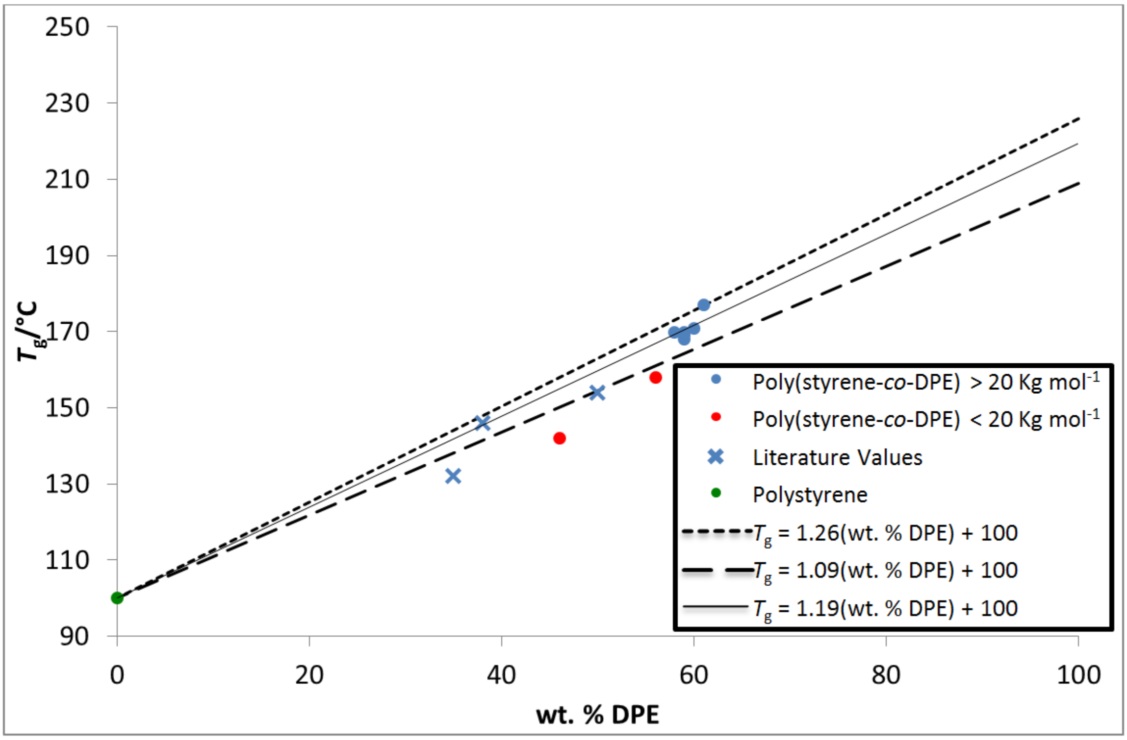

Figure 3.103: Graph showing the correlation between T_g and wt. % DPE for poly(styrene-co-DPE) copolymers.

an empirical parameter, related to the free volume contribution of chain ends, which for polystyrene is 1.7 x 10^5 mol K g^{-1},[1] and hence T_g decreases rapidly below about 20,000 g mol^{-1} but is relatively constant above this value. It should be noted that the value of K for poly(styrene-*co*-DPE) may not be the same as the value of K for polystyrene however due to the similarity in chemical structure it is unlikely that poly(styrene-*co*-DPE) will have a significantly different value of K from polystyrene and hence it has been assumed that values above 20,000 g mol^{-1} will have a relatively constant T_g. For this reason copolymers with a lower molecular weight (< 20,000 g mol^{-1}) have been excluded from the calculation of the dependence of T_g on the wt. % DPE. The T_g for 0 wt. % DPE (i.e. a homopolymer of polystyrene) has been obtained from literature as 100 °C and set as the intercept.[1] For comparison the values obtained by Xu and Bates (shown as crosses) have been included as well as both trend lines representing the correlation of T_g to wt. % DPE found by Xu *et al*. and Knoll *et al*. (shown by dashed lines).

This relationship between the wt. % of the co-monomers and T_g is approximately linear and can be approximated by the equation:

$$T_{gco} = T_{gSty}\omega_{Sty} + T_{gDPE}\omega_{DPE} \qquad [3.2]$$

where T_{gco} is the T_g of the copolymer, T_{gSty} and T_{gDPE} are T_g values of the respective homopolymers and ω_{Sty} and ω_{DPE} are the respective weight fractions.[6] Although it is not possible for DPE to homopolymerize, this equation can be used to calculate the theoretical T_g of poly(1,1-diphenylethylene) as 219 °C which can be seen graphically by extrapolating the values to 100 wt. % DPE in Figure 3.5. The theoretical maximum T_g can also be determined for a perfectly alternating copolymer of poly(styrene-*alt*-DPE) to be 175 °C (wt. % DPE = 63.4 %). The T_g values obtained herein for the poly(styrene-*co*-DPE) samples are in good agreement with the correlations with wt. % DPE that are found in literature. Furthermore, due to the high incorporation of DPE, the copolymers obtained herein have very high T_g values (~ 170 °C) which are higher than any previously reported T_g values for poly(styrene-*co*-DPE) copolymers.[3]

3.2. Thermal Analysis of Poly(Butadiene-*co*-1,1-Diphenylethylene) with a Microstructure of 64 % 1,4-Polybutadiene

There is no reported comparable equation to estimate the relationship between composition and T_g for P(Bd-*co*-D) copolymers. Herein the T_g for a near-perfectly alternating copolymer of P(Bd-*co*-D) is reported. The T_g for a homopolymer of polybutadiene varies with microstructure (i.e. 1,4- and 1,2-PBd content). The *cis*-to-*trans* ratio does not significantly affect the T_g,[7] and attempts to quantify this effect have been inconclusive,[8] for example whilst Colby *et al*. reported that T_g increases with an increase in *cis*-to-*trans* ratio[7] Groenewoud reported the opposite trend.[9-10] High 1,4-PBd has a T_g of approximately -110 °C (99.6 % 1,4-PBd) whereas high 1,2-PBd has a T_g of approximately -30 °C (79 % 1,2-PBd).[8] The P(Bd-*co*-D) copolymers in question (both with the same composition but with different molecular weights) were found to contain 64 % 1,4- and 36 % 1,2-PBd by ^{1}H NMR analysis and comparable homopolymers of polybutadiene with a 62 – 66 % 1,4-PBd content have a T_g of –73 °C reported by Makhiyanov and Temnikova.[8] Herein a T_g of 117 °C and 67 °C was obtained for the high and low molecular weight sample of P(Bd-*co*-D) (PBdD-1 and PBdD-2) respectively (DSC thermograms are shown in Figures 3.6 and 3.7 and molecular weight data in Table 3.2). These values of T_g are both substantially higher than the

Table 3.23: Copolymer composition and glass transition temperatures measured by DSC for the copolymerization of butadiene and 1,1-diphenylethylene.

Sample	DPE mole %	DPE wt. %	Glass Transition Temperature/ °C	M_n/g mol^{-1}
PBdD-1	49	76	117	70,200
PBdD-2	49	76	67	2,000

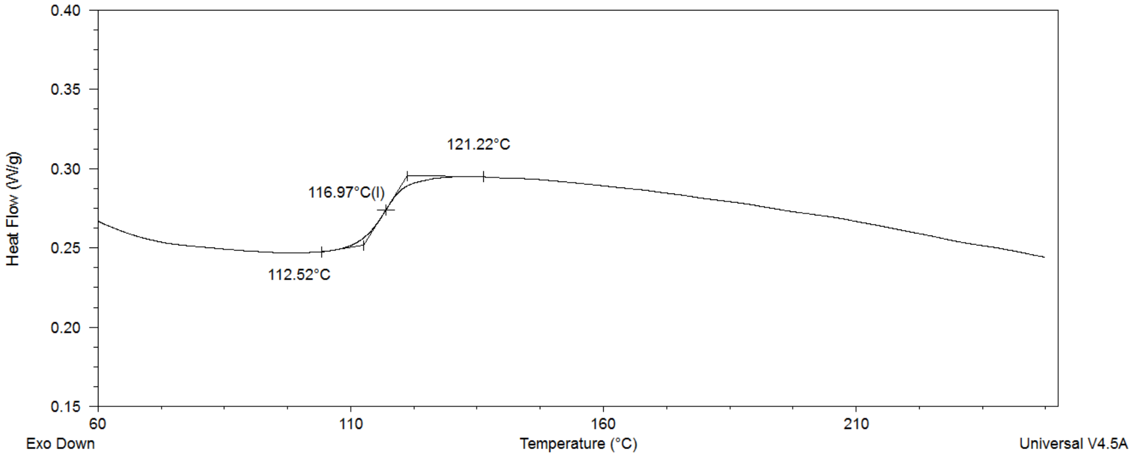

Figure 3.104: DSC thermogram obtained for the poly(butadiene-*co*-DPE) copolymer, PBdD-1, heated at a rate of 10 °C/min.

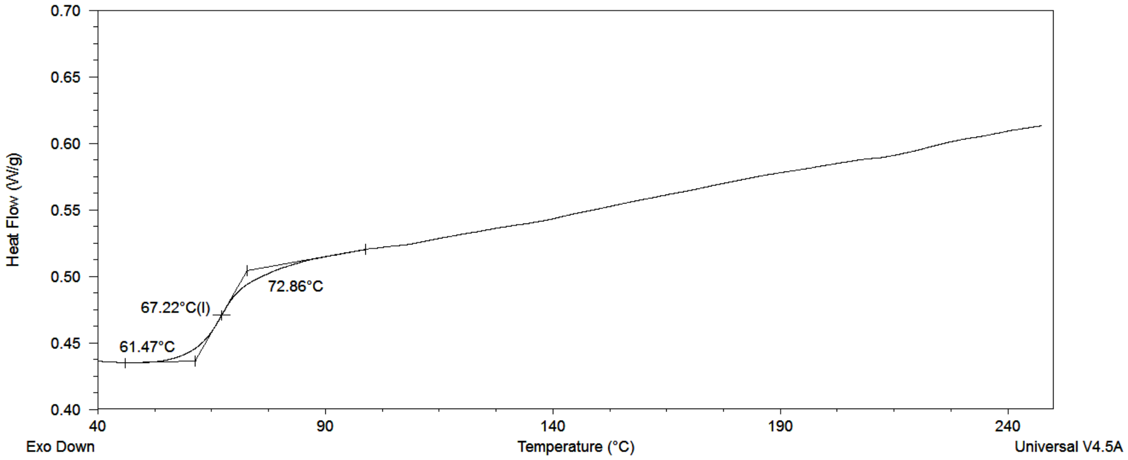

Figure 3.105: DSC thermogram obtained for the poly(butadiene-*co*-DPE) copolymer, PBdD-2, heated at a rate of 10 °C/min.

homopolymer of polybutadiene, as expected. As the relationship between T_g and composition is determined from the weight fractions, it is the weight difference between units of butadiene and DPE which accounts for this large increase in T_g, i.e. a perfectly alternating copolymer of poly(butadiene-*alt*-DPE) would have a DPE weight % of 76.9 %.

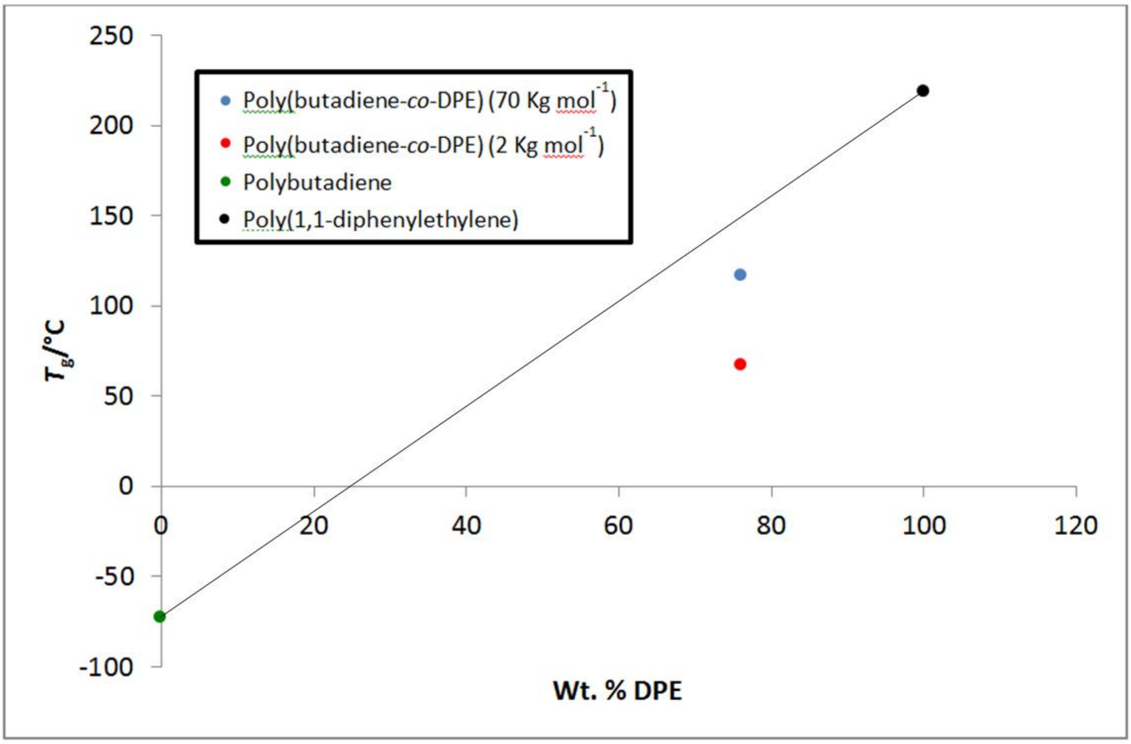

Figure 3.106: Graph showing the correlation between T_g and wt. % DPE for poly(butadiene-*co*-DPE) copolymers.

As there is only one high molecular weight sample of P(Bd-*co*-D) in this study, it is not possible to obtain an accurate correlation between T_g and composition. However, to illustrate that the T_g values obtained for P(Bd-*co*-D) approximately fall onto a linear relationship between the two respective homopolymers, a plot showing these copolymer T_g values, the theoretical T_g value of poly(1,1-diphenylethylene) (obtained from extrapolating the T_g of poly(styrene-*co*-DPE) to 100 % DPE) and the T_g value for polybutadiene (62 – 66 % 1,4-PBd) is shown in Figure 3.8. However, it should be noted that this plot is only for comparison as the T_g for poly(1,1-diphenylethylene) was found by extrapolation and the T_g for polybutadiene strongly depends on the microstructure.

3.3. Thermal Analysis of Poly(Styrene-*co*-1,1-Diphenylethylene)-*block*-Polybutadiene Prepared by Sequential Addition of Butadiene

For alternating, statistical and random copolymers a single combined T_g is observed. This T_g is approximately a linear function of the weight fraction of the constituent monomers. In the case of block copolymers the number of observed transitions depends on the number of blocks, the block length and the interactions between monomer units. A single T_g is observed if the blocks are short and not too incompatible, and in some cases a single T_g can be observed even if the blocks are long but both monomer units are well mixed due to the block copolymer consisting of a one-phase morphology. If the blocks are high molecular weight and incompatible then microphase separation occurs and two (or more) T_g values will be observed which are close to the T_g of the corresponding homopolymers. Furthermore, if the microphase separation results in a diffuse interface then a shell of mixed M_1 and M_2 units (where M_1 and M_2 represent the constituent monomers in each block) may surround the domains, and can give rise to an additional T_g which will have a value between the T_g of each constituent block.[11]

For the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymers prepared in the current study, the T_g of the polybutadiene block could not be detected by DSC due to the limitation in temperature range or the calorimeter, it could however, be found using dynamic mechanical analysis (DMA). Furthermore, when the poly(styrene-*co*-DPE) block was relatively short compared to the polybutadiene block it was also not possible to detect the T_g of this block, such as in copolymers P(SD)-PBd-6 to 8 where the butadiene content is between 62 and 75 wt. %. For this reason a poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer, P(SD)-PBd-3, was prepared specifically for thermal analysis with a composition of styrene : DPE : butadiene = 1.00 : 0.85 : 2.28 (mole fraction), 32 wt. % PBd and a total M_n of 66,600 g mol^{-1} (calculated using the *dn*/*dc* value of polystyrene). The DMA analysis (shown in Figure 3.9) shows a T_g at -65.0 °C on the heating cycle and -96.2 °C on the cooling cycle. The difference between these two values is most likely caused by the thermal lag in the polymer sample; however, taking an average indicates a T_g of -81 °C which is consistent with the T_g of a homopolymer of polybutadiene.

The T_g for the poly(styrene-*co*-DPE) block can be determined by DSC analysis (Figure 3.10). The heating rate was varied from 10 – 40 °C/min and the resulting T_g value varied from 172.8 – 174.0 °C and an average value of 173.4 °C was obtained (Figure 3.11). However, with a heating rate of 10 °C/min the T_g was visible but too small to be analysed. The T_g of the glassy block was also obtained by DMA; the DMA shows a T_g at

198 °C on the heating cycle. However, because of the large thermal lag when analysed by DMA, this value is likely to be less accurate than the value obtained by DSC.

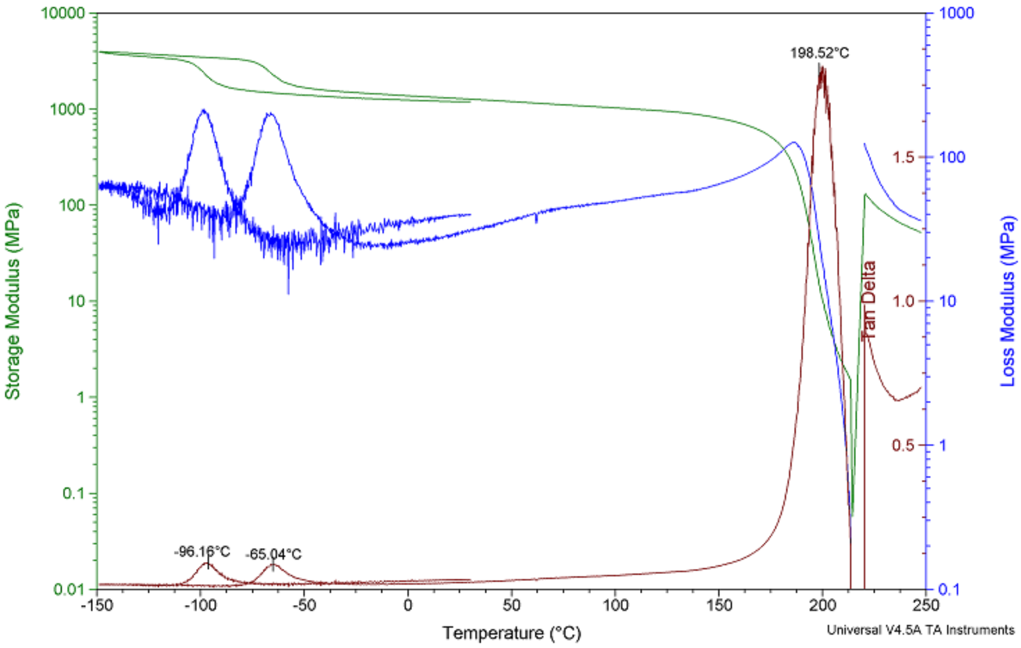

Figure 3.107: DMA analysis on the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer, PSD-PBd-3, showing the T_g observed upon heating and cooling at 5 °C/min.

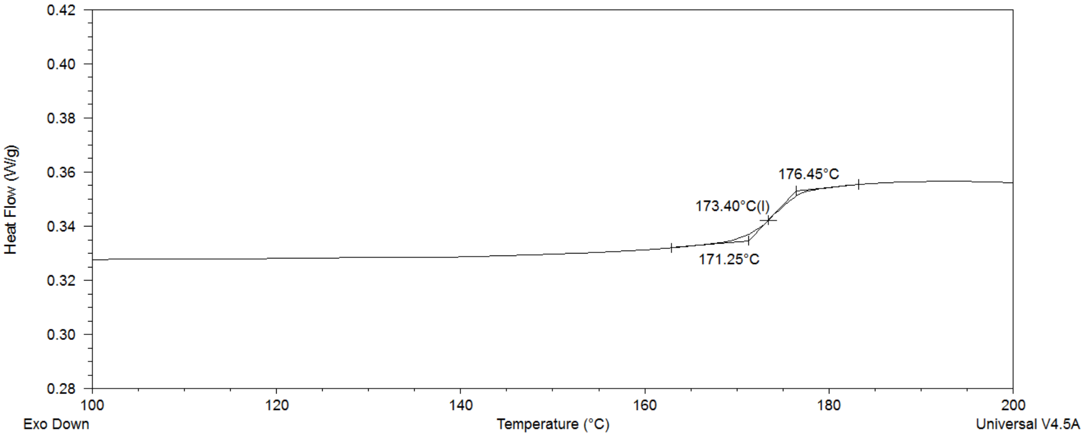

Figure 3.108: DSC thermogram obtained for the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer, PSD-PBd-3, showing the T_g observed upon heating at 40 °C/min.

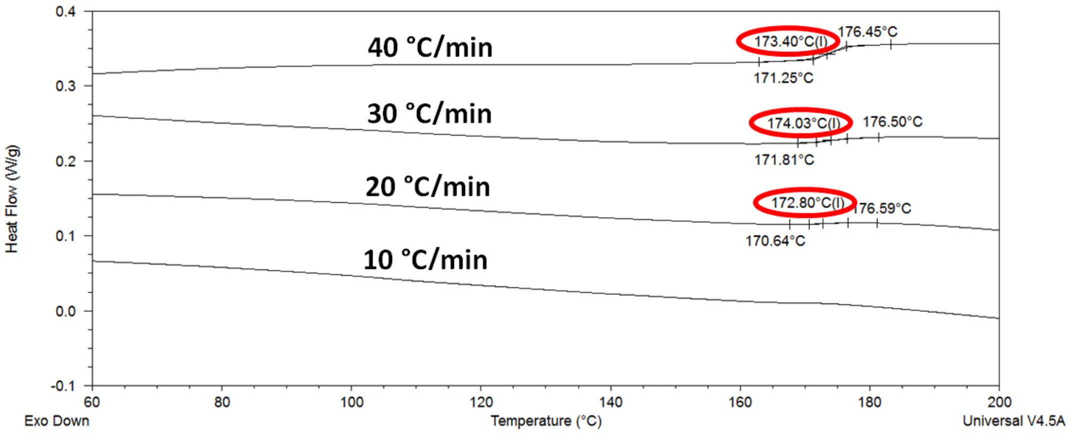

Figure 3.109: DSC thermogram obtained for the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer, PSD-PBd-3, showing the T_g observed upon heating at 10 °C/min; 20 °C/min; 30 °C/min and 40 °C/min with the T_g highlighted by red circles.

3.4. Thermal Analysis of Poly(Butadiene-*co*-Styrene-*co*-1,1-Diphenylethylene) Prepared by Simultaneous Copolymerization

To compare whether an analogous copolymer prepared by simultaneous copolymerization (fire and forget approach) has similar thermal properties to one prepared by the more common approach of sequential addition of monomers, a copolymer was prepared by the simultaneous copolymerization of styrene, DPE and butadiene for thermal analysis, PBdSD-4d. To allow comparison with P(SD)-PBd-3, this copolymer was prepared with a composition of styrene : DPE : butadiene = 1.00 : 0.83 : 2.94 (mole fraction), 38 wt. % PBd and a total M_n of 58,500 g mol^{-1}. Again the T_g of the polybutadiene 'block' had to be determined from DMA (Figure 3.12). Upon heating, the T_g was found to be -57.7 °C and upon cooling it was found to be -92.3 °C, and taking the average value gives a T_g of -75 °C. Again this is approximately the expected value of the homopolymer polybutadiene, and also only differs by 5 °C from the T_g found for the analogous block copolymer synthesized by sequential addition, P(SD)-PBd-3.

The DSC data shows an average T_g of 172.0 °C for the poly(styrene-*co*-DPE) 'block' when the heating rate is varied from 10 – 40 °C/min (Figures 3.13 – 3.14). Again, this is very close to the T_g obtained for the analogous block copolymer, P(SD)-PBd-3, which was found to be 173.4 °C.

The thermal analysis of P(SD)-PBd-3 (prepared by sequential addition) and PBdSD-4d (prepared by the simultaneous copolymerization) shows that the simultaneous copolymerization of styrene, DPE and butadiene produces a copolymer with very similar thermal properties to a copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene prepared by the sequential addition of butadiene. This suggests that the simultaneous copolymerization creates a copolymer in which the resulting structure is 'block-like' with distinguishable blocks of poly(styrene-*co*-DPE) and polybutadiene. Whilst it is likely that there will be a monomer gradient in the middle section of this copolymer, it would appear as if this does not impact significantly upon the thermal properties of the copolymer.

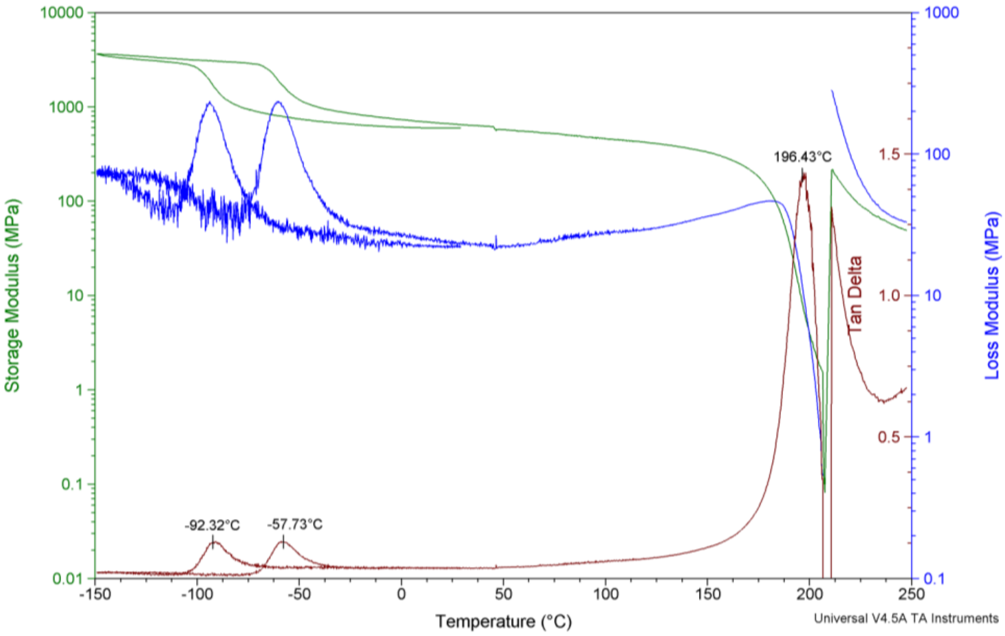

Figure 3.110: DMA analysis on the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-4d, showing the T_g observed upon heating and cooling at 5 °C/min.

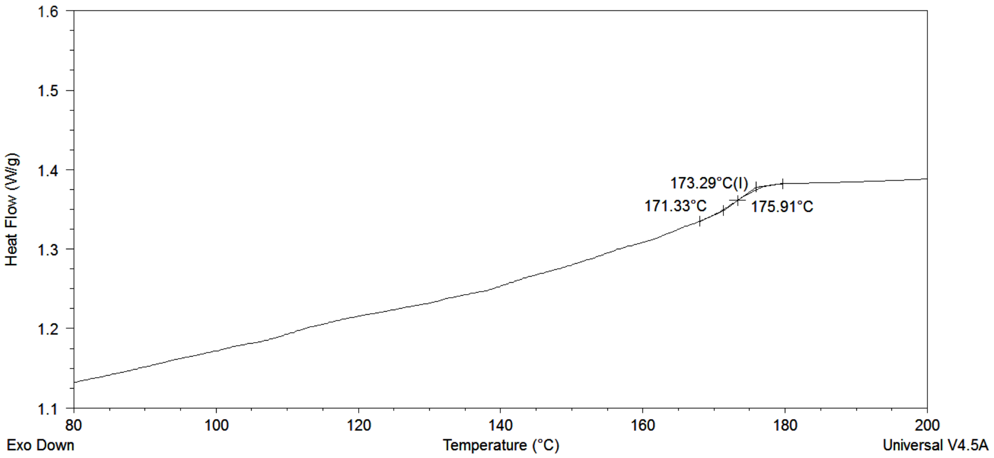

Figure 3.111: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-4d, showing the T_g observed upon heating at 40 °C/min.

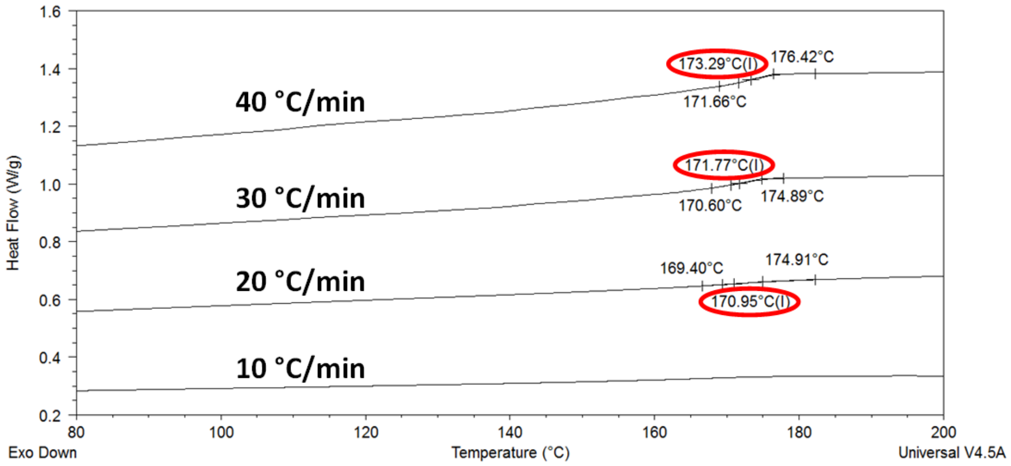

Figure 3.112: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-4d, showing the T_g observed upon heating at 10 °C/min; 20 °C/min; 30 °C/min and 40 °C/min.

3.5. TEM Analysis of the Solid State Morphology of Styrene, 1,1-Diphenylethylene and Butadiene Terpolymers

There are currently no literature reports of the phase separation and resultant solid state morphology of block copolymers containing DPE. A more commonly studied block copolymer with respect to morphology is that of polyisoprene-*block*-polystyrene (Figure 3.15).[12] It was assumed, for a preliminary basis, that the phase diagram of polybutadiene-*block*-poly(styrene-*co*-DPE) would show similarities to that of polyisoprene-*block*-polystyrene. However, whilst polybutadiene and polyisoprene are chemically quite similar, poly(styrene-*co*-DPE) is likely to be much stiffer than polystyrene. In the present study, the phase separated morphology of the styrene, DPE and butadiene terpolymers was analysed by transmission electron microscopy (TEM). As seen in the phase diagrams by Bates and Fredrickson (Figure 3.15),[12] to obtain a copolymer with a clearly defined phase-separated morphology, a suitably high degree of polymerization, *N*, is required, and as *N* is directly proportional to the molecular weight, a copolymer with a high molecular weight is required.

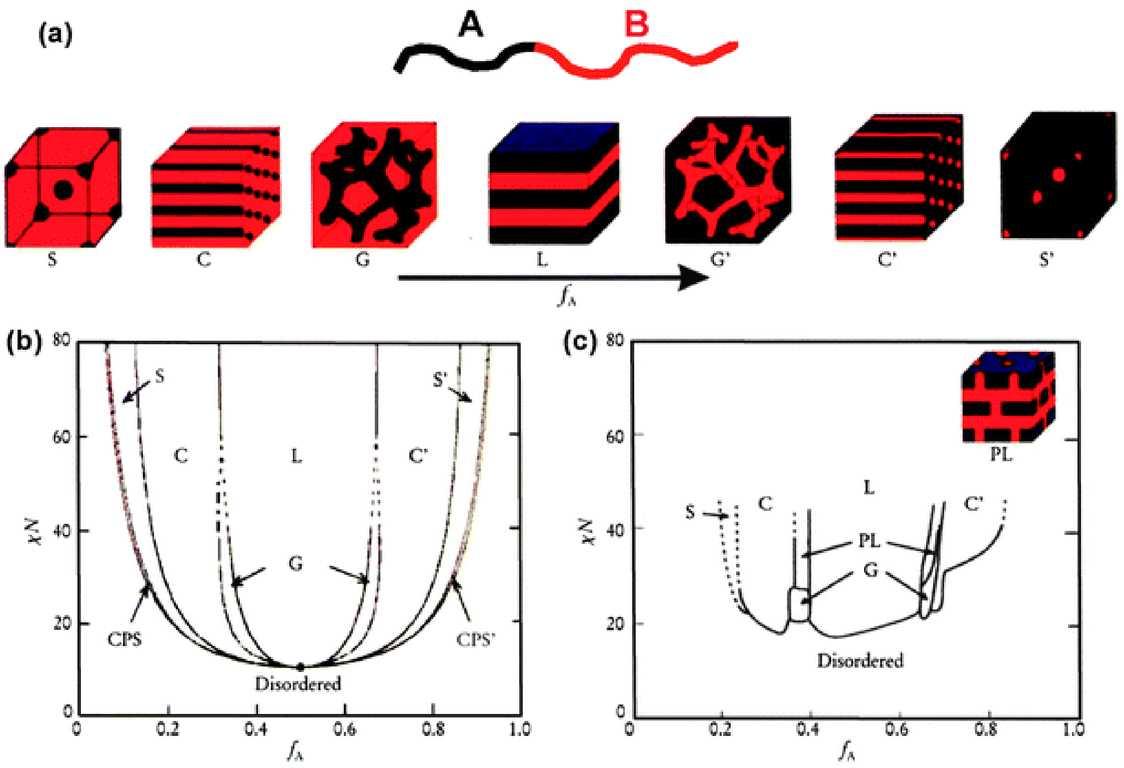

Figure 3.113: (a) Theoretical and (b) Experimental Phase diagram for a Polyisoprene-block-Polystyrene copolymer, and (c) microstructure schematics of (S) spherical (C) cylindrical (G) gyroid (L) lamellar and (PL) perforated layers. f_A is the volume fraction of polyisoprene, χ is the interaction parameter, *N* is the degree of polymerization and CPS are close packed spheres. Reprinted with permission from Bates, F. S., Fredrickson, G. H., Physics Today, Vol. 52/2, Page 32-38, 1999. Copyright 1999, American Institute of Physics.[12]

The phase diagrams of ABA tri-block copolymers are more complicated than those of AB di-blocks due to the addition of a third block of variable length. Not only does one need to be concerned about the volume fraction of each monomer but in the case of the 'A' monomer, how this monomer is distributed between the two 'A' blocks. Therefore the morphology of 'di-blocks' polybutadiene-*block*-poly(styrene-*co*-DPE) and poly(butadiene-*co*-styrene-*co*-DPE) copolymers were first investigated in order to establish whether both synthetic routes (copolymerization with sequential addition of butadiene or 'fire and forget') resulted in copolymers with similar morphologies prior to investigating the morphology of DPE containing tri-block copolymers. It was desirable to obtain copolymers with a well-ordered morphology, and in this case it was decided to target a cylindrical morphology.

The theoretical phase diagram shown in Figure 3.15 shows that to obtain a cylindrical morphology for a di-block copolymer of polyisoprene-*block*-polystyrene a styrene volume fraction of 0.15 – 0.35 is required. It was assumed that a similar styrene-*co*-DPE volume fraction of 0.15 – 0.35 would be required to obtain a cylindrical morphology in a block copolymer of polybutadiene-*block*-poly(styrene-*co*-DPE). As mentioned previously, this was based on the (cautious) assumption that a block copolymer of polybutadiene-*block*-poly(styrene-*co*-DPE) would behave similarly to polyisoprene-*block*-polystyrene. The volume fraction can be determined from the weight fraction and density of each block. The density of polybutadiene varies depending on microstructure but high 1,4-polybutadiene is typically quoted between 0.91 – 0.97 g cm^{-3}, which gives an average of 0.94 g cm^{-3}.[13-15] Although the density of polystyrene is quoted between 1.04 – 1.12 g cm^{-3},[13-14] to accurately determine the density of poly(styrene-*co*-DPE), salt solutions (calcium chloride in water) were used with known densities. The copolymer, PSD-3c (41.3 wt. % styrene), was found to have neutral buoyancy in a calcium chloride solution of 11.9 % w/w which corresponds to a density of 1.10 g cm^{-3}, and hence the density of poly(styrene-*co*-DPE) is not significantly different from that of polystyrene. The required weight fraction of styrene-*co*-DPE for a cylindrical morphology is therefore found from the following equation:

$$\omega_A = \frac{V_A \rho_A}{V_A \rho_A + \rho_B (1 - V_A)} \qquad [3.3]$$

where ω_A is the weight fraction of block A, V_A is the volume fraction of block A and ρ_A and ρ_B are the densities of block A and B respectively. Using equation 3.3 and values of 1.10 g cm^{-3} for the density of poly(styrene-*co*-DPE) and 0.94 g cm^{-3} for the density of polybutadiene it was calculated that a copolymer with a styrene-*co*-DPE weight fraction of 0.17 – 0.39 should result in a cylindrical morphology assuming poly(styrene-*co*-DPE)-*block*-polybutadiene and polystyrene-*block*-polyisoprene will have the same morphology with the same volume fraction of the glassy block.

Copolymer PSD-PBd-6 (poly(styrene-*co*-DPE)-*block*-polybutadiene) was synthesized with a number average molecular weight, M_n, of 102,000 g mol^{-1} and a monomer mole ratio of styrene : DPE : butadiene = 1.00 : 0.85 : 14.29, which corresponds to a styrene-

co-DPE weight fraction of 0.25. The TEM images of PSD-PBd-6 are shown in Figure 3.16. This shows that the morphology is not cylindrical as targeted, however, the target composition was based on that required for polyisoprene-*block*-polystyrene. Moreover, since the experimental and theoretical phase diagrams for polyisoprene-*block*-polystyrene (Figure 3.15) differ it is perhaps not surprising that the first attempt did not result in a cylindrical morphology. Instead the TEM images show a predominantly spherical morphology with spheres of styrene-*co*-DPE (white) in a butadiene matrix (black), which would suggest that the weight % of the butadiene block is too high for cylinders to form. However, whilst the TEM images clearly show a spherical morphology it should be noted that the long range order is not perfect.

It could be argued that the lack of perfect long range order in the observed TEM images suggests that the composition of the copolymer puts the polymer close to the phase boundary between spherical and cylindrical morphologies. Furthermore, this copolymer contains some heterogeneity, introduced as a result of its preparation by the sequential addition of monomers. The block copolymer contained a small quantity of poly(styrene-*co*-DPE) copolymer calculated as approximately 10 % (by mass) of the amount of the poly(styrene-*co*-DPE)-*block*-polybutadiene copolymer from the area under the curve in the RI response resulting from inadvertent premature termination. In this case it is likely that the poly(styrene-*co*-DPE) copolymer will be situated within

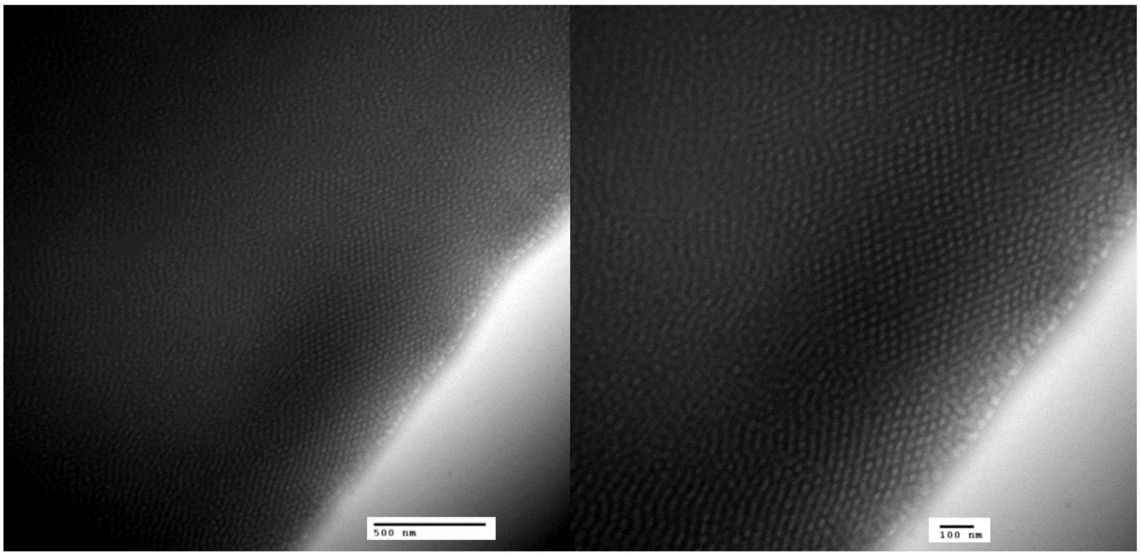

Figure 3.114: TEM images of the copolymer poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-6, with the butadiene blocks stained black with OsO_4.

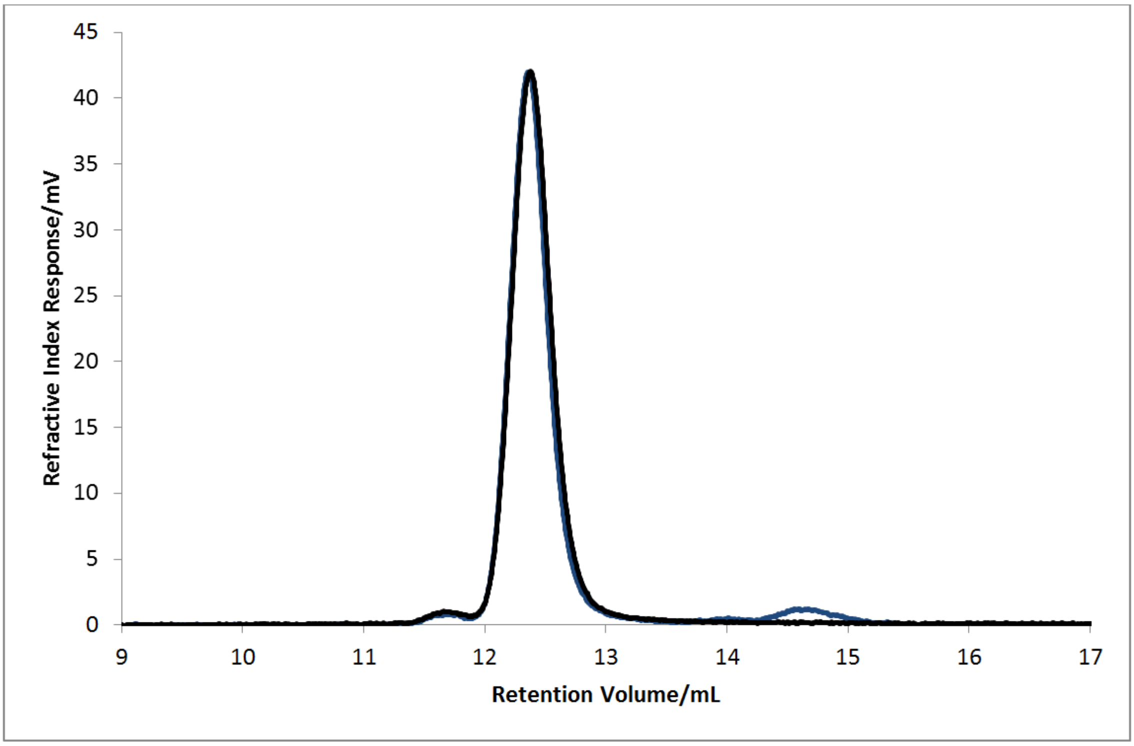

Figure 3.115: SEC chromatogram (refractive index) for the copolymer poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-6, before fractionation (blue) and after fractionation (black).

the styrene-*co*-DPE domains formed from the block copolymer and should therefore not have a significant impact upon the morphology as the styrene-*co*-DPE domains should still have the desired volume. However, a consequence of partial termination of these chains means that the resulting polybutadiene block will have a higher molecular weight than desired which will affect the composition of the final copolymer and could

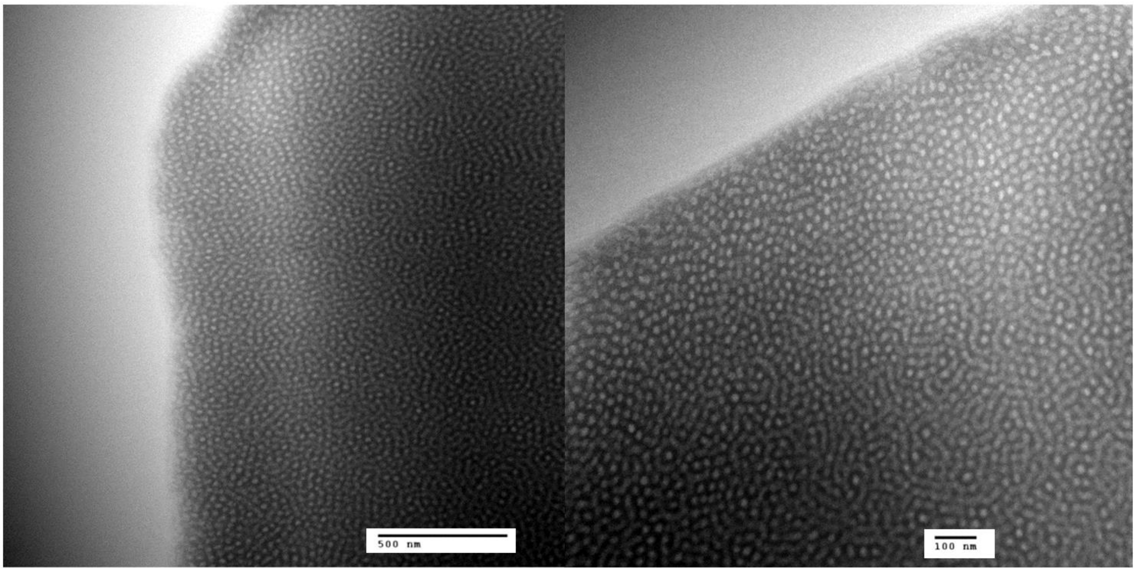

Figure 3.116: TEM images of the copolymer poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-6, after removal of the poly(styrene-*co*-DPE) impurity by fractionation with the butadiene blocks stained black with OsO_4.

potentially change the morphology. To investigate the impact that the poly(styrene-*co*-DPE) copolymer has upon the morphology of the poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-6, the crude product was purified by fractionation. The overlay of the SEC chromatograms of the sample before and after fractionation can be seen in Figure 3.17. Analysis of the ^{1}H NMR spectrum of the fractionated sample of PSD-PBd-6 indicated that the block copolymer composition was in fact styrene : DPE : butadiene = 1.00 : 0.85 : 17.30, and hence the weight fraction of styrene-*co*-DPE is only 0.22 (rather than 0.25). The TEM images of the fractionated copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-6, are shown in Figure 3.18 and indicate that the morphology of the purified block copolymer appears to be spherical but lacking long range order. Indeed the morphology appears to be less well-ordered than the crude copolymer indicating that removal of the poly(styrene-*co*-DPE) copolymer has shifted the resulting morphology closer to a phase boundary, presumably due to the reduction of the volume size of the styrene-*co*-DPE domains.

In light of this and with the desire to produce a sample with an unambiguous morphology, a new copolymer, PBdSD-5 (poly(butadiene-*co*-styrene-*co*-DPE)) was synthesized with a number average molecular weight, M_n, of 111,900 g mol^{-1} and a mole fraction of styrene : DPE : butadiene = 1.00 : 0.85 : 12.60 which corresponds to a styrene-*co*-DPE weight fraction of 0.27. The TEM images of PSD-PBd-5 are shown in Figure 3.19. The morphology of the poly(butadiene-*co*-styrene-*co*-DPE) copolymer,

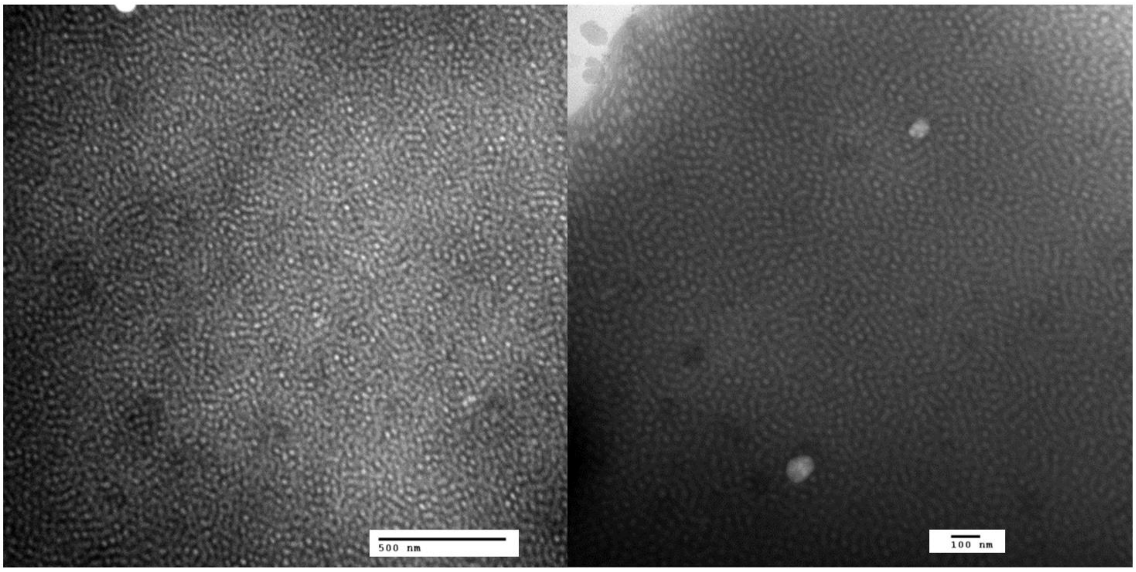

Figure 3.117: TEM images of the copolymer poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-5, with the butadiene blocks stained black with OsO_4.

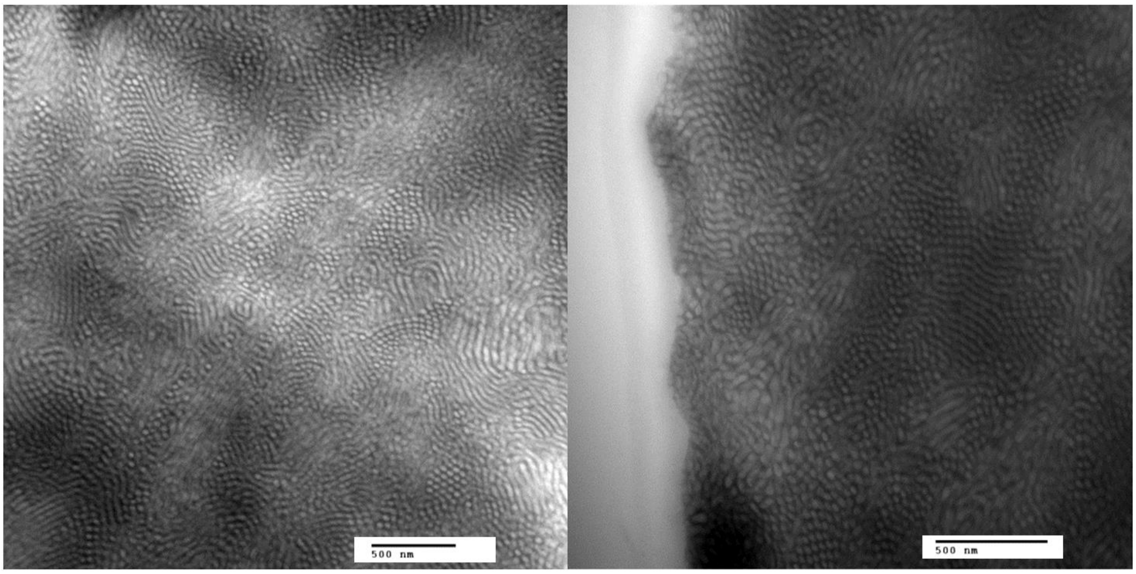

Figure 3.118: TEM images of the copolymer poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-8, with the butadiene blocks stained black with OsO_4.

PBdSD-5, is very similar to that of P(SD)-PBd-6 before and after fractionation, and again it is believed this morphology lies close to the spherical boundary.

If a weight fraction of 0.22 – 0.27 is indeed on the spherical/cylindrical morphology phase boundary, then a styrene-*co*-DPE weight fraction of 0.35 should be well within the cylindrical morphology phase and copolymers with a target styrene-*co*-DPE weight fraction of 0.35 were therefore synthesized. The copolymer PSD-PBd-8 (poly(styrene-*co*-DPE)-*block*-polybutadiene) was synthesized with a number average molecular

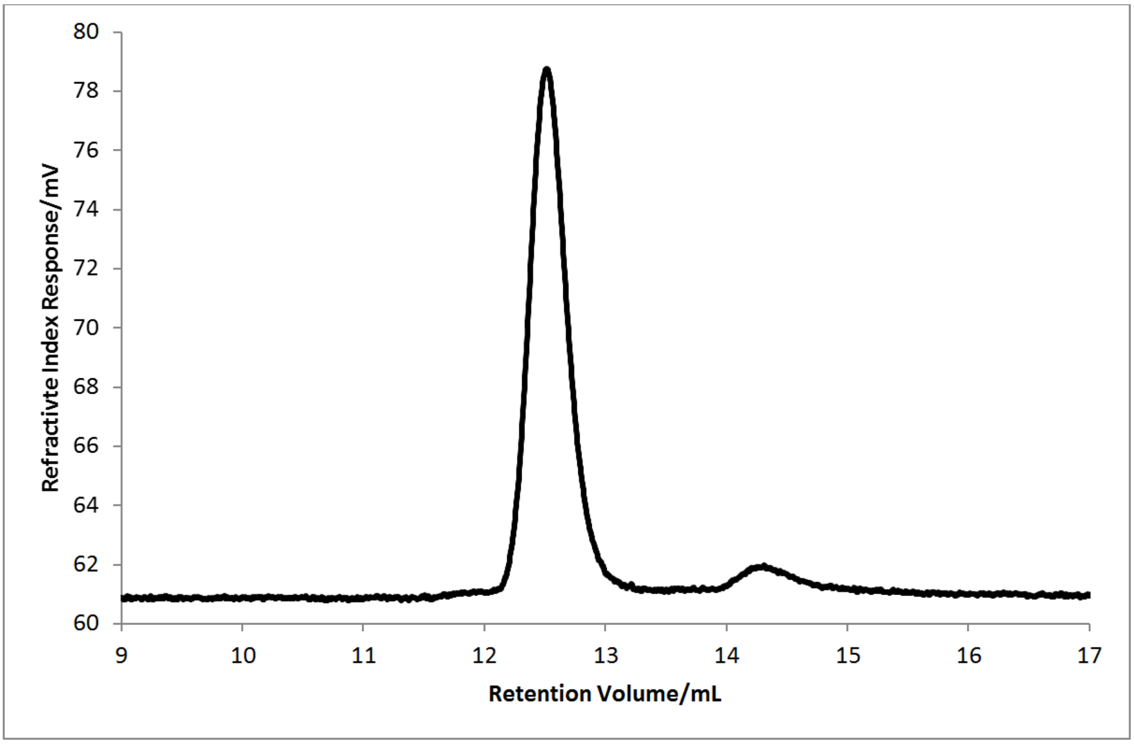

Figure 3.119: SEC chromatogram (refractive index) for the copolymer poly(styrene-*co*-DPE)-*block*-polybutadiene, PSD-PBd-8.

weight, M_n, of 135,500 g mol^{-1} and a mole ratio of styrene : DPE : butadiene = 1.00 : 0.85 : 7.78 and hence a styrene-*co*-DPE weight fraction of 0.38. The TEM images of PSD-PBd-8 are shown in Figure 3.20 and although the long range order is not great, there is an indication of cylindrical morphology as evidenced by hexagonally packed cylinders in both the side-on and head-on orientations. It should however be noted that the copolymer sample 'as-prepared' is contaminated with some poly(styrene-*co*-DPE) copolymer as shown in the SEC chromatogram (Figure 3.21) and the styrene-*co*-DPE weight fraction in the block copolymer of 0.38 will therefore be a slight overestimation.

In contrast the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-8, was synthesized by the 'fire and forget' approach but with a comparable composition and molecular weight to the copolymer PSD-PBd-8 which was prepared by sequential addition of monomers. The number average molecular weight, M_n, of PBdSD-8 (fire and forget) was 122,500 g mol^{-1} with a monomer mole ratio of styrene : DPE : butadiene = 1.00 : 0.85 : 9.32 and hence a styrene-*co*-DPE weight fraction of 0.34. The

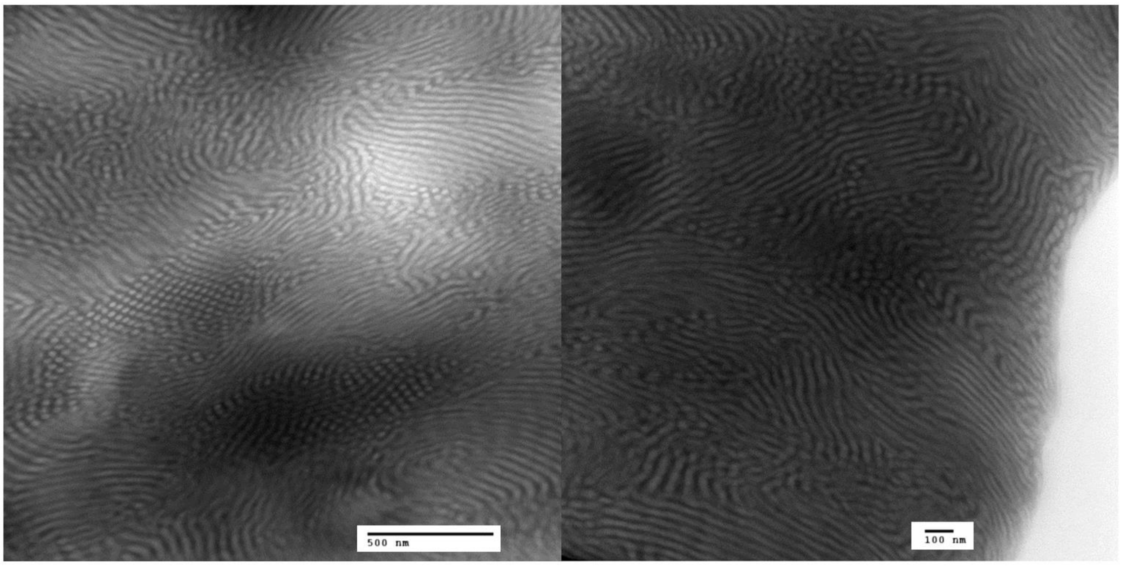

Figure 3.120: TEM images of the copolymer poly(butadiene-*co*-styrene-*co*-DPE), PBdSD-8, with the butadiene blocks stained black with OsO_4.

TEM images of PBdSD-8 are shown in Figure 3.22 and both the side-on and head-on orientations of hexagonally packed cylinders indicate a cylindrical morphology. These results show that poly(butadiene-*co*-styrene-*co*-DPE) prepared by a 'fire and forget' approach has very similar morphology to that prepared by the sequential addition of monomers at a comparable molecular weight and composition. However, the 'fire and forget' approach is a much more facile approach and bypasses the possibility of heterogeneities through premature termination.

3.6. TEM Analysis of the Solid State Morphology of Poly(Styrene-*co*-1,1-Diphenylethylene)-*co*-Polybutadiene-*co*-Poly(Styrene-*co*-1,1-Diphenylethylene) prepared with a Difunctional Initiator

Phase diagrams of tri-block copolymers contain a third variable parameter that arises from the length of the third block and are therefore typically represented using a constant value of χN. The theoretical phase diagram of an ABA tri-block copolymer with χN = 20, 30 and 40 is shown in Figure 3.23.[16] The composition of the polymer is specified by $0 \leq f_A \leq 1$, and the asymmetry in the block lengths of A is defined by τ where:

$$\tau = \frac{N_{A1}}{N_{A1} + N_{A2}} \qquad [3.4]$$

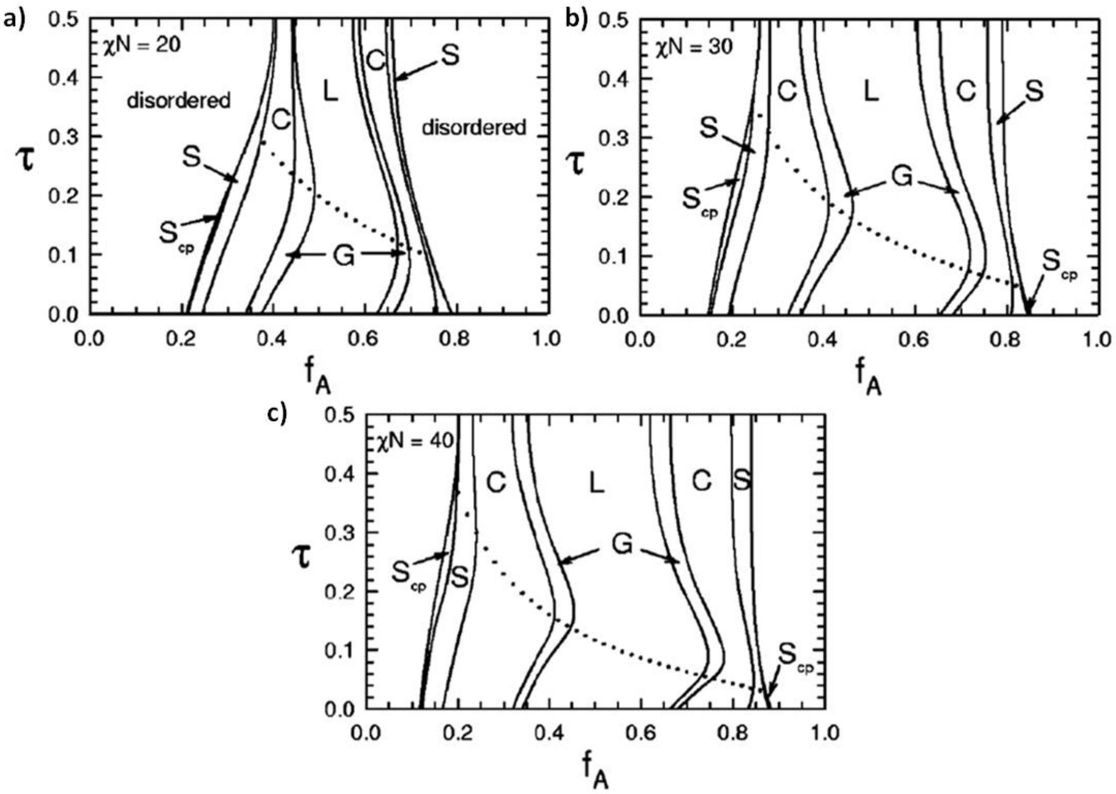

Figure 3.121: Phase diagrams for asymmetric ABA tri-block copolymers spanning the di-block (τ = 0.0) and symmetric tri-block (τ = 0.5) limits for (a) χN = 20, (b) χN = 30 and (c) χN = 40. Reprinted with permission from Matsen, M. W., The Journal of Chemical Physiscs, Vol. 113/13, Page 5539-5544, 2000. Copyright 2000, American Institute of Physics.[16]

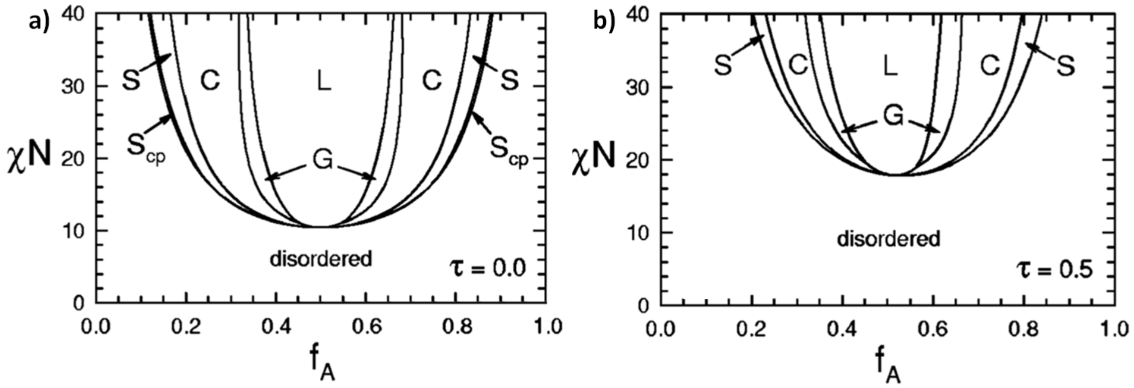

Figure 3.122: Phase diagrams for (a) a di-block copolymer (τ = 0.0) and (b) a symmetric ABA tri-block copolymer (τ = 0.5). Reprinted with permission from Matsen, M. W., The Journal of Chemical Physiscs, Vol. 113/13, Page 5539-5544, 2000. Copyright 2000, American Institute of Physics.[16]

and N_{A1} is the degree of polymerization of the shorter block of monomer A, and N_{A2} is the degree of polymerization of the longer block, such that $0 \leq \tau \leq ½$. The phase diagrams shown in Figure 3.23 show how the morphology varies as the asymmetry changes from the di-block system (τ = 0) to a symmetric ABA tri-block copolymer (τ = ½). As the copolymers (synthesized by ‘fire and forget’ and sequential addition) investigated herein are symmetric, only the phase diagram when τ = ½ needs to be considered. For comparison, a phase diagram for a di-block ($\tau = 0$) and a symmetric ($\tau = ½$) ABA tri-block copolymer are shown in Figure 3.24.[16] This shows that symmetric tri-block copolymers tend to be less strongly ordered than a di-block copolymer of equal molecular weight with narrower ordered regions, particularly at small values of χN.[16]

It is therefore quite likely that a symmetric tri-block copolymer may have a different morphology from a di-block copolymer with the same f_A value. In order to obtain a tri-block copolymer with thermoplastic elastomeric properties either a spherical or cylindrical morphology is required. This allows the middle rubbery block to form a flexible, continuous matrix whilst the two outer glassy blocks constrain the polymer with either spherical or cylindrical glassy domains which act as physical reversible cross-links. A tapered "tri-block" poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer, $P(BdSD)_2$-I (as shown in Figure 2.59 in Chapter 2), was synthesized by the simultaneous copolymerization of butadiene, styrene and DPE with a difunctional initiator. This copolymer had an M_n, of 317,700 g mol^{-1} and a monomer molar ratio of styrene : DPE : butadiene = 1.00 : 0.83 : 15.62 which corresponds to a styrene-*co*-DPE weight fraction of 0.23.

The TEM images (Figure 3.25) show that this copolymer appears to be close to spherical but without well-defined long range order, similar to the morphology of the analogous di-block copolymers with a 0.22 – 0.27 weight fraction of styrene-*co*-DPE. The theoretical phase diagram for a symmetric tri-block (Figure 3.24b) is very similar to that of a di-block copolymer (Figure 3.24a) except that the phase boundaries have been shifted to a higher value of χN. Therefore it is perhaps not surprising that the tapered "tri-block" copolymer, $P(BdSD)_2$-I has a similar morphology to that of the analogous di-block copolymers as the molecular weight is over twice as large as those di-block copolymers. Hence the value of χN will also be twice as large, and based on the theoretical phase diagrams shown in Figure 3.24, it is therefore quite plausible that the symmetric tri-block copolymer would show the same morphology as a di-block copolymer with an equal weight fraction of styrene-*co*-DPE.

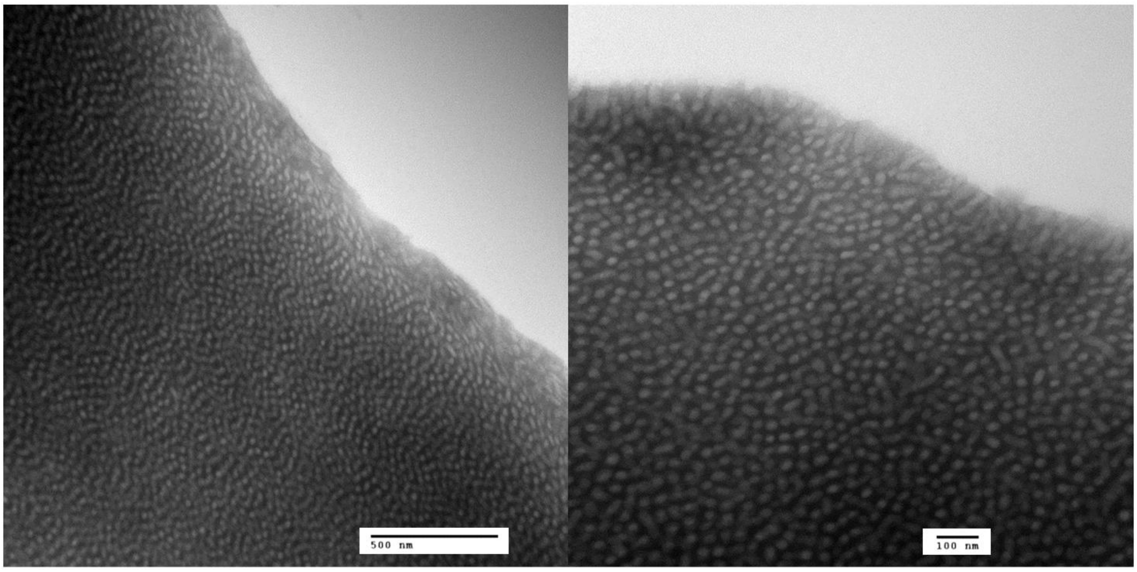

Figure 3.123: TEM images of a tapered poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE), P(BdSD)$_2$-I, synthesized by the simultaneous copolymerization of butadiene, styrene and DPE with a difunctional initiator, with the butadiene blocks stained black with OsO_4.

3.7. TEM Analysis of the Solid State Morphology of a Commercial Polystyrene-*block*-Polybutadiene-*block*-Polystyrene Copolymer

For comparison with the poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer, P(BdSD)$_2$-I, prepared by the 'fire and forget' approach, a commercial copolymer of polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer, PS-PBd-PS, was obtained. Ideally the phase separated morphology of the copolymer P(BdSD)$_2$-I would have been compared to an analogous poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer synthesized by sequential addition of monomers, however, it was not possible to obtain such a copolymer due to the challenging synthesis and time constraints. It would also have been preferable to compare the commercial copolymer, PS-PBd-PS, with that of an analogous poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer synthesized by sequential addition to investigate the impact of DPE on the phase separation. As the analogous poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) could not be obtained, the phase separated morphology of the commercial copolymer, PS-PBd-PS, was compared with the copolymer, P(BdSD)$_2$-I, prepared by the 'fire and forget' approach.

The molecular weight, M_n, of the commercial copolymer, PS-PBd-PS, was calculated as 47,000 g mol^{-1} (analysed by triple detection SEC using the *dn*/*dc* value of polystyrene),

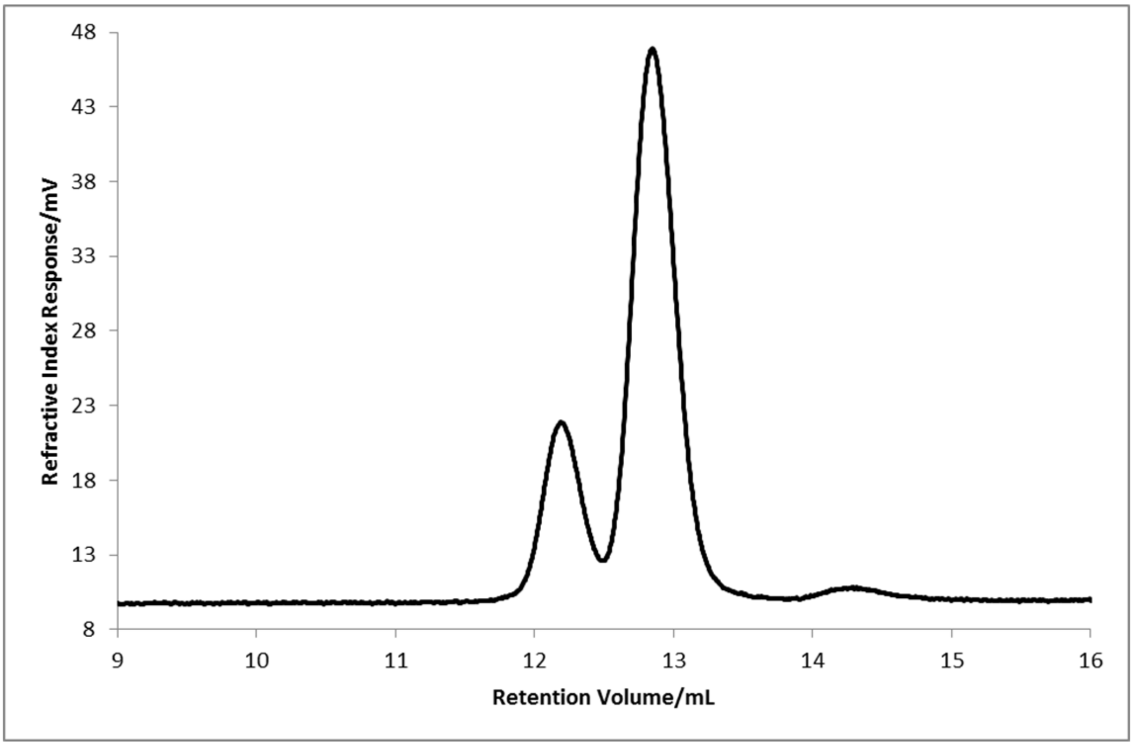

Figure 3.124: SEC chromatogram (refractive index) for the commercial copolymer polystyrene-*block*-polybutadiene-*block*-polystyrene, PS-PBd-PS.

which is significantly lower than that of P(BdSD)$_2$-I and the molar ratio of styrene : butadiene was 1.00 : 3.55 (91 % 1,4-polybutadiene) corresponding to a styrene weight fraction of 0.35 is higher than that of P(BdSD)$_2$-I. Additionally the SEC chromatogram (Figure 3.26) reveals that the molecular weight distribution of the commercial copolymer is multi-modal. The largest peak at a retention volume of 12.9 ml is likely to be the desired PS-PBd-PS copolymer, whereas that at 12.2 ml presumably corresponds to the cross-coupled material and therefore is a PS-PBd-PS-PBd-PS penta-block copolymer assuming it was made by sequential addition. Finally the peak at 14.3 ml is likely to either correspond to a homopolymer of polystyrene (prematurely terminated by impurities introduced with the addition of butadiene) or a polystyrene-*block*-polybutadiene copolymer (terminated by impurities introduced with the addition of a second batch of styrene) depending on the synthetic process. This further demonstrates that premature termination caused by the sequential addition of monomer approach is also a problem for commercially prepared copolymers and highlights the drawbacks of preparing block copolymers by the sequential addition of monomers.

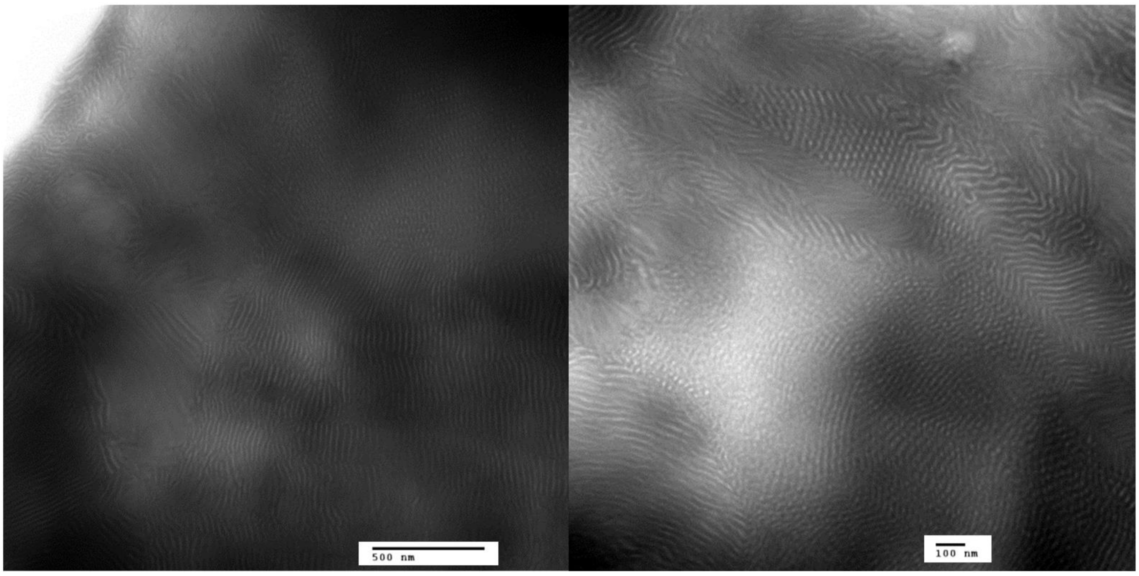

Figure 3.125: TEM images of a commercial polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer, with the butadiene blocks stained black with OsO_4.

Whilst it would have been preferable to synthesize a polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer with a comparable molecular weight and mole fraction this was not possible due to time constraints. The TEM images shown in Figure 3.27 show that the commercial tri-block copolymer, PS-PBd-PS, adopts a cylindrical morphology as evidenced by the hexagonal cylinders in both side-on and head-on orientations. Since the weight fraction of the glassy block is 0.35 wt. %, and the copolymer $P(BdSD)_2$-I appeared to be on the spherical/cylindrical phase boundary with a weight fraction of 0.23 wt. % it seems likely that both the commercial PS-PBd-PS copolymer and $P(BdSD)_2$-I would have the same morphology if the weight fraction of the glassy blocks were comparable. This suggests that both the impact of DPE, and the tapered section do not significantly affect the morphology. However, further investigations with copolymers of comparable molecular weight would be required to confirm this.

In conclusion a terpolymer of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) prepared by a 'fire and forget' methodology with high molecular weight and a styrene-*co*-DPE weight fraction of 0.23 wt. % appeared to be on the spherical/cylindrical morphology phase boundary. As di-block copolymers of poly(styrene-*co*-DPE)-*block*-polybutadiene also appeared to be on the spherical/cylindrical morphology phase boundary with a weight fraction of 0.22 – 0.27 wt. % styrene-*co*-DPE, this would suggest that, at this composition, the terpolymer prepared by simultaneous copolymerization has a comparable morphology to that of a sequentially prepared di-block copolymer. Furthermore a commercially obtained terpolymer of polystyrene-*block*-polybutadiene-*block*-polystyrene with a weight fraction of 0.35 wt. % styrene had a cylindrical morphology. It seems likely that a small increase in the styrene-*co*-DPE weight fraction would push the poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) terpolymer into the cylindrical morphological region, as was the case for the di-block copolymers. This would suggest that the presence of DPE in the styrene blocks does not significantly affect the morphology. If time had allowed, a high molecular weight terpolymer with a weight fraction of 0.35 wt. % styrene-*co*-DPE would have been synthesized by a 'fire and forget' approach to unequivocally demonstrate that a copolymer of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) prepared by a 'fire and forget' approach had the same morphology as that of a commercial polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer. Furthermore if time had allowed, the mechanical properties of the poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer would be compared with the commercial polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer to demonstrate that the 'fire and forget' approach could be used to prepare a copolymer with comparable mechanical properties but with a higher operating temperature due to the presence of DPE.

3.8. Thermal Analysis of Poly(Butadiene-*co*-Styrene-*co*-1,1-Diphenylethylene) Synthesized in THF

As a result of the impact of solvent polarity on reactivity ratios it was expected that when styrene, butadiene and DPE were copolymerized in THF, a tapered copolymer of poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE) would be formed, where DPE is highly incorporated to form a near-alternating copolymer and styrene would preferentially be incorporated over butadiene (Figure 3.28b). Whilst this has generally been shown to be the case and discussed in the previous chapter, butadiene monomer is still incorporated in the early stages of the reaction suggesting that the tapered middle section could extend along the majority of the chain. In an attempt to more deeply understand the outcome of this copolymerization, the T_g values of poly(butadiene-*co*-styrene-*co*-DPE) copolymers, PBdSD-10a-e, were analysed by DSC.

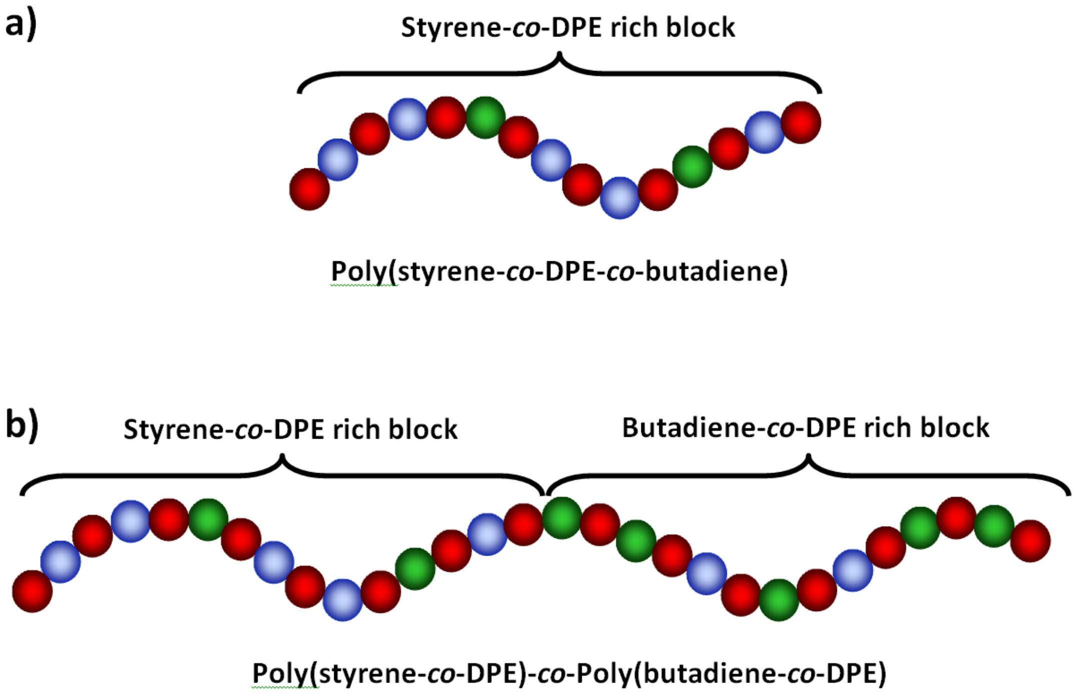

Figure 3.126: Schematic diagram to show the potential structure of (a) poly(styrene-*co*-DPE-*co*-butadiene) collected during the early stages of the reaction and (b) the final poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE) terpolymer when butadiene (green balls), styrene (blue balls) and DPE (red balls) are copolymerized in THF with a molar feed ratio of styrene : DPE : butadiene = 1 : 2 : 1.

If the hypothetical monomer sequence (as illustrated in Figure 3.28b) is correct then samples collected during the early stages of the reaction should contain a higher content of styrene and DPE than butadiene and a T_g similar to that of poly(styrene-*co*-DPE) should be observed. From DSC analysis a T_g could be observed at 10 and 20 °C/min for PBdSD-10a, although the magnitude of the transition at 10 °C/min was very small (Figure 3.29). However, a T_g was only observable at a heating rate of 40 °C/min for the samples collected later in the reaction and hence for comparison the DSC thermograms run at a heating rate of 40 °C/min are shown for all the samples (Figures 3.30 – 3.34). The T_g of the first sample, PBdSD-10a (Figures 3.29 – 3.30), was found to be 153 °C. This value is between the theoretical T_g of 175 °C for a perfect alternating copolymer of poly(styrene-*alt*-DPE) and approximately 117 °C for a copolymer of poly(butadiene-*co*-DPE) suggesting that PBdSD-10a is not a perfectly alternating copolymer of poly(styrene-*co*-DPE) and does contain some butadiene units. It is possible that a T_g of 153° C could indicate a copolymer of poly(styrene-*co*-DPE) with a modest content of DPE, however, previous results in Chapter 2 (Section 2.44), namely reaction PBdSD-11, indicated that DPE was fully incorporated when copolymerized with styrene and butadiene in THF. It should be noted that the molecular weight of sample PBdSD-10a is 14,300 g mol^{-1} (using the *dn*/*dc* value for polystyrene), and as shown in equation 3.1, T_g is not independent of molecular weight. If it is assumed that the empirical parameter, K, in this equation is the same value as that for polystyrene, 1.7 x 10^5 mol K g^{-1}, then equation 3.1 would suggest that a perfectly alternating copolymer of poly(styrene-*alt*-DPE) with a molecular weight, M_n, of 14,300 g mol^{-1} would have a T_g of 163 °C, and a Tg of 153 °C is therefore consistent with the copolymer structure shown in Figure 3.28a, i.e. a rich styrene-*co*-DPE composition.

It was anticipated that the T_g of samples collected later in the experiment would be slightly lower, as the incorporation of butadiene increased relative to styrene. As shown in Chapter 2 (Section 2.44), the reaction was complete upon collection of the final sample, PBdSD-10d, and hence PBdSD-10d and PBdSD-10e should have identical compositions. The T_g of all the samples (Figures 3.29 – 3.34) were found to be in a very narrow range – between 153 and 159 °C. Whilst it was expected that the T_g would decrease if butadiene is incorporated in the later stages it is possible that the change in composition is not sufficient to affect the T_g value of the initial block. Indeed from the equation correlating T_g and composition:

$$T_{gco} = T_{g(Sty-co-DPE)}\omega_{(Sty-co-DPE)} + T_{g(Bd-co-DPE)}\omega_{(Bd-co-DPE)}\ , \qquad [3.5]$$

a statistical copolymer containing 25 mol % of poly(butadiene-*co*-DPE) would have a T_g that is only approximately 10 °C higher than a copolymer containing 50 mol % poly(butadiene-*co*-DPE). It is also worth noting that the T_g is higher for PBdSD-10b than PBdSD-10a, however, this is likely to be due to the lower molecular weight of PBdSD-10a.

It is possible to obtain further information about the copolymer structure from the T_g; the breadth of the transition appears to be broader for the samples extracted at the latter stages of the reaction. This broader transition is indicative that the domains are not so well-defined suggesting the copolymer samples extracted at the latter stages of the reaction contain a less defined structure, i.e. are tapered copolymers with a higher incorporation of butadiene.[17] It is possible to quantify the breadth of T_g by plotting the derivative of the heat flow (∂HT/∂T) against temperature and calculating the peak width at half the peak height ($W_{0.5}$). The plots of ∂HT/∂T vs. temperature for

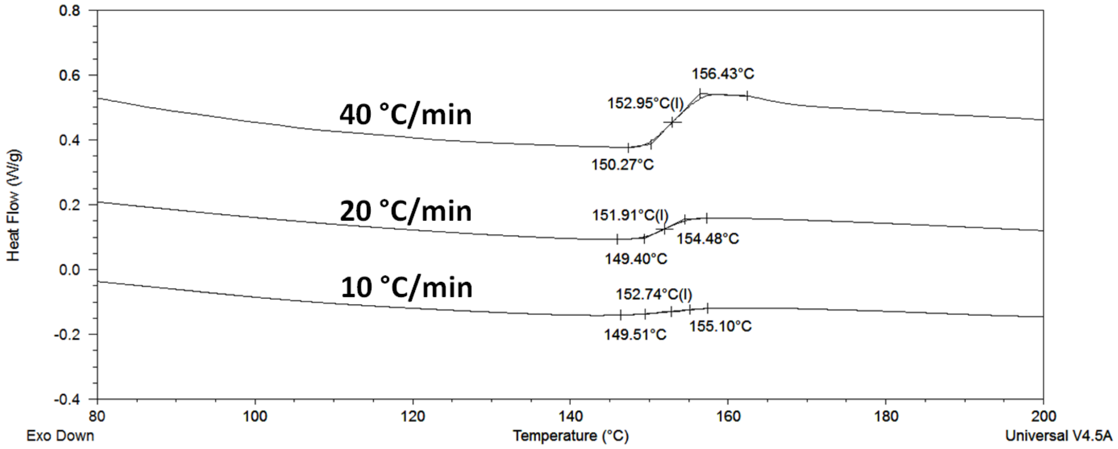

Figure 3.127: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10a, showing the T_g observed upon heating at 10 °C/min; 20 °C/min and 40 °C/min.

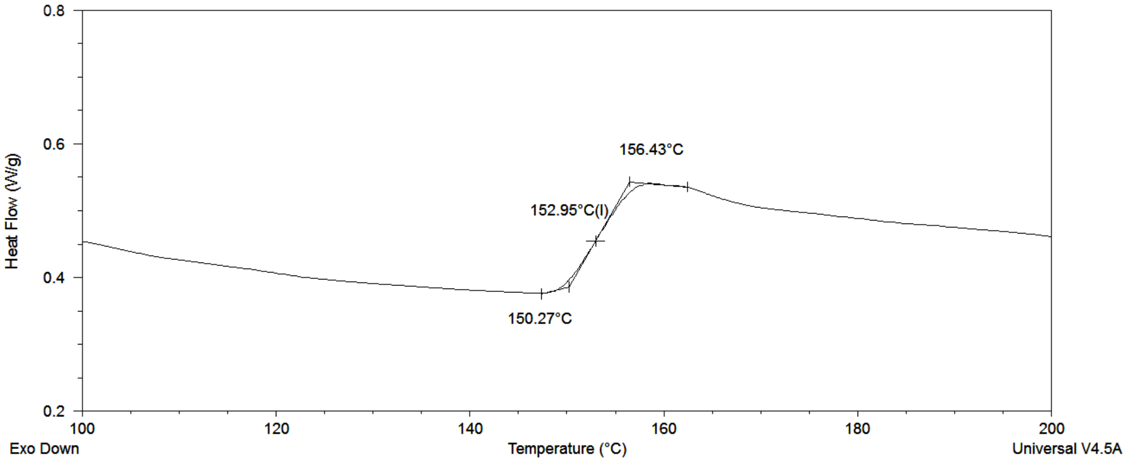

Figure 3.128: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10a, showing the T_g observed upon heating at 40 °C/min.

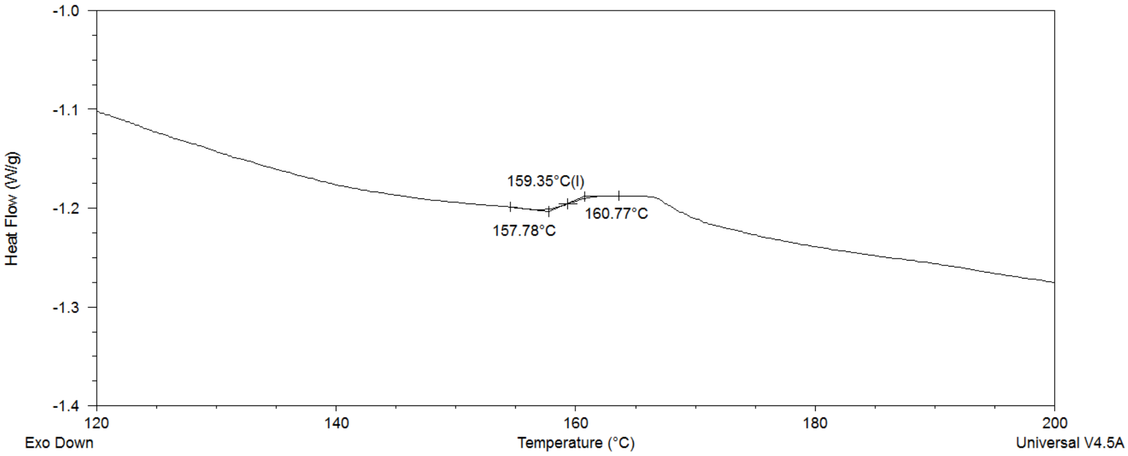

Figure 3.129: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10b, showing the T_g observed upon heating at 40 °C/min.

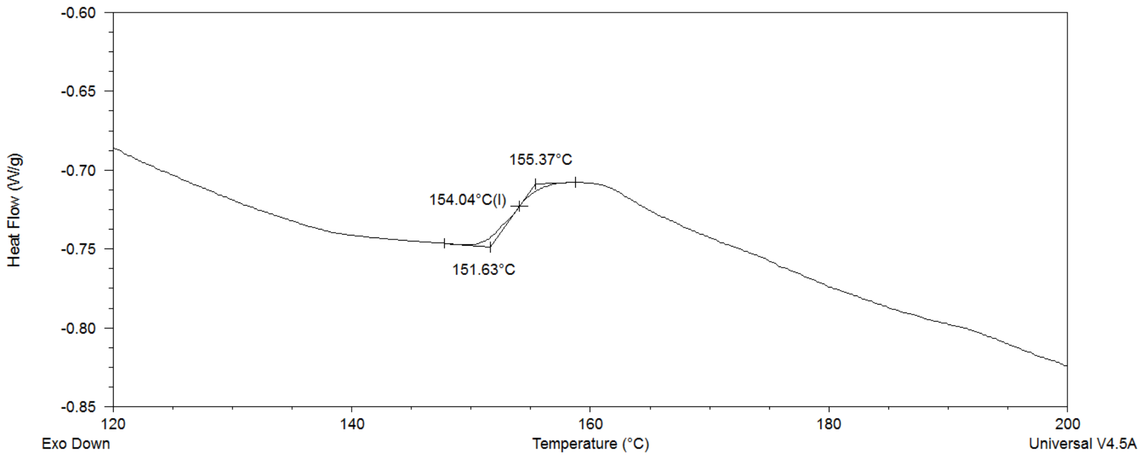

Figure 3.130: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10c, showing the T_g observed upon heating at 40 °C/min.

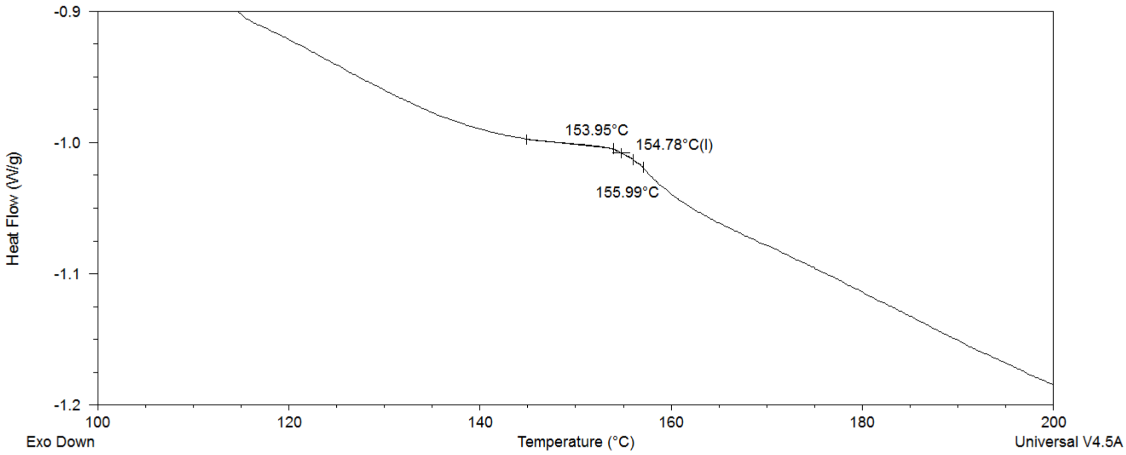

Figure 3.131: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10d, showing the T_g observed upon heating at 40 °C/min.

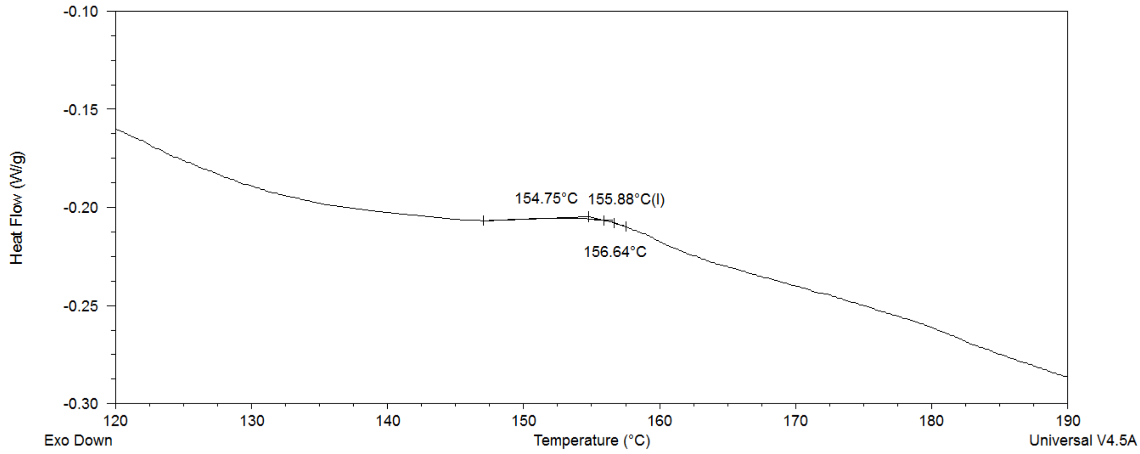

Figure 3.132: DSC thermogram obtained for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10e, showing the T_g observed upon heating at 40 °C/min.

Table 3.24: Peak Width for the change in Heat Flow for poly(butadiene-*co*-styrene-*co*-DPE), PSD-10a-e.

Sample	Peak Height (PH)/mW K^{-1}	1^{st} Temperature at (0.5 x PH)/°C	2^{nd} Temperature at (0.5 x PH)/°C	$W_{0.5}$/°C
PBdSD-10a	0.100	149.9	157.2	7.3
PBdSD-10b	0.022	157.7	161.7	4.0
PBdSD-10c	0.053	151.0	156.2	5.2
PBdSD-10d	0.016	139.0	154.0	15.0
PBdSD-10e	0.012	134.2	155.7	21.5

PBdSD-10a-e are shown in Figures 3.35 – 3.39 and shows that the copolymers PBdSD-10a-c have a fairly narrow transition, whereas those of PBdSD-10d-e have a broad transition. The breadth of T_g is quantified by the values of $W_{0.5}$, shown in Table 3.3, which clearly indicate there is a significant change between PBdSD-10c and PBdSD-10d. Hence, since the T_g is broader for the samples collected towards the end of the reaction, it can be surmised that the copolymers extracted in the latter stages have less well-defined domains which in turn suggests that butadiene is incorporated in the later stages of the reaction.[17]

In conclusion these results provide further evidence that when styrene, DPE and butadiene are copolymerized in THF with a 1 : 2 : 1 molar feed ratio an alternating tapered copolymer with a gradient of styrene to butadiene, poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE), is formed as shown in Figure 3.28.

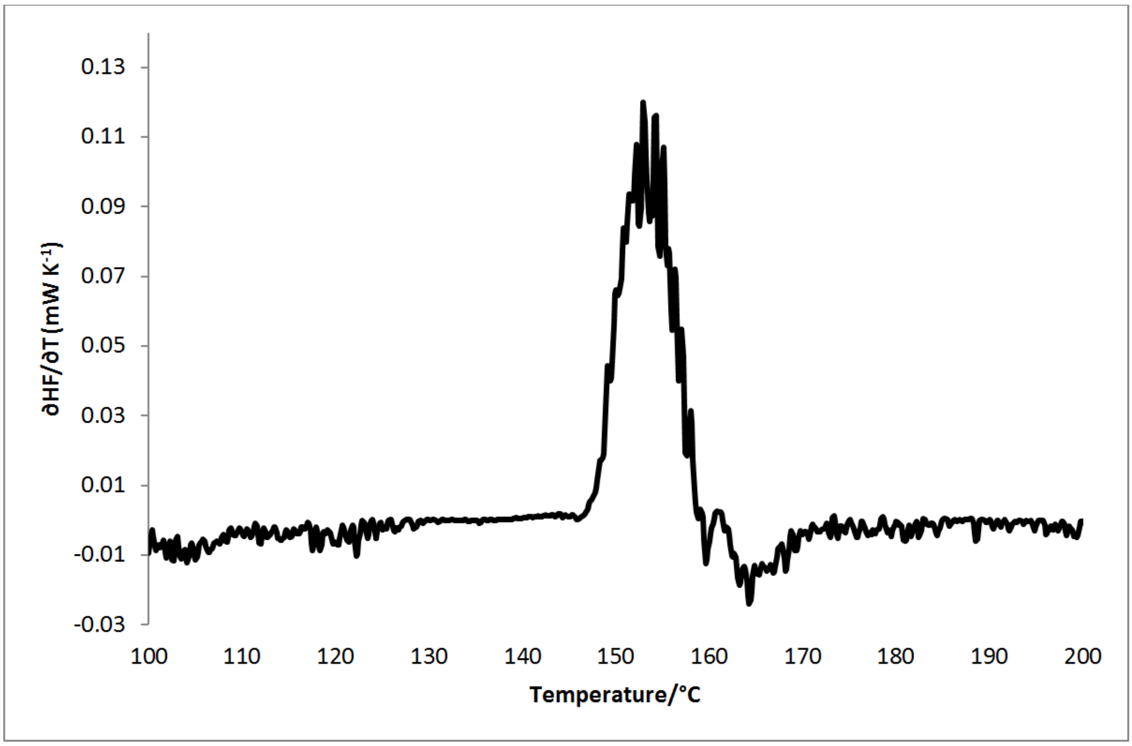

Figure 3.133: Derivative of Heat Flow (HF) vs Temperature (T) for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10a.

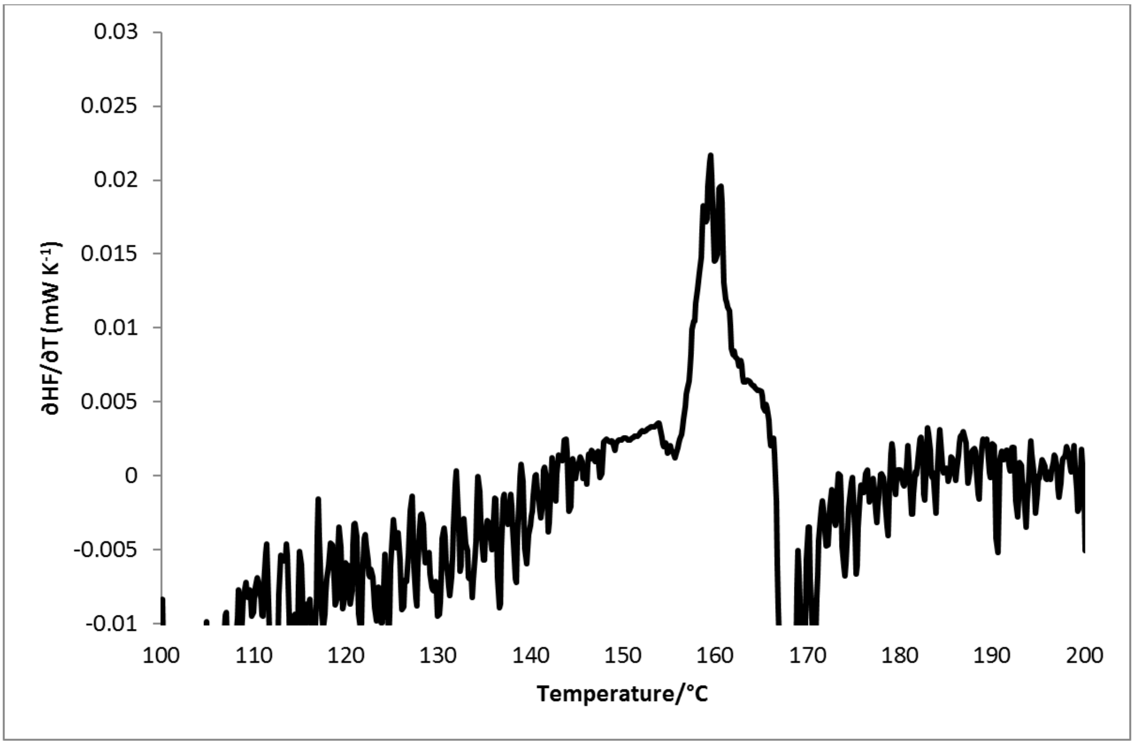

Figure 3.134: Derivative of Heat Flow (HF) vs Temperature (T) for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10b.

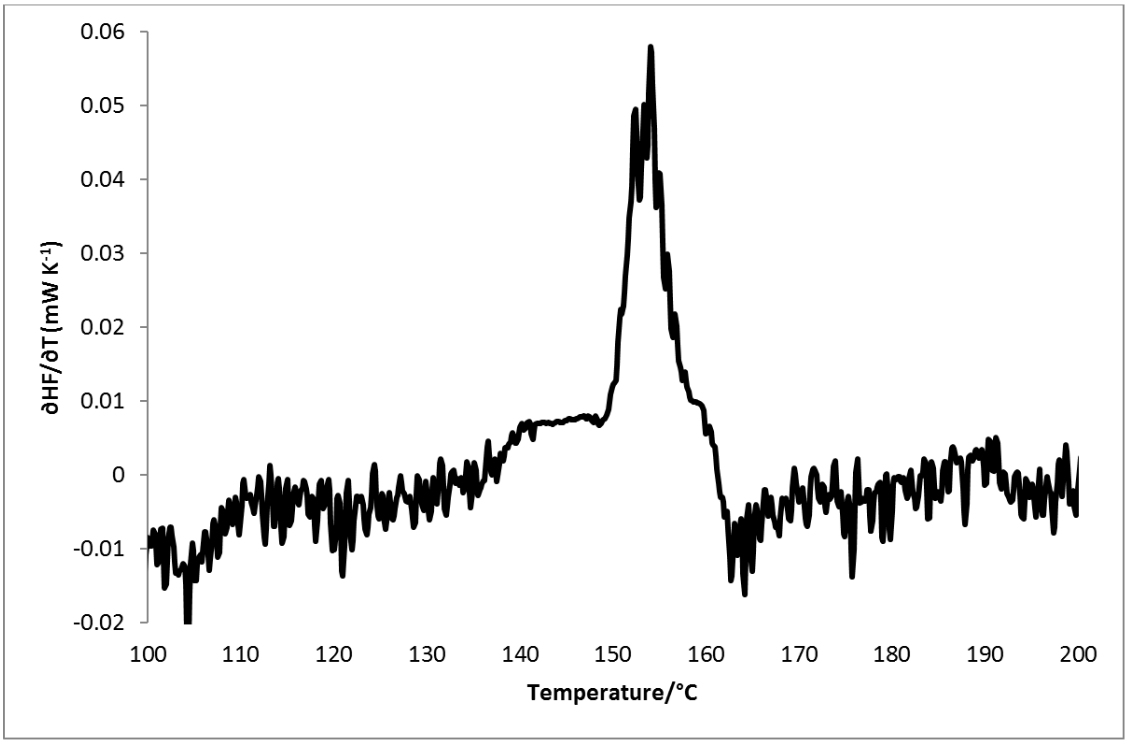

Figure 3.135: Derivative of Heat Flow (HF) vs Temperature (T) for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10c.

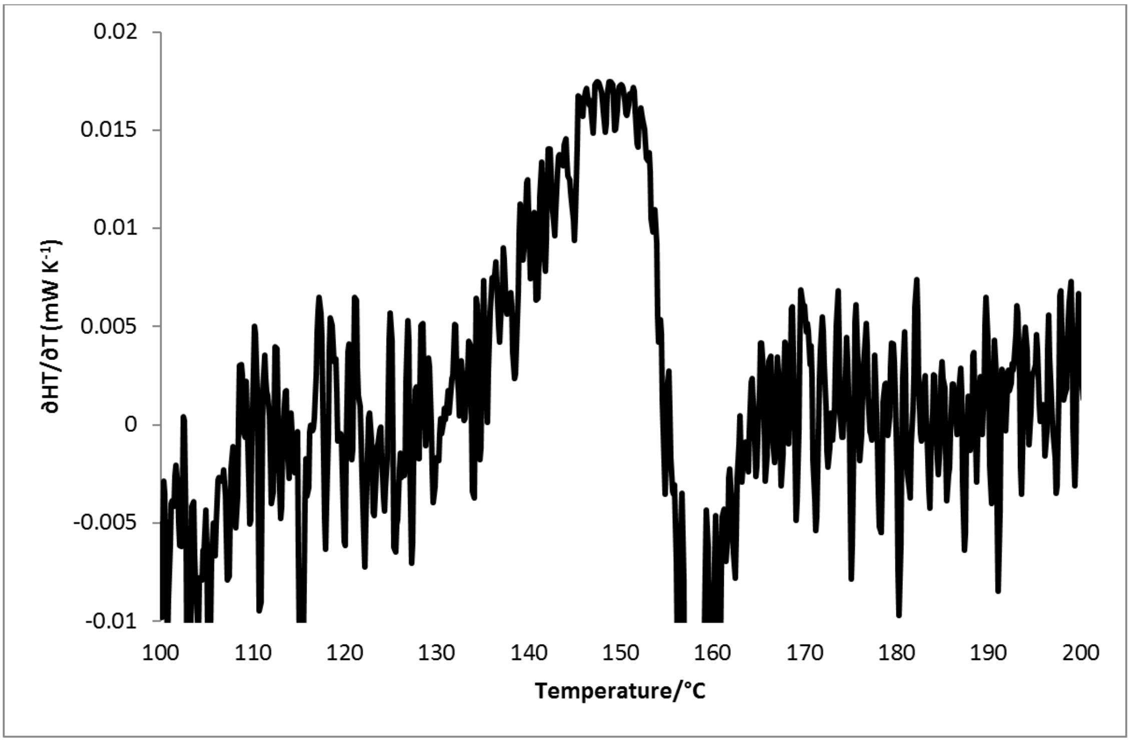

Figure 3.136: Derivative of Heat Flow (HF) vs Temperature (T) for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10d.

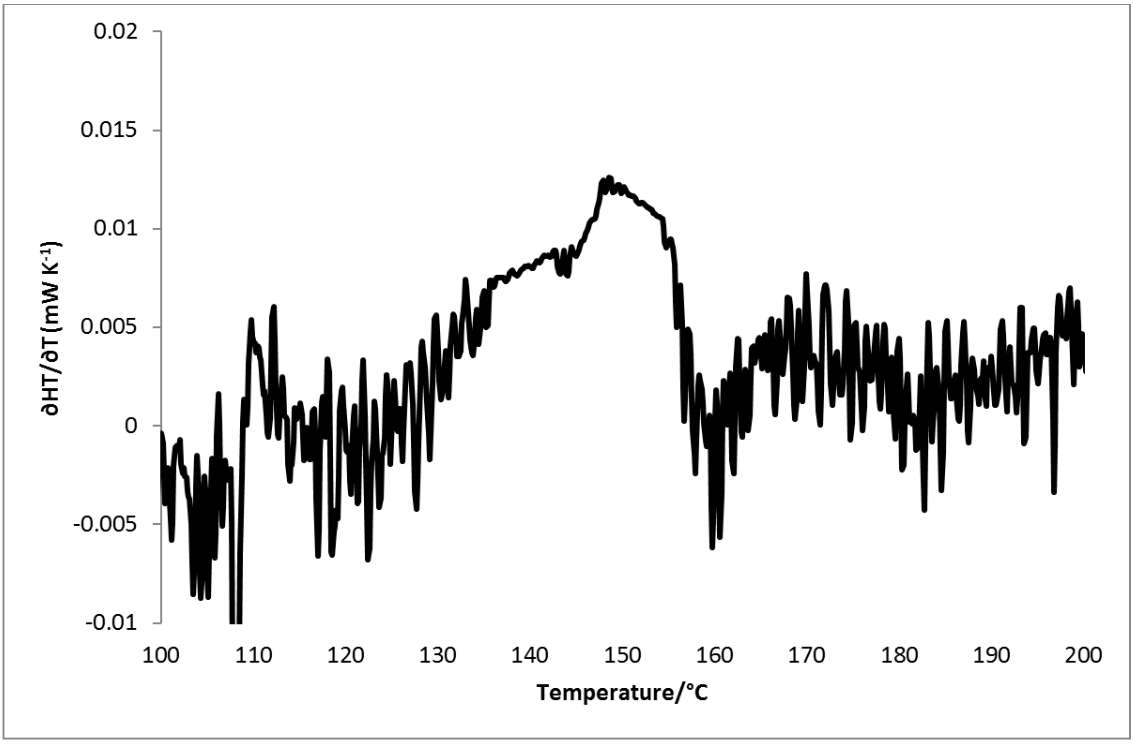

Figure 3.137: Derivative of Heat Flow (HF) vs Temperature (T) for the poly(butadiene-*co*-styrene-*co*-DPE) copolymer, PBdSD-10e.

3.9 References

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CHAPTER 4

Copolymers Containing Functional Derivatives of 1,1-Diphenylethylene

4. Copolymers Containing Functional Derivatives of 1,1-Diphenylethylene

The reactivity of 1,1-diphenylethylene (DPE) can be drastically modified by the addition of electron-withdrawing or donating groups on the para-position of the phenyl ring. The addition of electron-donating groups in the para position (such as the siloxy groups shown in Figure 4.1) will increase the electron density in the double bond by conjugation thereby deactivating the DPE to nucleophilic attack by a propagating carbanion – the same electron donating group will also increase the reactivity of DPE as a propagating species. Conversely, electron-withdrawing groups will increase the reactivity of DPE as a monomer, but decrease the reactivity of DPE as a propagating species.

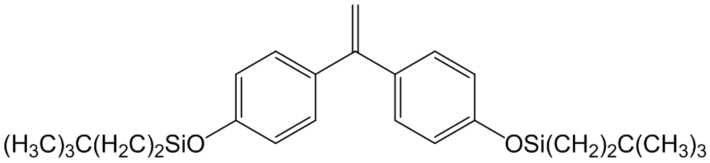

Figure 4.138: Structure of 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi).

Hutchings *et al*. reported that during the copolymerization of 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) with styrene in benzene, the reactivity ratio, r_1, was between 3 and 4 (if styrene is M_1) indicating a strong preference for styrene to undergo self-propagation.[1] Changing the solvent to THF and using diphenylmethyl potassium (DPMK) as the initiator yielded similar results with a reactivity ratio, r_1, of 6.1. Only by the slow addition of styrene (under starved monomer conditions) was it possible to generate copolymers with a higher incorporation (40 mol. %) of DPE-OSi.[1]

Hutchings *et al*. then investigated a terpolymerization of styrene, DPE and DPE-OSi. A terpolymerization is characterized by nine possible rate constants, however it is only the relative magnitude of k_{11}, k_{12} and k_{13} that are significant in determining the resulting monomer sequence (k_{22}, k_{33}, k_{23} and k_{32} are zero, and the cross-propagation rate constants, k_{21} and k_{31} will not impact upon the monomer sequence only on the overall rate of polymerization). It was reported that a terpolymerization with a molar feed ratio of styrene, DPE and DPE-OSi = 3 : 3 : 1 resulted in a nearly alternating copolymer of poly(styrene-*co*-DPE) with DPE-OSi being almost entirely excluded from the reaction, indeed the composition of the final copolymer was found to have a ratio

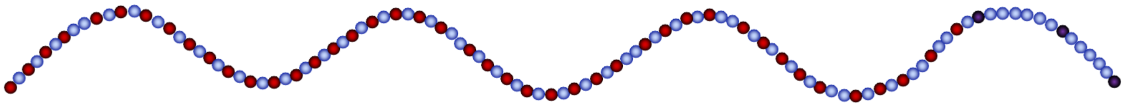

Figure 4.139: Schematic representation of the proposed structure of the polymer chains formed during the anionic terpolymerization of styrene (blue), DPE (red) and DPE-OSi (purple) with a monomer molar feed ratio of styrene : DPE : DPE-OSi = 4 : 3 : 1.

of 59 : 52 : 1 styrene : DPE : DPE-OSi. When the feed ratio of styrene was increased, such that the molar feed ratio of styrene : DPE : DPE-OSi = 4 : 3 : 1, the composition of the final copolymer was found to have a ratio of 17 : 13.5 : 1 styrene : DPE : DPE-OSi showing a much higher incorporation of DPE-OSi. Hence it was concluded that the structure of the polymer was likely to consist of an initial section which has a nearly alternating sequence of styrene and DPE and a second shorter section which is a statistical copolymer of styrene and DPE-OSi. The predicted structure is shown by the schematic representation in Figure 4.2.[1]

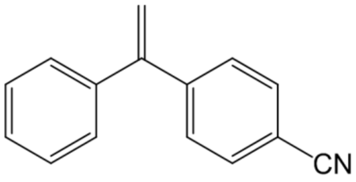

Figure 4.140: Structure of 4-cyanodiphenylethylene (DPE-CN).

Hutchings *et al*. also investigated the copolymerization of styrene (monomer 1) with 4-cyanodiphenylethylene, DPE-CN (monomer 2) (Figure 4.3) which due to the electron-withdrawing nature of the cyano group in the para-position strongly enhances the cross propagation rate constant k_{12} and accelerates the nucleophilic attack of the styryl carbanion on the double bond of DPE-CN creating a highly activated monomer.[1] The presence of the substituent also influences the rate of attack of the diphenylethyl carbanion on styrene (k_{21}) as it can withdraw electron density from the carbanion and therefore reduce the reactivity of the diphenylethyl carbanion. The reactions were initiated with DPMK and carried out in THF at -78 °C to avoid potential side reactions involving DPE-CN.[2] In the first reaction the molar feed ratio of styrene : DPE-CN was 9 : 1 and the copolymerization was sampled after 15 and 24 hours. As the rates of propagation are an order of magnitude faster in THF than non-polar solvents such as

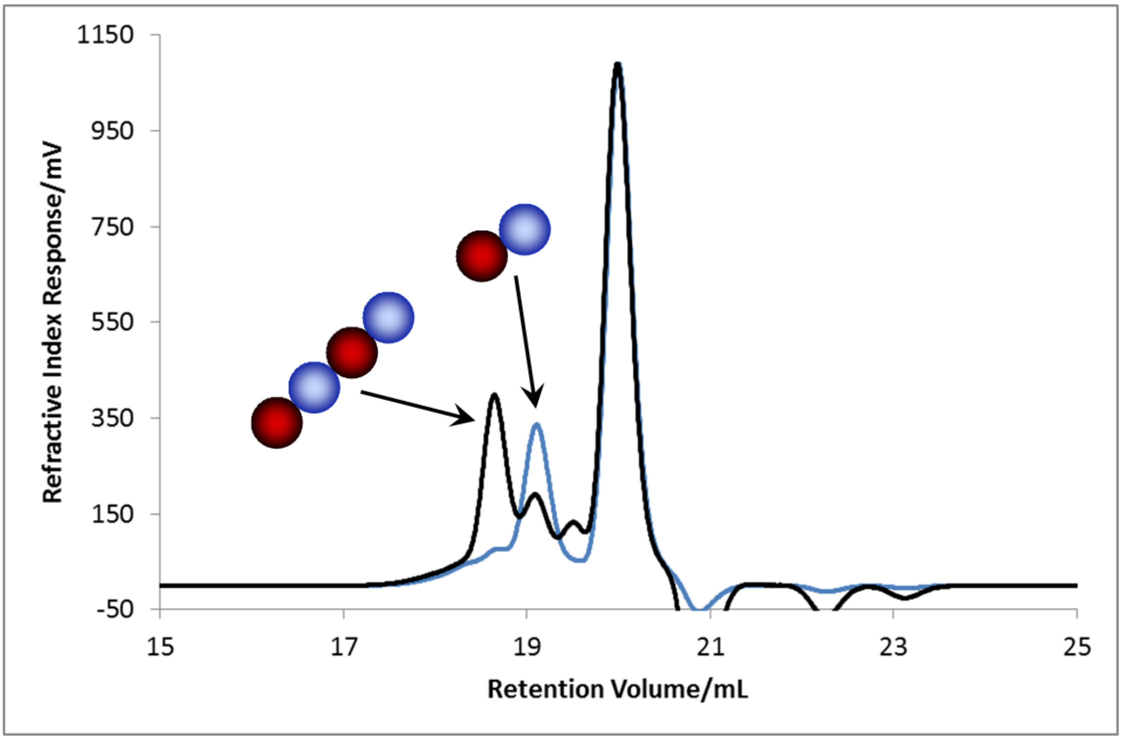

Figure 4.141: Size exclusion chromatography (RI) data for the copolymerization of styrene (blue balls) and DPE-CN (red balls) after 15 hours (blue line) and 24 hours (black line).

benzene,[3-5] it was expected that the copolymerization of styrene and DPE-CN would still be reasonably rapid at -78 °C. However, the size exclusion chromatography (SEC) data showed that even after 24 hours only oligomers had formed (Figure 4.4). During the initiation step, due to the steric bulk of the initiator, it is most likely that DPMK reacts exclusively with styrene. The activation effect of the cyano group on the DPE double bond is so strong that it is very likely that any styryllithium rapidly reacts with DPE-CN. However, the DPE-CN was then so strongly deactivated by the cyano group that the reaction was extremely slow, hence the peaks in the SEC chromatogram (Figure 4.4) can be assigned to the monomer, the dimer and the tetramer.

However, when the monomer molar feed ratio of styrene : DPE-CN was increased to 100 : 1, quantitative conversion of monomer to polymer occurred. The same result was observed for ratios of 50 : 1, 25 : 1 and 18 : 1, suggesting that when the relative amount of styrene is sufficiently high, the concentration of styrene can overcome the low rate of cross-propagation from DPE-CN to styrene.[1] When *sec*-butyllithium was used as the initiator (still in THF at -78 °C) the rate of propagation increased due to the smaller lithium counter ion being more easily solvated by THF.[3] SEC analysis of a

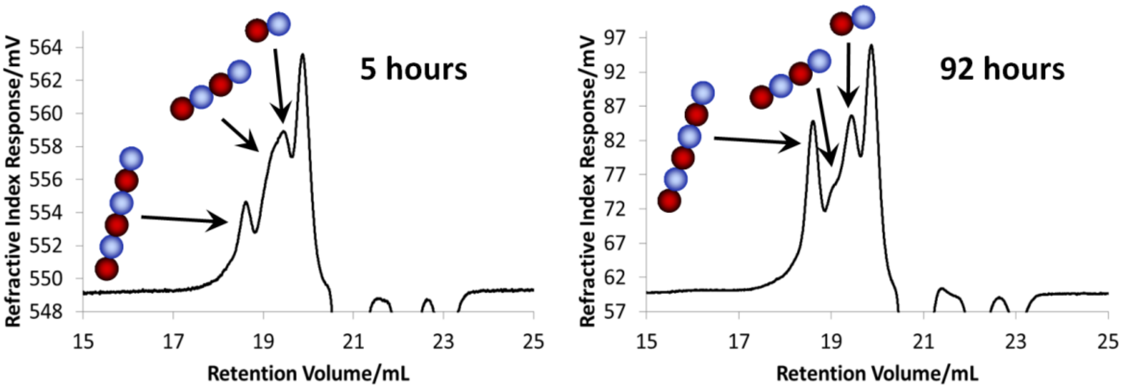

Figure 4.142: Size exclusion chromatography (RI) data for the copolymerization of styrene (blue balls) and DPE-CN (red balls) after 5 hours and 92 hours (initiated with *sec*-butyllithium).

copolymerization with a molar feed ratio of styrene : DPE-CN of 10 : 1 revealed the dimer, tetramer and hexamer species were present even after 5 hours (Figure 4.5).[6]

4.1. Copolymerization of 4-Cyanodiphenylethylene with Methyl Methacrylate

Previous reactions revealed that when 4-cyanodiphenylethylene (DPE-CN) was copolymerized with styrene, the rate of cross-propagation of DPE-CN to styrene was so low that only oligomers were obtained. In order to increase the rate of cross-propagation of DPE-CN, a more reactive co-monomer was required. Methyl methacrylate (MMA) has a resonance stabilized vinyl group resulting in an electron deficient double bond; hence it is a very reactive monomer and therefore a potential co-monomer for the copolymerization with DPE-CN. Due to resonance stabilization, the carbanion of MMA will not react with styrene or DPE, however, it was believed it might be able to cross-propagate to the more reactive monomer DPE-CN. The copolymerization of MMA and DPE-CN were performed in-house by the co-worker Karina Bley. In order to investigate the incorporation of DPE-CN when copolymerized with MMA, two copolymerizations of DPE-CN and MMA were performed with different molar feed ratios. The molar feed ratios of MMA : DPE-CN were 10 : 1 and 1 : 1 in THF, (P(MMA-*co*-D_{CN})-1 and P(MMA-*co*-D_{CN})-2).

Due to the presence of the carbonyl group on the MMA monomer alkyllithium initiators are unsuitable as initiators as they are too reactive and will partially react with the carbonyl group (approximately 51 %).[7] One of the commonly used initiators for MMA is 1,1-diphenylhexyllithium which is formed by the reaction of DPE with

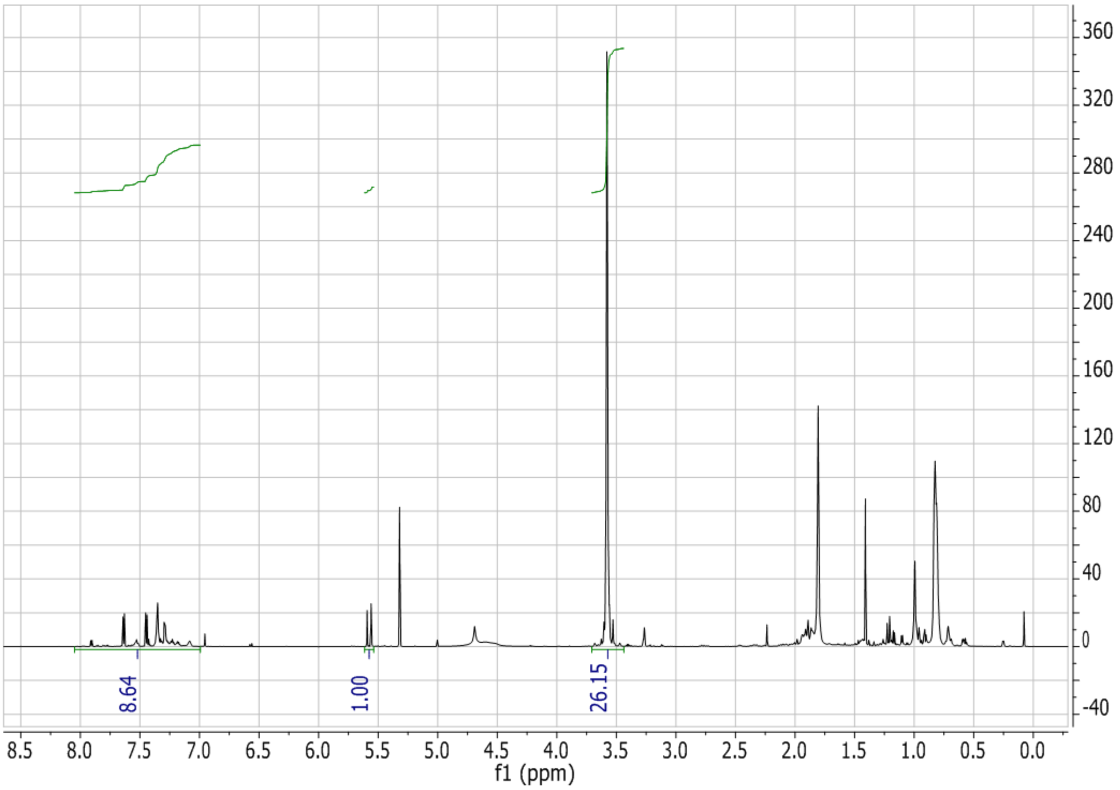

Figure 4.143: ^{1}H NMR spectrum (in CD_2Cl_2) of poly(MMA-*co*-DPE-CN), P(MMA-*co*-D_{CN})-1, synthesized in THF with a molar feed ratio 10.0 : 1.0 MMA : DPE-CN.

butyllithium.[7] In this case as DPE-CN was being used as a co-monomer, the initiator was generated by the reaction of DPE-CN with *sec*-butyllithium prior to the addition of MMA. An advantage of this is that it also ensures that any environmental impurities present in DPE-CN can be titrated out with BuLi prior to the copolymerization and thus prevent the inadvertent termination of the reaction. Additionally this means that the first unit in every sequence will have to be DPE-CN, although as DPE-CN cannot undergo homopolymerization this should not greatly impact the following sequence. This first unit of DPE-CN can either be considered as the first monomer unit or as the end-group but in the following analysis it will be considered as the first monomer unit. Upon analysis of the resulting copolymers by ^{1}H NMR spectroscopy (Figure 4.6) and MALDI-ToF mass spectrometry (MS) (Figure 4.7) it was discovered that MMA had predominantly self-propagated and hence MMA is a more reactive monomer than DPE-CN ($r_1 >> 1$ where MMA is monomer 1 and DPE-CN is monomer 2).

The ratio of MMA : DPE-CN in the copolymer, P(MMA-*co*-D_{CN})-1, can be determined from the ^{1}H NMR spectrum shown in Figure 4.6. The signals at 5.5 – 5.6 ppm

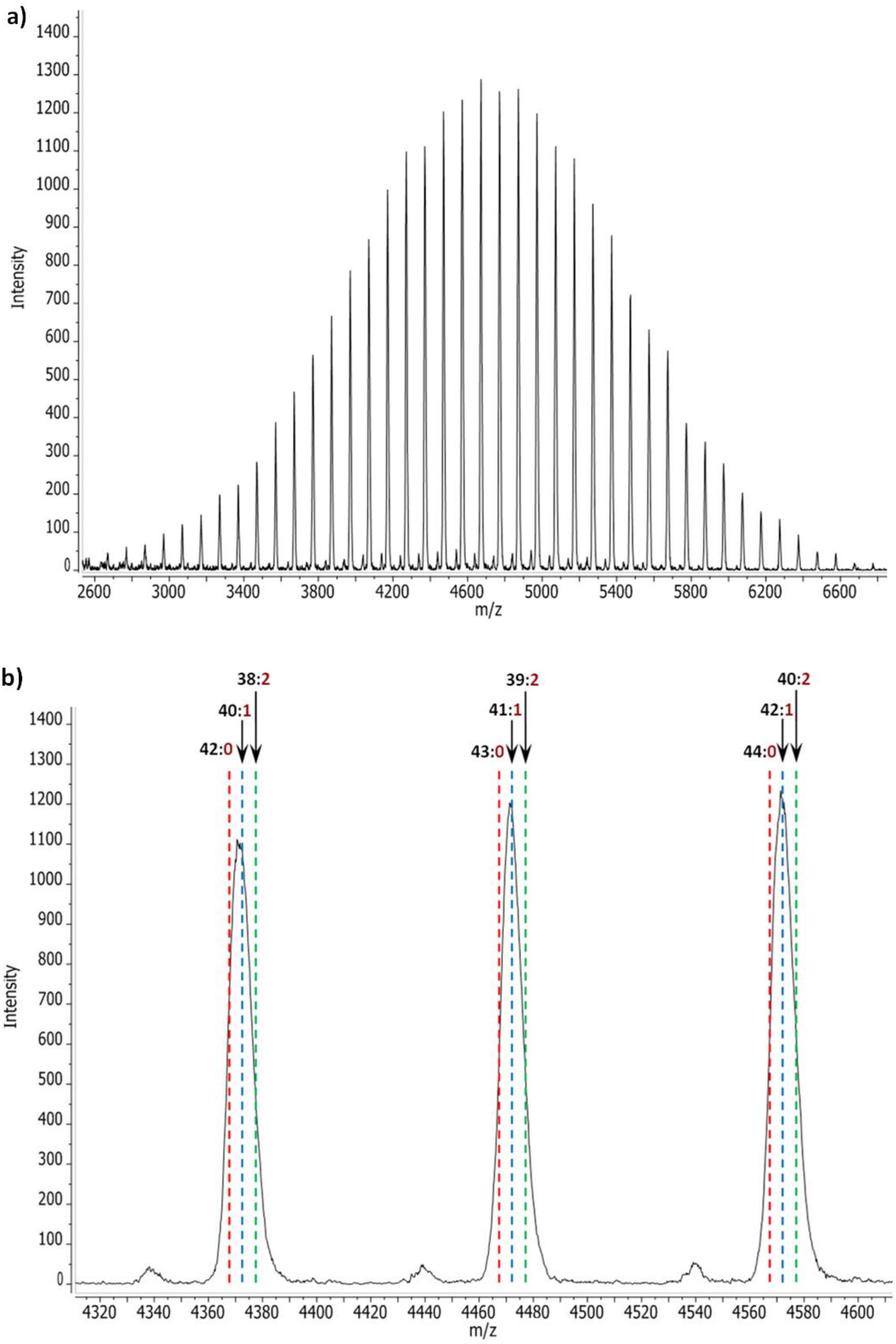

Figure 4.144: (a) MALDI-ToF mass spectrum of poly(MMA-*co*-DPE-CN), P(MMA-*co*-D_{CN})-1, synthesized in THF with a molar feed ratio 10.0 : 1.0 MMA : DPE-CN and (b) expansion showing the range m/z = 4320 – 4600 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-CN respectively, would be expected to appear. The mole ratio of MMA : DPE-CN for any given chain is labelled with MMA in black and DPE-CN in red.

correspond to 2 protons on the DPE-CN monomer and therefore indicate the presence of unreacted DPE-CN monomer. The DPE-CN monomer also contains 9 aromatic protons (present “underneath” the polymer aromatic protons at 7.1 – 7.9 ppm) and hence 4.5 x (the integral at 5.5 – 5.6 ppm) were subtracted from the aromatic region. The ratio of MMA : DPE-CN (x : y) repeat units in the copolymer can be calculated from the integral of the aromatic signal (7.0 – 7.9 ppm) ($9y = 4.32$), and from the integral of the OCH_3 peak at 3.6 ppm ($3x = 25.69$). This gives a ratio of MMA : DPE-CN = 18.9 : 1.0 in the resulting copolymer compared with a feed ratio of MMA : DPE-CN = 10 : 1.

MALDI-ToF MS analysis of P(MMA-*co*-D_{CN})-1 (Figure 4.7) shows that there is one predominant single sequence with repeating units equal to MMA, however, as the mass difference between two units of MMA and one unit of DPE-CN is only about 5 g mol^{-1}, and whilst the MALDI-ToF mass spectrum suggests that the chains contain a single unit of DPE-CN, it was not possible to accurately determine the exact composition by MALDI-ToF MS alone (as shown by Figure 4.7b). There is also a very small sequence a few mass units (31 g mol^{-1}) below the main peaks which are likely to correspond to the loss of an OCH_3 group from one methyl methacrylate unit.

The average number DPE-CN units per chain, $N_{\text{DPE-CN}}$, can be calculated using the total number of MMA units relative to DPE-CN units, MMA/DPE-CN, (obtained by ^{1}H NMR analysis) and the average molecular weight of the polymer. Ideally the mean molecular weight would be used, however, only the modal molecular weight could be reliably obtained from the MALDI-ToF mass spectra. MALDI-ToF MS revealed that the modal molecular weight was approximately 4,700 g mol^{-1}, and after subtracting the silver cation (107.0 g mol^{-1}) and the end-groups (57.1 g mol^{-1} and 1.0 g mol^{-1}, assuming the first unit of DPE-CN is a monomer and not an end-group) the modal molecular weight of the copolymer is approximately 4,500 g mol^{-1}. From the modal molecular weight and the molecular weight of the monomer units (100.1 g mol^{-1} for MMA and 205.3 g mol^{-1} for DPE-CN) the following equation can be obtained:

$$100.1x + 205.3y = 4500 \pm 500 \qquad [4.1]$$

where x : y is the ratio of MMA : DPE-CN and assuming a 10 % error of the molecular weight. It was calculated from the ^{1}H NMR spectroscopy that x/y = 18.9, however, due to the low intensity of the aromatic peaks corresponding to polymeric DPE-CN and the contribution from the monomer signals in the aromatic region, the error on this value could be as high as 40 %. Ideally the copolymer would be purified by a series of sequential re-precipitations until all the DPE-CN monomer had been removed, however, in this case time did not allow for the purification of this sample. Solving equation 4.1 and propagating the errors reveals that there are approximately 2.1 ± 0.8 units of DPE-CN per chain. Due to this significant error, these results are therefore inconclusive and there are two likely possibilities. One possibility is that MMA preferentially self-propagates until the monomer is fully consumed, at which point the final MMA unit can cross-propagate to the remaining DPE-CN monomer, incorporating 2 units of DPE-CN per chain, and thereby creating a telechelic copolymer by kinetic control. The other possibility is that MMA may be too unreactive as a propagating species to react with DPE-CN resulting in a single unit of DPE-CN per chain.

Similar analysis on the copolymer P(MMA-*co*-$\mathrm{D_{CN}}$)-2 which was synthesized by Karina Bley with a 1 : 1 molar ratio of MMA : DPE-CN indicated a ratio of MMA : DPE-CN of 17.3 : 1.0 in the copolymer (calculated from the ^{1}H NMR spectrum in Figure 4.8) and 1.4 ± 0.3 units of DPE-CN also using the modal molecular weight determined from the MALDI-ToF mass spectrum (Figure 4.10). The error was calculated assuming a 10 % error on the molecular weight, however, in this case the error from the ^{1}H NMR was fairly minimal as the DPE-CN monomer was removed by a series of re-precipitations. It should be noted that the peak at 4.7 ppm is likely to be due to water present in the sample which is supported by the HSQCAD NMR spectrum (Figure 4.9) which shows that the protons at 4.7 ppm are not connected to any carbon signals. Whilst the results are inconclusive as to whether the copolymer has been end-capped with DPE-CN, it does suggest a potential method to obtain a telechelic copolymer using kinetic control, provided the right co-monomer pair is found (i.e. where k_{11} is much higher than k_{12} but k_{12} is not negligible). In order to determine whether there is one or two units of DPE-CN, future work will involve a polymerization of MMA and the subsequent addition of DPE-CN monomer in an attempt to end-cap the reaction. ^{1}H NMR analysis can then be

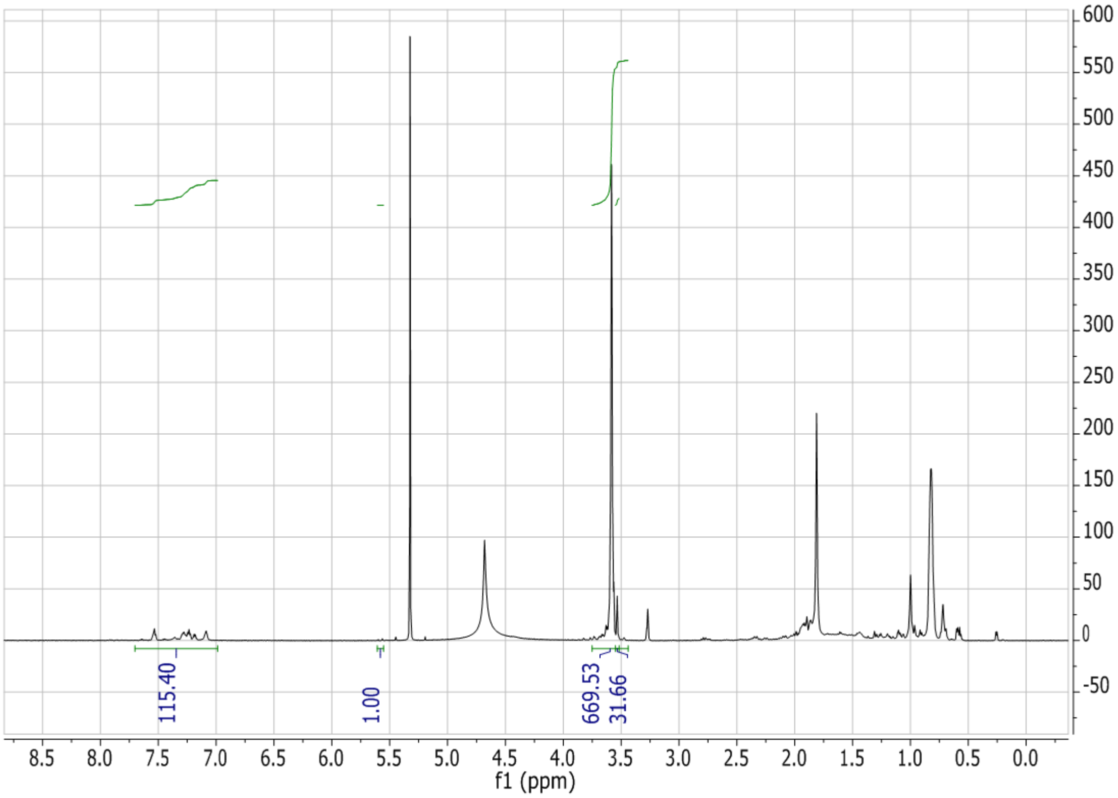

Figure 4.145: ^{1}H NMR spectrum (in CD_2Cl_2) of poly(MMA-*co*-DPE-CN), P(MMA-*co*-D_{CN})-2, synthesized in THF with a molar feed ratio 1.0 : 1.0 MMA : DPE-CN.

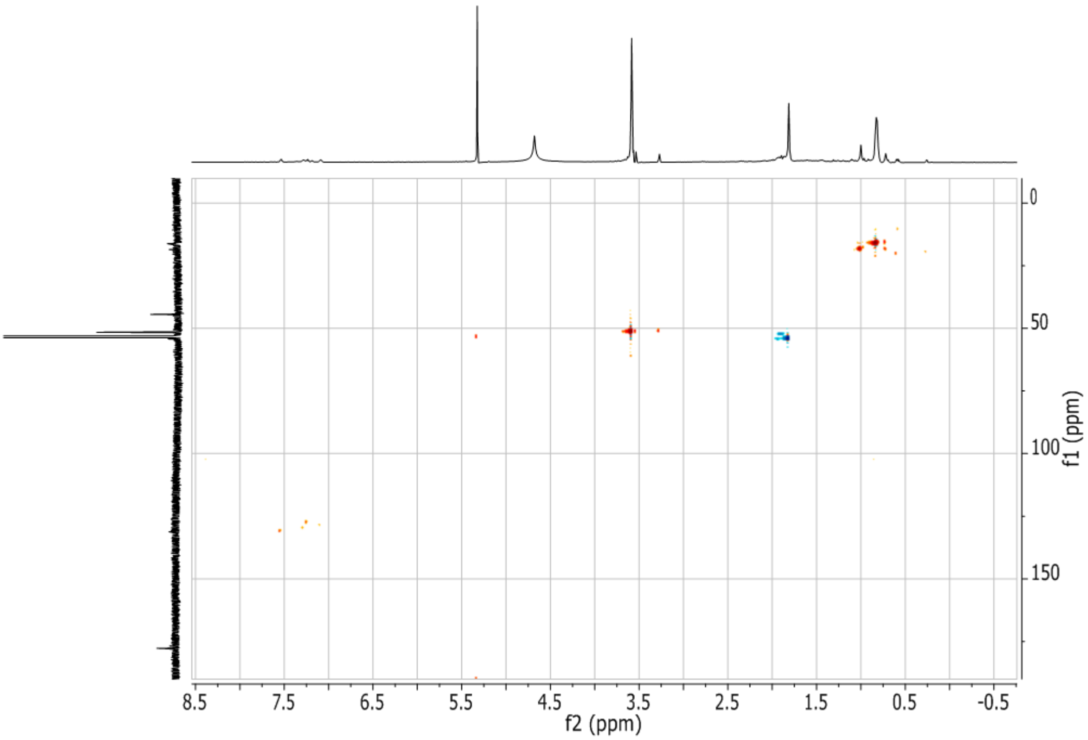

Figure 4.146: HSQCAD NMR spectrum (in CD_2Cl_2) of poly(MMA-*co*-DPE-CN), P(MMA-*co*-D_{CN})-2, synthesized in THF with a molar feed ratio 1.0 : 1.0 MMA : DPE-CN.

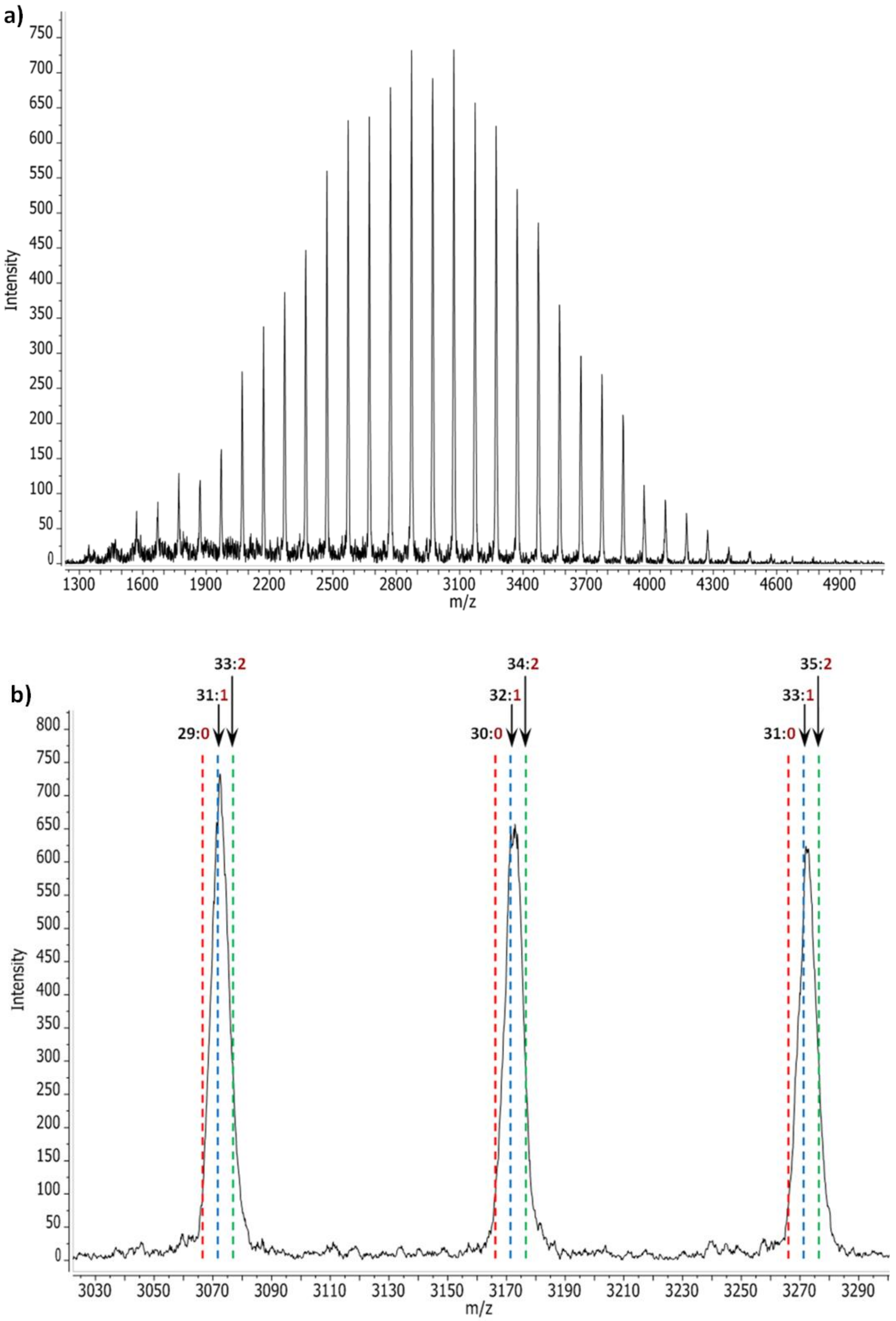

Figure 4.147: (a) MALDI-ToF mass spectrum of poly(MMA-*co*-DPE-CN), P(MMA-*co*-D_{CN})-2, synthesized in THF with a molar feed ratio 1.0 : 1.0 MMA : DPE-CN and (b) expansion showing the range m/z = 3030 – 3290 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-CN respectively, would be expected to appear. The mole ratio of MMA : DPE-CN for any given chain is labelled with MMA in black and DPE-CN in red.

used to determine whether there are zero or one units of DPE-CN per chain which is much more facile than distinguishing between one or two units of DPE-CN.

4.2. Copolymerization of 1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene with Butadiene in THF

The presence of substituents on DPE is particularly useful both in terms of controlling the reactivity of the DPE monomer and also for introducing functionality into the resulting copolymer. Upon the deprotection of DPE-OSi two phenol groups per DPE-OSi repeat unit are introduced into the copolymer which can be used either in subsequent reactions (i.e. as a macromonomer)[8-9] or to increase the hydrophilicity and other properties of the copolymer. It is therefore desirable to investigate the extent of incorporation of DPE-OSi in copolymerizations under various conditions. It is known from previous work that DPE-OSi is weakly incorporated when copolymerized with styrene even in THF.[1] Herein the copolymerization of DPE-OSi with butadiene was also investigated. The copolymerization of butadiene and DPE in non-polar solvents strongly favours the homopolymerization of polybutadiene with DPE almost totally excluded from the reaction. Given the deactivating impact of the protected phenol groups in DPE-OSi the tendency for cross-propagation reactions will be extremely low and it is likely there will be little or no incorporation of DPE-OSi when DPE-OSi is copolymerized with butadiene in non-polar solvents. However, in THF butadiene and DPE form an alternating copolymer, hence it is of interest to investigate the level of incorporation of DPE-OSi when copolymerized with butadiene in THF.

A series of copolymerizations of DPE-OSi with butadiene in THF were attempted to determine the reactivity ratios. Despite rigorously dry/high vacuum conditions it was found that termination appeared to be a problem for these copolymerizations, which was most likely due to impurities present in the DPE-OSi monomer. The first attempted copolymerization (P(Bd-*co*-D_{OSi})-1) with a target molecular weight with 2,500 g mol^{-1} was performed at -78 °C and assisted by Serkan Sevinc. DPE-OSi, butadiene and THF were added to the main reaction flask and initiated with *sec*-BuLi. Upon addition of *sec*-BuLi the colour of the reaction mixture became red indicating a proportion of the chains contained a terminal unit of living DPE-OSi. However, SEC analysis (Figure 4.11)

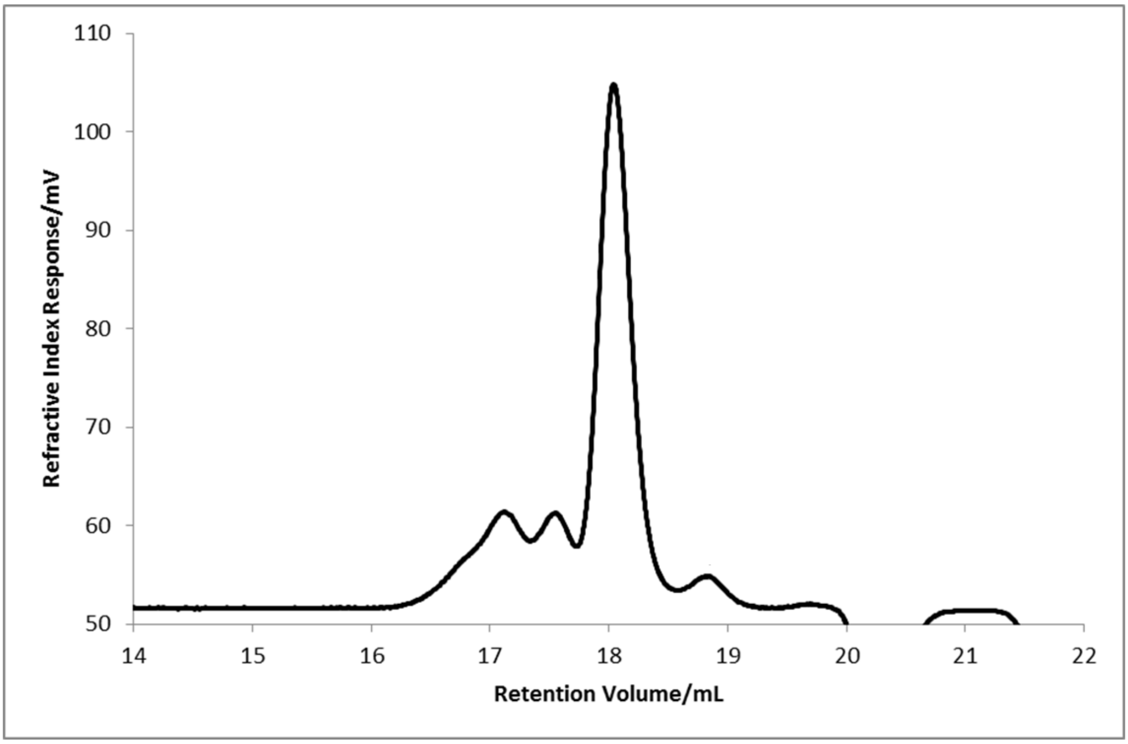

Figure 4.148: SEC trace for poly(butadiene-*co*-DPE-OSi) copolymer, P(Bd-*co*-D_{OSi})-1, showing the refractive index response.

revealed that after being stirred at -78 °C for 50.5 hours only oligomers had been obtained and the ^{1}H NMR spectrum was dominated by unreacted DPE-OSi monomer (Figure 4.12). Whist it was not possible to obtain any information from the integrals, the expansion from 3.7 – 7.3 ppm shown in Figure 4.13 does show that both butadiene and DPE-OSi have been incorporated. The SEC chromatogram is multi-modal and shows a series of peaks, the one at a retention volume of 18.8 ml is likely to arise from the solvent. The most intense peak, at a retention volume of 18.1 ml is calculated as 500 g mol^{-1} using conventional analysis relative to polystyrene standards. Although low molecular weight analysis, particularly when analysed relative to a different polymer, is likely to be inaccurate, it seems likely that this peak could correspond to either the DPE-OSi monomer or sequences containing 1 unit of DPE-OSi and one or two units of butadiene. The next peak at a retention volume of 17.5 ml is calculated as 850 g mol^{-1}, and as the monomer is 441 g mol^{-1} it seems likely that this peak corresponds to sequences containing two units of DPE-OSi. Finally the peak at a retention volume of 16.2 – 17.3 ml is broader and appears to have a higher molecular weight shoulder. This peak is calculated as 1,500 g mol^{-1} and therefore presumably corresponds to

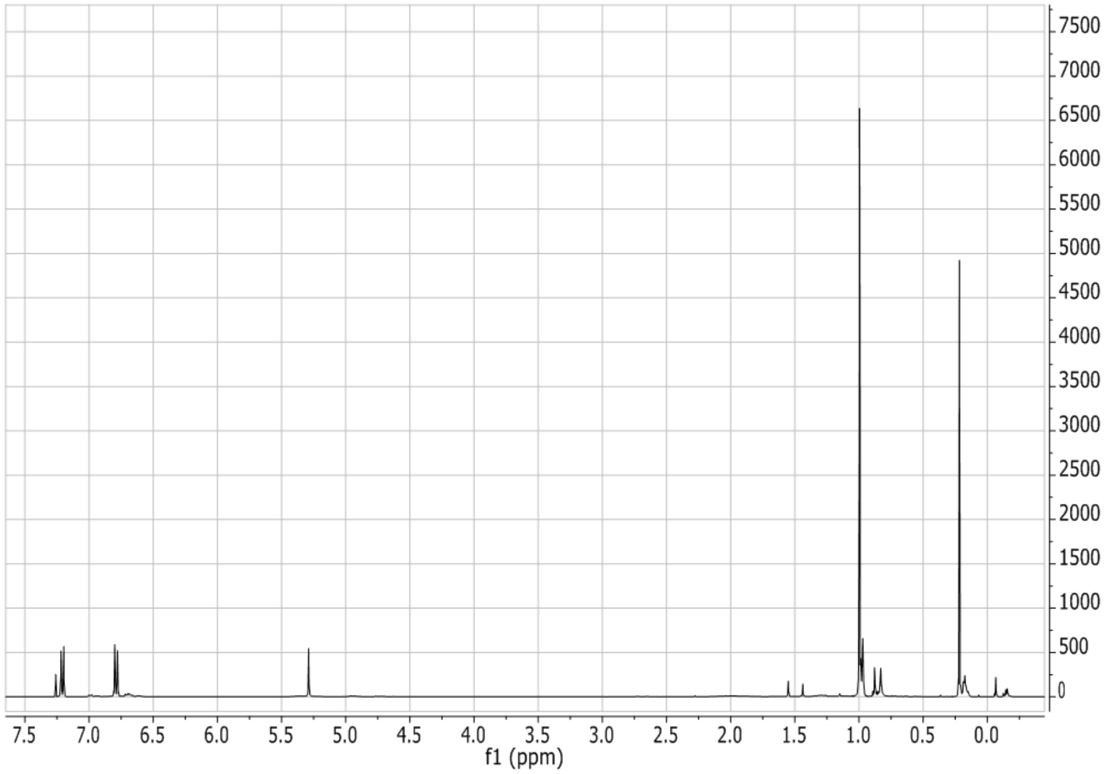

Figure 4.149: ^{1}H NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE-OSi), P(Bd-*co*-D_{OSi})-1, synthesized in THF with a molar feed ratio 1.0 : 1.0 butadiene : DPE-OSi.

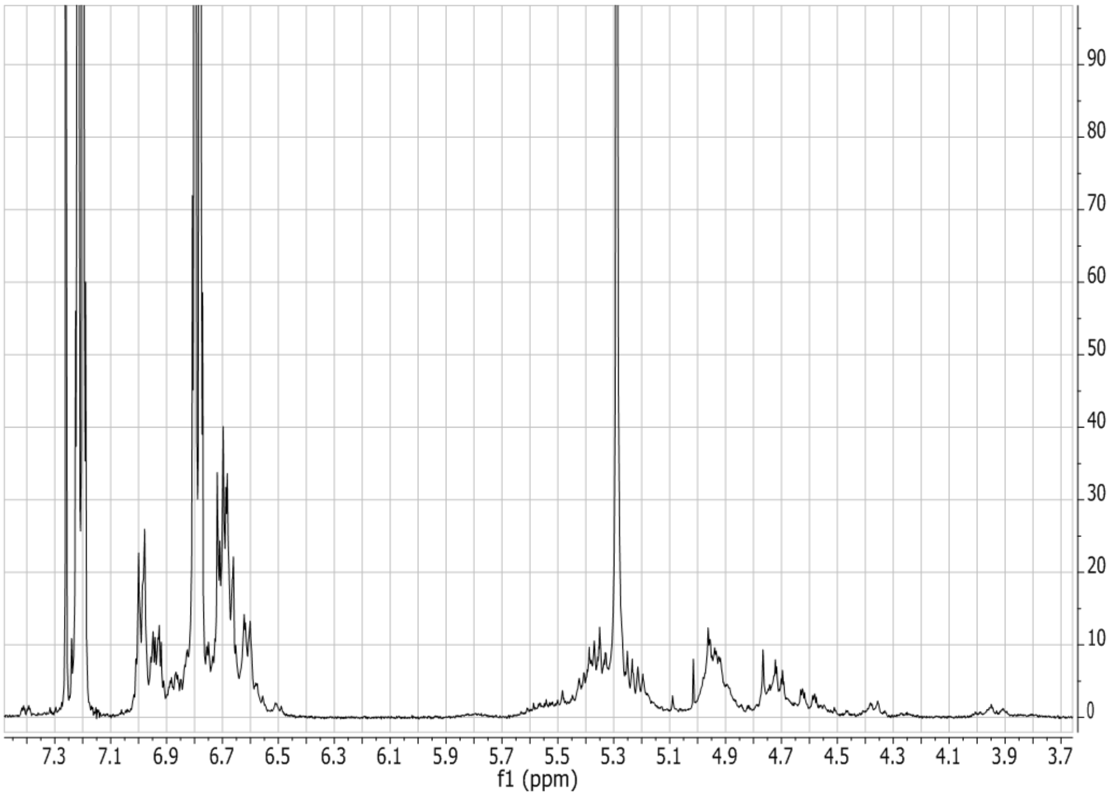

Figure 4.150: ^{1}H NMR spectrum (in $CDCl_3$) of poly(butadiene-*co*-DPE-OSi), P(Bd-*co*-D_{OSi})-1, synthesized in THF with a molar feed ratio 1.0 : 1.0 butadiene : DPE-OSi and expanded over the region 3.7 – 7.3 ppm.

sequences containing three or more units of DPE-OSi. Due to the large presence of DPE-OSi monomer it was not possible to obtain a meaningful yield for this reaction.

It was possible that the reason only oligomers were obtained in P(Bd-*co*-D_{OSi})-1 was due to the slow rate of polymerization at -78 °C, hence the reaction was repeated at 0 °C (P(Bd-*co*-D_{OSi})-2). DPE-OSi, butadiene and THF were added to the main reaction flask and initiated with *sec*-BuLi with a target molecular weight of 2,500 g mol^{-1}. Upon addition of *sec*-BuLi the colour of the reaction mixture became red indicating a proportion of the chains contained a terminal unit of living DPE-OSi, however, within one minute the reaction mixture had become colourless. It was possible that the colourless reaction mixture may be indicative of polybutadienyllithium so the reaction was split into three portions; one portion ((PBd-*co*-D_{OSi})-2a) was re-initiated with a further addition of *sec*-BuLi and a low target molecular weight of approximately 1,700 g mol^{-1}, the second portion ((PBd-*co*-D_{OSi})-2b) was allowed to proceed with no further addition of *sec*-BuLi, and the third portion ((PBd-*co*-D_{OSi})-2c) was re-initiated with *sec*-BuLi, added dropwise until a permanent yellow colour was observed for a higher (but unspecified) target molecular weight. The reactions were allowed to proceed at 0 °C for a further 12 days before being terminated with methanol; during which time P(Bd-*co*-D_{OSi})-2a remained red throughout; P(Bd-*co*-D_{OSi})-2b remained colourless throughout and P(Bd-*co*-D_{OSi})-2c remained pale yellow throughout. Analysis revealed that the sample that had not been re-initiated, (P(Bd-*co*-D_{OSi})-2b), had not polymerized. Both the re-initiated samples (P(Bd-*co*-D_{OSi})-2a and P(Bd-*co*-D_{OSi})-2c) contained only oligomers as shown by the SEC traces (Figures 4.14 and 4.15). Both SEC traces appear to show five peaks, the latter peak is a high molecular weight shoulder on the fourth peak. The most intense peak at a retention volume of 18.5 ml (calculated as 500 g mol^{-1} using conventional calibration relative to polystyrene standards) is likely to correspond to DPE-OSi monomer or sequences containing one unit of DPE-OSi. The second peak (at a retention volume of 17.7 ml) which is calculated as 850 g mol^{-1} is more intense for the sample of P(Bd-*co*-D_{OSi})-2a than P(Bd-*co*-D_{OSi})-2c. This peak is likely to correspond to sequences containing 2 units of DPE-OSi and therefore the lower concentration of this peak in P(Bd-*co*-D_{OSi})-2c is consistent with the fact a smaller

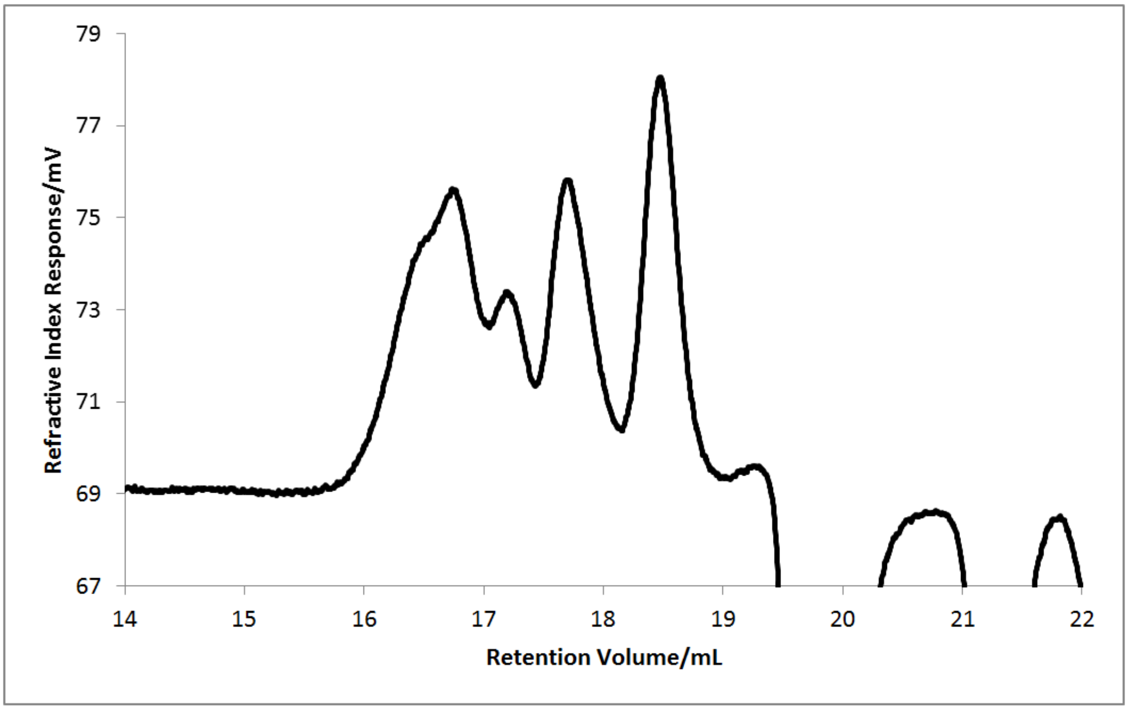

Figure 4.151: SEC trace for poly(butadiene-*co*-DPE-OSi) copolymer, P(Bd-*co*-D_{OSi})-2a, showing the refractive index response.

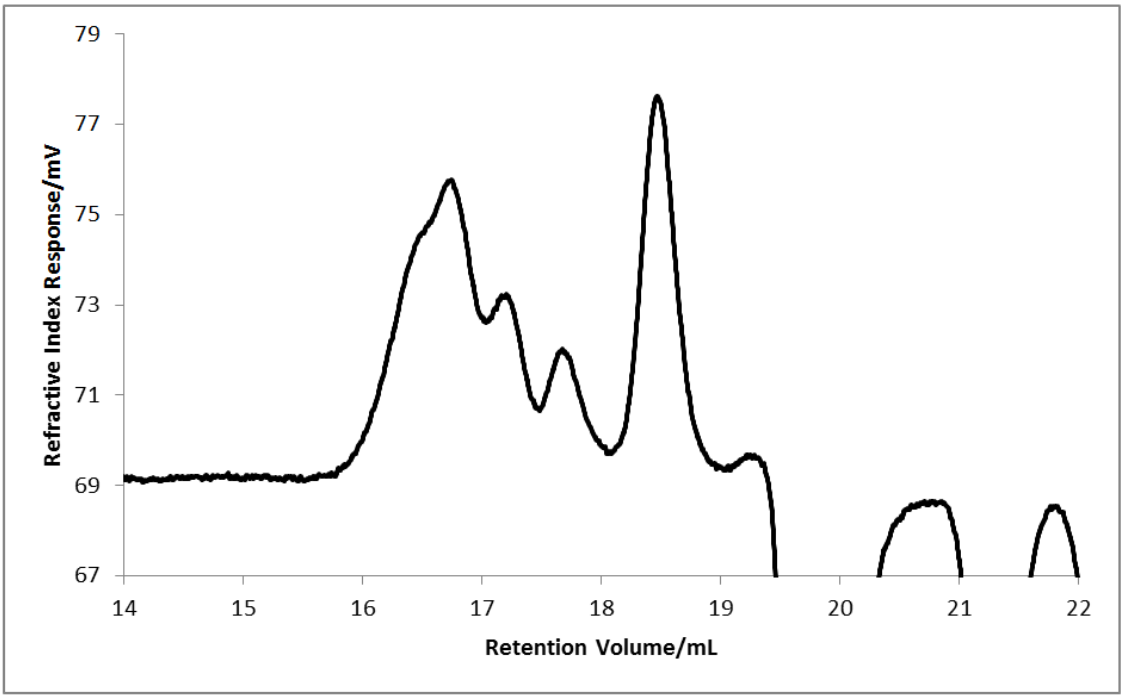

Figure 4.152: SEC trace for poly(butadiene-*co*-DPE-OSi) copolymer, P(Bd-*co*-D_{OSi})-2c, showing the refractive index response.

amount of *sec*-BuLi was added to this sample. The peaks at a retention volume of 17.2 ml are calculated as 1,400 g mol^{-1} and are likely to correspond to sequences containing three units of DPE-OSi. Finally the peaks at a retention volume of 15.8 – 17.0 ml are calculated as 2,700 g mol^{-1} and could correspond to sequences containing four or more units of DPE-OSi. Similarly to the analysis of P(Bd-*co*-D_{OSi})-1, the presence of DPE-OSi monomer meant that no meaningful data could be obtained from the yield or the ^{1}H NMR spectrum.

The objective of the previous copolymerizations, (P(Bd-*co*-D_{OSi})-1) and (P(Bd-*co*-D_{OSi})-2), had been to prepare a low molecular weight copolymer with a view of analysing the resulting copolymers by MALDI-ToF MS, however, it was possible that the reason only oligomers were being obtained was due to the low target molecular weight. It was decided that subsequent copolymerizations would be performed with a high target molecular weight. The copolymerization of DPE-OSi and butadiene with a high target molecular weight on such a low scale (due to limited amount of DPE-OSi) means the required amount of initiator was less than 3 x 10^{-5} moles (for a 2.6 g reaction this gives a target molecular weight between 10,000 g mol^{-1} and 91,400 g mol^{-1} depending on the incorporation of DPE-OSi) and hence these are inherently difficult reactions. With a high target molecular weight, impurities are a much more significant problem. One of the most likely sources of impurities is from the DPE-OSi monomer which could contain bi-products as this monomer was synthesized in house from dihydroxybenzophenone.

Hence in the next reaction, (P(Bd-*co*-D_{OSi})-3), synthesized in THF at 0 °C which had a target molecular weight of 91,400 g mol^{-1} (assuming a full incorporation of DPE-OSi), DPE-OSi was purified by the dropwise addition of *sec*-BuLi prior to the addition of butadiene. Upon the dropwise addition of *sec*-BuLi to a solution of DPE-OSi in THF, initially a blue colour is observed. As the amount of *sec*-BuLi is increased the colour of the mixture goes through various shades of blue, green and brown before finally a red colour signifies the end-point and the presence of living DPE-OSi. This colour transition is analogous to that observed for DPE. Upon attaining the red colour indicative of the presence of living DPE-OSi the final amount of 3 x 10^{-5} moles of *sec*-BuLi were added. However, upon addition of butadiene the reaction mixture became blue. This blue colour may indicate that the red colour obtained upon addition of *sec*-BuLi was a false end-point and impurities were still present. As the butadiene had been used in many previous reactions it seemed unlikely that the butadiene monomer was the source of the impurities. In this case it was decided to allow the copolymerization to continue to determine whether any polymerization was indeed ongoing. The reaction was stirred overnight at 0 °C by which time the colour of the reaction mixture had become pale yellow although this further colour change could not provide further information on whether polymerization was occurring or if the reaction had been terminated by impurities. The reaction was stirred at 0 °C for a further 4 days at which point the reaction was stopped and analysis revealed that no polymerization had occurred suggesting that impurities had indeed terminated the reaction.

The reaction was repeated once more (P(Bd-*co*-D_{OSi})-4) by the dropwise addition of *sec*-BuLi until a permanent red colour was observed and the required amount of sec-BuLi added for a target molecular weight of 124,800 g mol^{-1} (assuming full incorporation of DPE-OSi). As in the previous reaction, upon the addition of butadiene the reaction mixture became blue; but this time subsequent additions of *sec*-BuLi were added dropwise to obtain a permanent red colour. It was however, extremely difficult to obtain a permanent red colour as upon each addition of *sec*-BuLi the instantaneous colour that developed would not persist for more than a few seconds. After 16 additions (2.7×10^{-3} moles) of *sec*-BuLi a brown/red colour was observed. A further 3 additions (7×10^{-4} moles) of sec-BuLi were added before a convincing permanent red colour was observed. At this point it was therefore very unlikely that a high molecular weight copolymer would be formed as it was not possible to determine how much of the *sec*-BuLi had been used to initiate the copolymerization and how much had been required to react with impurities. The reaction was allowed to proceed at 0 °C for 4 days (during which time the colour of the reaction mixture remained red) before the reaction was terminated with methanol. SEC analysis (Figure 4.16) indicated that polymerization had occurred but only to produce oligomers. Again, the same characteristic peaks are observed which again are assumed to correspond to sequences containing one, two, three and four units of DPE-OSi respectively.

The MALDI-ToF mass spectrum (Figure 4.17) analysis allowed the compositions of these oligomers to be identified. The results confirm that there are indeed sequences with one, two, three and four units of DPE-OSi, supporting the assignment of the peaks in the SEC chromatogram. The MALDI-ToF MS analysis shows that there is a significant

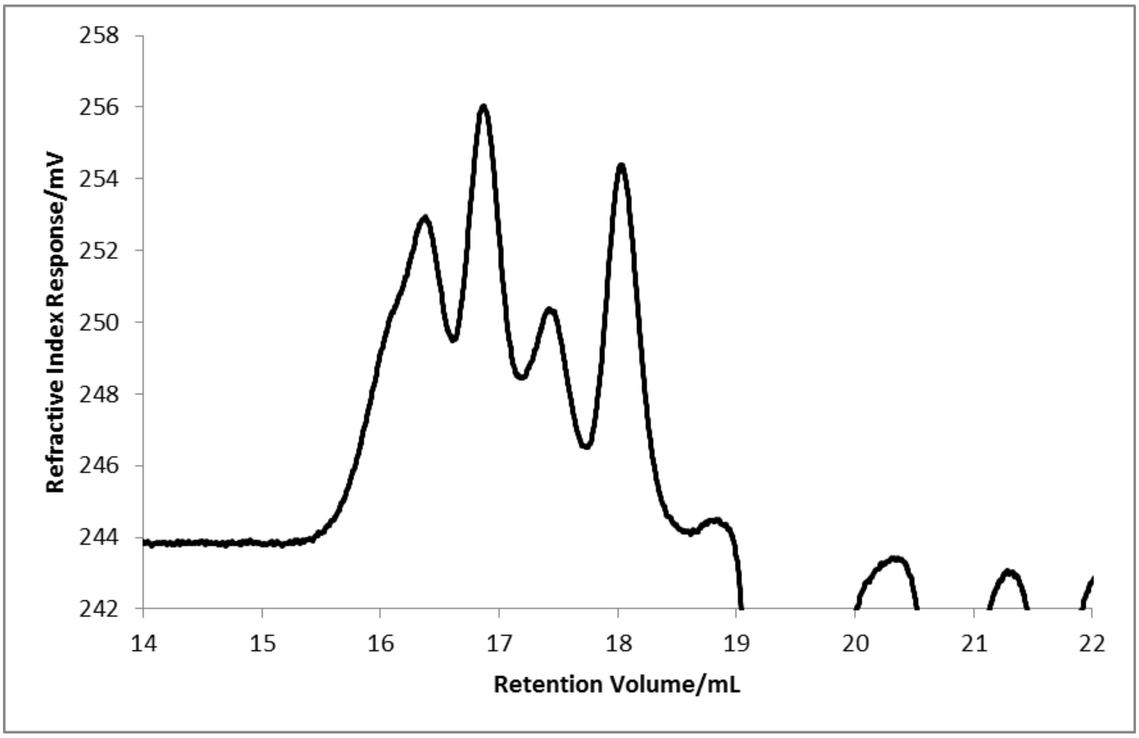

Figure 4.153: SEC trace for poly(butadiene-*co*-DPE-OSi) copolymer, P(Bd-*co*-D_{OSi})-4, showing the refractive index response.

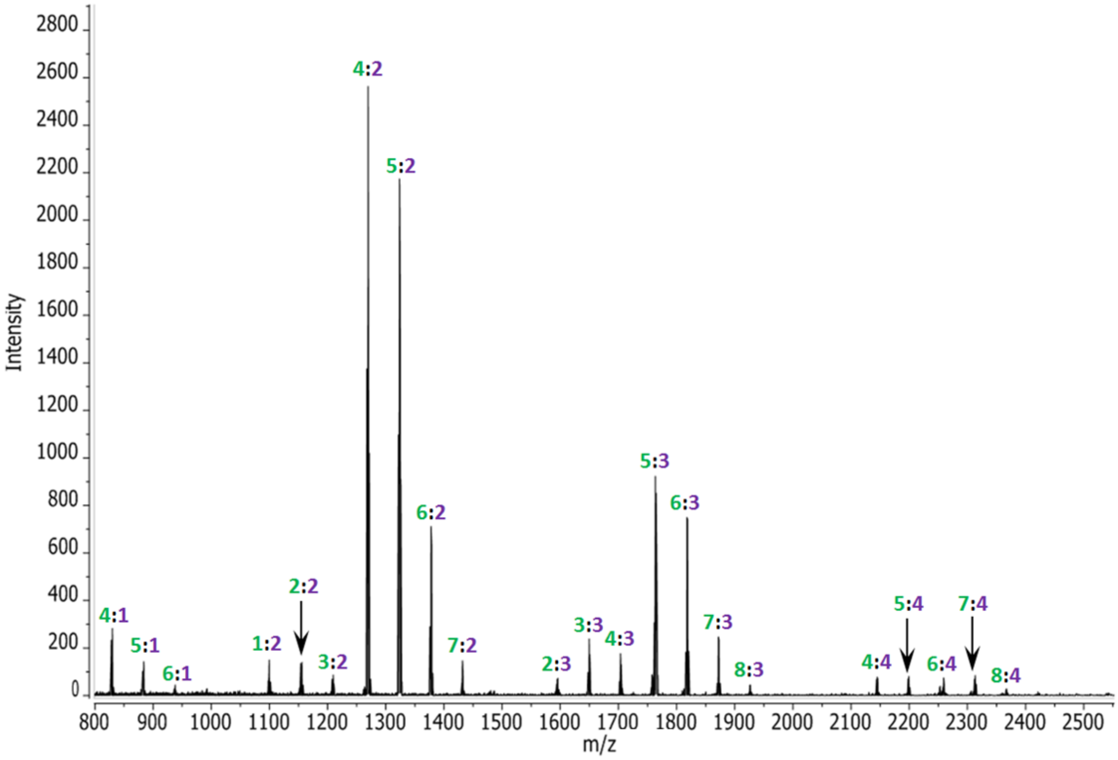

Figure 4.154: MALDI-ToF mass spectrum for the copolymer P(Bd-*co*-D_{OSi})-4 prepared by the copolymerization of butadiene and DPE-OSi (monomer molar feed ratio of butadiene : DPE-OSi = 1.09 : 1.00) in THF. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

incorporation of DPE-OSi and whilst the majority of chains (unsurprisingly) contain more units of butadiene than DPE-OSi, there are some chains which are perfectly alternating, such as the peak at 1,650 g mol^{-1} which contains a butadiene : DPE-OSi ratio of 3 : 3.

High molecular weight copolymers of poly(butadiene-*co*-DPE-OSi) were not successfully prepared. However, one possible future approach would be to synthesize a large batch of the monomer, DPE-OSi, allowing a copolymerization to be performed on a larger scale, thereby reducing the impact of the impurities and allowing a more facile synthesis.

4.3. Telechelic Copolymerizations

As mentioned in Section 4.1, it should be possible to prepare a telechelic copolymer using the 'fire and forget' approach in which the monomer sequence is under kinetic control. The strategy would require a co-monomer pair in which k_{11} is much higher than k_{12} but k_{12} is not negligible. Hutchings *et al*. had previously reported that DPE-OSi can copolymerize with styrene but cross-propagation to the DPE-OSi is highly dis-favoured.[1] This might suggest that a copolymerization of DPE-OSi and styrene in a non-polar solvent with a low concentration of DPE-OSi should be an ideal system to enable the synthesis of telechelic copolymers in a simultaneous (fire and forget) copolymerization following the initiation of DPE-OSi.

When considering the copolymerization of butadiene with DPE-OSi, since butadiene undergoes preferential self-propagation when copolymerized with DPE in non-polar solvents, when butadiene is copolymerized with DPE-OSi (a less reactive monomer than DPE), DPE-OSi should be excluded entirely until all the butadiene is consumed allowing a perfect telechelic copolymer to be formed. A further attractive advantage of using DPE-OSi as the co-monomer in this reaction is that mild acid hydrolysis of this monomer results in the cleavage of the silyl groups to produce a telechelic polymer with 4 reactive terminal phenol groups.

4.3.1. Synthesis of Telechelic Polystyrene by the Copolymerization of Styrene and 1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene in Benzene

Telechelic copolymers are effectively homopolymers which are functionalized at each chain end and as such, in the present work, the successful synthesis of telechelic polystyrene requires only two units of DPE-OSi per chain. Hence, styrene and DPE-OSi were copolymerized using 2.5 mole equivalents of DPE-OSi with respect to the initiator (*sec*-butyllithium) and a monomer molar feed ratio of styrene : DPE-OSi = 9.6 : 1.0. The hypothesis was that the reaction between *sec*-butyllithium and (2.5 mole equivalents) of DPE-OSi would introduce one unit of DPE-OSi at the α-chain end and the excess DPE-OSi would remain unreacted since its homopolymerization is not possible. Subsequent addition of styrene monomer would result in polymerization but a reactivity ratio r_1 of 3 – 4,[1] coupled with a monomer feed ratio containing a very low concentration of DPE-OSi, would result in homopolymerization of styrene and exclusion of the DPE-OSi until all of the styrene is consumed. Only then would the DPE-OSi react, effectively end-capping the polymer (Figure 4.18).

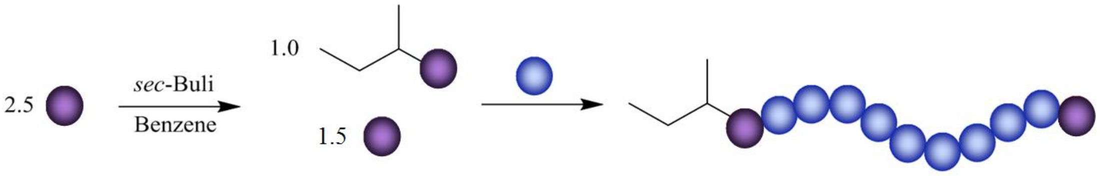

Figure 4.155: Reaction scheme showing the formation of a telechelic copolymer using a ‘fire and forget’ approach with styrene (blue) and DPE-OSi (purple).

DPE-OSi was initially allowed to react with *sec*-BuLi for 1 hour to introduce the first DPE-OSi at the α-chain end of the chain before the addition of styrene. Whilst the use of DPE-OSi in Section 4.2 was problematic, which was assumed to be due to impurities in the DPE-OSi, in this case the amount of DPE-OSi is much lower and hence any impurities will not be so significant. Hutchings *et al*. have previously reported the use of DPE-OSi as a functional initiator in the synthesis of PMMA HyperMacs[10] and as an end capping monomer for the synthesis of AB_2 macromonomers for the preparation of polystyrene[11] and polybutadiene[12] DendriMacs, polystyrene,[13-14] PMMA and polybutadiene HyperMacs[10] and asymmetric stars[15] and polystyrene-polyisoprene-polystyrene HyperBlocks.[10] In hydrocarbon non-polar solvents the rate of end-capping

Table 4.25: DPE-OSi content and molecular weight analysis of Poly(Styrene-*co*-DPE-OSi) copolymers.

Sty : DPE-OSi molar feed ratio	Total Reaction Time/ hours	TMEDA	M_n/ g mol^{-1} (SEC)	Modal Molecular Weight (MALDI-ToF)	Đ	Sty : DPE-OSi by ^{1}H NMR	DPE-OSi per chain
9.6 : 1.0	48	No	3,100	3,300	1.07	11.7 : 1.0	1.9 ± 0.2
9.6 : 1.0	48	Yes	3,100	3,300	1.21	10.0 : 1.0	2.1 ± 0.2

was very slow and tetramethylethylenediamine (TMEDA) (one mole equivalent with respect to Li) was added to enhance the rate of end-capping. Whilst it was found in Chapter 2 that TMEDA inhibited the incorporation of DPE in a copolymerization with styrene, this indicated that the value of k_{11}/k_{12} increases (where styrene is monomer 1 and DPE is monomer 2), not that the value of k_{12} decreased. Furthermore, it is known from literature that the addition of TMEDA enhances the rate of end-capping of polystyryllithium and polybutadienyllithium with DPE-OSi.[10] In the current work the polymerization of styrene in benzene was initiated by the BuLi-DPE-OSi adduct and in the presence of DPE-OSi monomer with a target molecular weight of 2,500 g mol^{-1} (P(S-*co*-D$_{OSi}$)-1). Upon addition of styrene the red colour of the living DPE-OSi could be seen to turn orange, indicative of propagating polystyrene. Within several minutes the orange colour darkened a little towards the red colour of living DPE-OSi. This early colour change may suggest that the polystyrene chains had begun to react with DPE-OSi via end-capping. Whilst this is possible since the polymer chains are very short and the time for propagation is short, previous results suggest the end-capping process can take up to 5 days even in the presence of TMEDA.[14] The reaction was allowed to proceed for 24 hours before the reaction mixture was split into two equal portions (P(S-*co*-D$_{OSi}$)-1a and 1b). TMEDA (2 moles with respect to the initiator) was added to one portion of polymer (P(S-*co*-D$_{OSi}$)-1b) to promote end-capping and then both portions were allowed to react for a further 24 hours. The resulting copolymers were analysed by ^{1}H NMR spectroscopy, SEC and MALDI-ToF MS (Table 4.1 and Figures 4.19 – 4.20). ^{1}H NMR spectroscopy enables the accurate calculation of the ratio of DPE-OSi : styrene repeat units using the intense signals resulting from the -Si(CH$_3$)$_2$ and -C(CH$_3$)$_3$ groups on DPE-OSi, from which it was possible to calculate a ratio

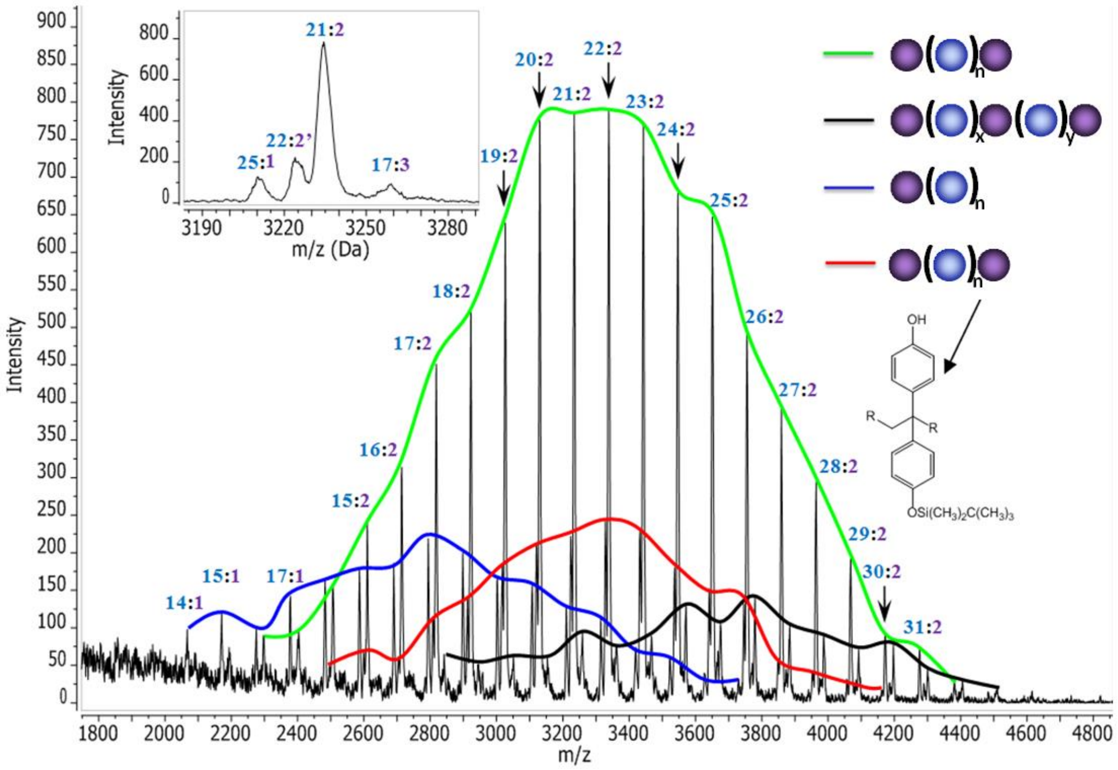

Figure 4.156: MALDI-ToF mass spectrum for the anionic copolymerization (in benzene) of styrene (blue) and DPE-OSi (purple), P(S-*co*-D_{OSi})-1a, (monomer molar feed ratio of Sty : DPE-OSi = 9.6 : 1.0). The mole ratio of styrene : DPE-OSi for any given chain is labelled with styrene in blue and DPE-OSi in purple.

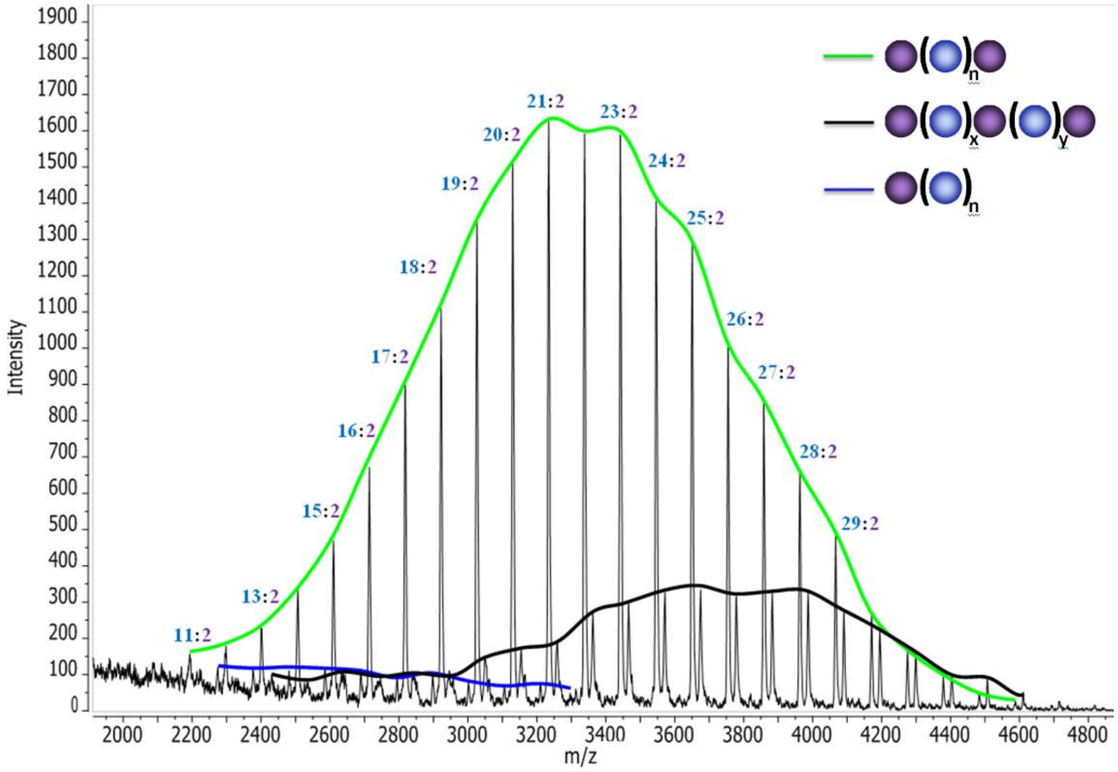

Figure 4.157: MALDI-ToF spectrum for anionic copolymerization (in benzene) of styrene (blue) and DPE-OSi, P(S-*co*-D_{OSi})-1b, (purple) (monomer molar feed ratio of Sty : DPE-OSi = 9.6 : 1.0) with TMEDA injected after 24 hours. The mole ratio of styrene : DPE-OSi for any given chain is labelled with styrene in blue and DPE-OSi in purple.

of 10.0 and 11.7 units of styrene per unit of DPE-OSi for the reactions carried out with and without TMEDA respectively. These values are in good agreement with the styrene : DPE-OSi feed ratio of 9.6 : 1.0. Of course the NMR data cannot provide information about the co-monomer sequence.

MALDI-ToF MS analysis of the reaction carried out *without* the addition of TMEDA (P(S-*co*-D_{OSi})-1a) (Figure 4.19) indicates chain sequences containing some variation in the number of DPE-OSi units. By far the most prevalent distribution of chains is indicated by the green line in Figure 4.19 and comprises of chains with '*n*' styrene units and 2 DPE-OSi units. One of these DPE-OSi units was introduced via the initiator and assuming the hypothesis described above is correct, this population of chains would be the intended telechelic polymers, further evidence to support this hypothesis is given below. Although the above described distribution represents the overwhelming majority of chains present, it is also clear from the data in Figure 4.19 that other types of chains are to be found in the polymer sample. The population of chains indicated by the red line also represents polystyrene chains containing two DPE-OSi units with appropriate *m*/*z* values – however in this case the *m*/*z* value is 115.27 g mol^{-1} lower than expected and these peaks correspond to chains in which one $Si(CH_3)_2CH(CH_3)$ group is missing from the DPE-OSi unit. As such, this population of chains also represents the successful production of telechelic polymers. The chains indicated by the blue line have *m*/*z* values of polystyrene chains containing a single DPE-OSi unit (introduced at the α-chain end) and therefore chains which have not been end-capped with a second DPE-OSi unit. The presence of these chains supports the hypothesis that DPE-OSi units will be *all but* excluded from the polymerization reaction until all the styrene has been consumed. If one considers the sum total of the populations represented by the green, red and blue lines – probably more than 90 % of the total number of chains – as being chains where DPE-OSi has been excluded from the polymerization it would appear that the hypothesis is valid. The remainder, and very small minority of chains represented by the black line have *m*/*z* values which are consistent with polystyrene chains containing 3 DPE-OSi units – most likely 1 DPE-OSi at each chain end and the additional DPE-OSi unit mid-chain.

Considering the MALDI-ToF mass spectrum in Figure 4.20 for the sample to which TMEDA was added after 24 hours (P(S-*co*-D_{OSi})-1b), it can be seen that the situation is slightly different. It is clear that by far the major portion of polystyrene chains contain 2 DPE-OSi units – again represented by the green line. However, it is equally clear that the number of chains containing only a single DPE-OSi unit at the α-chain end is significantly reduced in comparison to Figure 4.19. This would suggest that the addition of TMEDA after 24 hours does indeed have an impact upon reactivity ratios and would appear to have promoted the end-capping of polystyrene chains with DPE-OSi. The same conclusion can be drawn from the fact that the proportion of polystyrene chains containing 3 DPE-OSi chains is also somewhat larger in Figure 4.20 than Figure 4.19.

The number of units of DPE-OSi per chain, $N_{\text{DPE-OSi}}$, can be calculated in a similar approach to the analysis for the P(MMA-*co*-D_{CN}) copolymers. The modal molecular weight for P(S-*co*-D_{OSi})-1a, obtained from MALDI-ToF MS, is 3,300 g mol^{-1}. Hence, after subtracting the end-groups (assuming DPE-OSi is a monomer and not an end-group) and the silver counter ion the molecular weight is approximately 3,100 ± 300 g mol^{-1} (assuming an error of 10 %). Using the molecular weight of the monomer units (104.1 g mol^{-1} for styrene and 440.8 g mol^{-1}) the following equation can be obtained:

$$104.1x + 440.8y = 3100 \pm 300 \qquad [4.2]$$

where x : y is the ratio of styrene : DPE-OSi. It was calculated from ^1H NMR spectroscopy that x/y = 11.7 and the error on this value is likely to be very small due to the intense signals arising from the $Si(CH_3)_2C(CH_3)_3$ groups. Solving equation 4.2 and propagating the errors gives a value of $N_{\text{DPE-OSi}}$ = 1.9 ± 0.2 and is consistent with the MALDI-ToF analysis which indicates the majority of chains contain 2 units of DPE-OSi. Similar analysis for P(S-*co*-D_{OSi})-1b, gives a value of $N_{\text{DPE-OSi}}$ = 2.1 ± 0.2 again indicating that the majority of chains contain 2 units of DPE-OSi.

It appears from the MALDI-ToF mass spectra (Figures 4.19 and 4.20) that the basis for the hypothesis is valid. The reactivity ratios for the copolymerization of styrene and DPE-OSi are such that the DPE-OSi is almost totally excluded from the reaction and the overwhelming majority of chains contain only 2 DPE-OSi units. One of these is at the α-

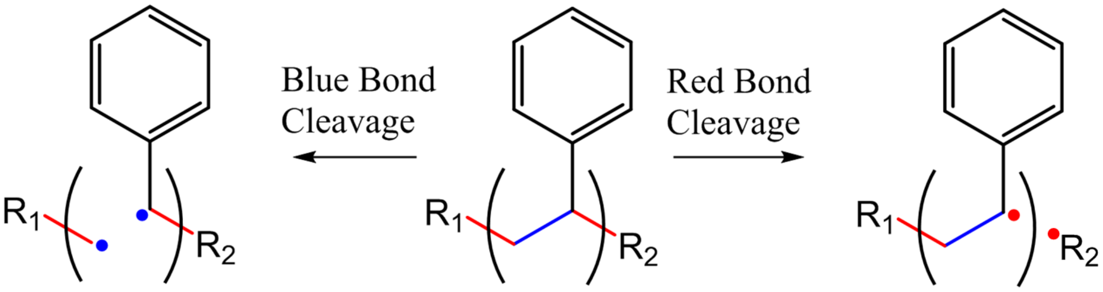

Figure 4.158: Schematic diagram showing the fragmentation of a styrene unit.

chain end and it is most likely that the other unit is at the ω-chain end. To provide further evidence that the second DPE-OSi unit is indeed located at the ω-chain end, a positive ion MSMS experiment using LIFT^{TM} was conducted to more deeply interrogate the monomer sequence of the chains by analysis of the fragmentation of a specific chain. The chains contributing to the peak at *m/z* = 3133.0 in Figure 4.20 corresponding to 20 : 2 (styrene : DPE-OSi) were isolated and fragmented – the fragmentation and MSMS analysis is described in detail by Wesdemiotis *et al.*[16] Fragmentation of these chains can occur at any position along the polymer backbone to generate two radical chain fragments of varying length (as shown in Figure 21 and 4.22a). Fragmentation occurs as a result of cleavage of either one of the two C-C backbone bonds in the polystyrene repeat unit indicated by the red bonds and blue bonds shown in Figure 4.21 and in Figure 4.22a where the representative chain is drawn with a DPE-OSi unit at each end of the chain. Following bond cleavage, the resulting fragments can either include the initiating chain end (α-chain end) or the terminating chain end (ω-chain end). Assuming that the chains all contain a DPE-OSi unit at both the α- and the ω- chain end then four possible sequences can arise. However, if the two DPE-OSi units are exclusively located at each chain end (as intended) then no matter where the fragmentation occurs, both of the resulting fragments must contain a DPE-OSi unit. The radical fragment containing the α-chain end resulting from breaking a red bond is denoted α-$D_1S_n^{\bullet}$, where *n* represents the number of styrene units in the fragment. The radical fragment containing the ω-chain end resulting from cleavage of a red bond is denoted ω-$D_1S_n^{\bullet}$. Whereas the radical fragments arising from cleavage of a blue bond are denoted α-$D_1S_{n+CH2}^{\bullet}$ and ω-$D_1S_{n-CH2}^{\bullet}$ for the fragment containing the α-chain end and the ω-chain end respectively, and

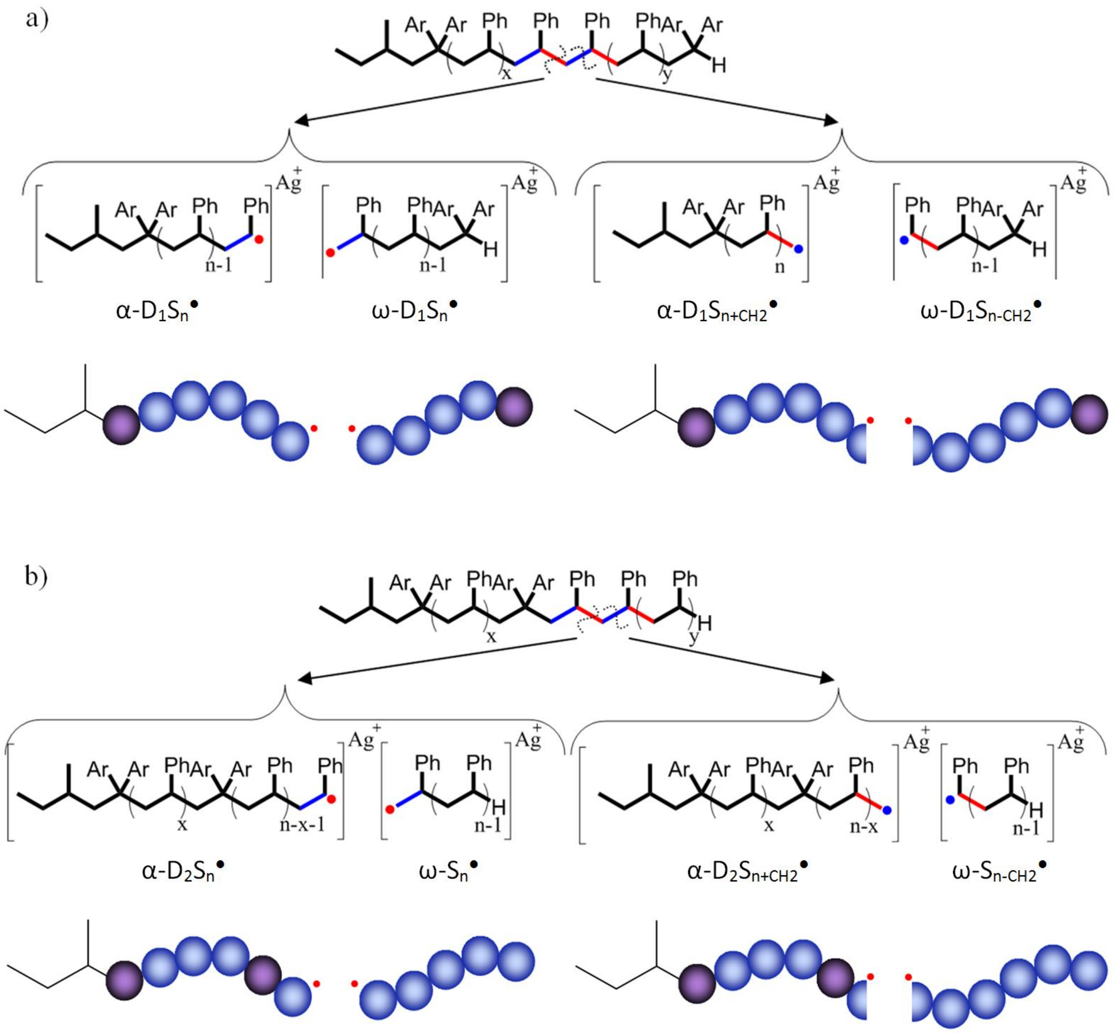

Figure 4.159: Possible sequences arising from fragmentation of (a) a perfect telechelic copolymer (b) a non-telechelic copolymer.

have therefore either gained or lost the CH_2 group – see Figure 4.22a. However, if the second DPE-OSi unit is not located at the ω-chain end but mid-chain, then fragmentation gives rise to a different set of possible sequences as shown in Figure 4.22b and depending where fragmentation occurs it is possible that one fragment will not contain any DPE-OSi units, denoted ω-$S_n^{\bullet}$ and ω-$S_{n\text{-}CH2}^{\bullet}$ for the breaking of the red and blue bond respectively, and the other fragment will contain two DPE-OSi units, denoted α-$D_2S_n^{\bullet}$ and α-$D_2S_{n+CH2}^{\bullet}$ for the breaking of the red and blue bond respectively. The radical fragments, α-$D_1S_n^{\bullet}$, ω-$D_1S_{n\text{-}CH2}^{\bullet}$, α-$D_2S_n^{\bullet}$ and ω-$S_{n\text{-}CH2}^{\bullet}$, can also undergo both a backbiting rearrangement followed by β-scission to yield common internal fragments which dominate in the lower region of the spectra (> 500 *m/z*). Other possible sequences arise from β-scission of an H atom on the radical fragments

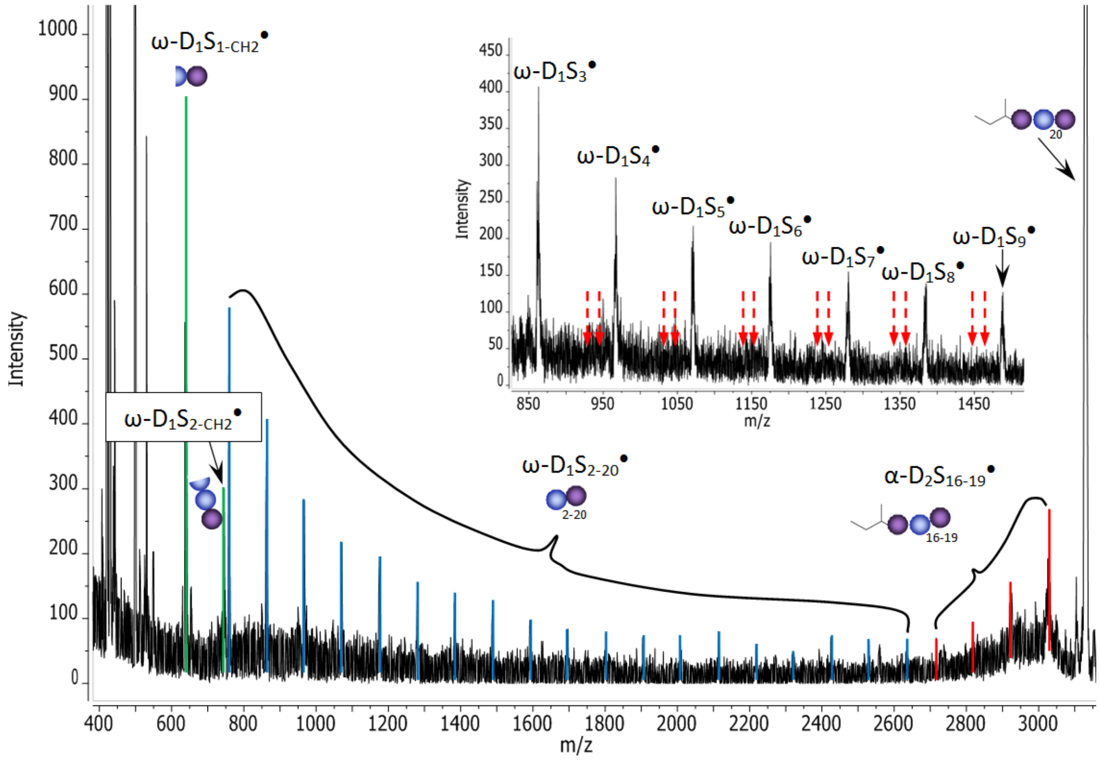

Figure 4.160: Positive Ion MSMS spectrum with LIFT^{TM} for the anionic copolymerization (in benzene) of styrene and DPE-OSi (monomer feed ratio of Sty : DPE-OSi = 9.6 : 1.0) with TMEDA injected after 24 hours with the expansion (inset) showing the range m/z = 850 – 1,500 g mol^{-1}. Red arrows indicate where the sequences of ω-$S_n^{\bullet}$ and ω-$S_{n\text{-}CH2}^{\bullet}$ corresponding to a non telechelic copolymers would appear.

which would differ from their radical counterparts by only the mass of an H atom (1.008 g mol^{-1}); however, these sequences are not observed in this case. It should also be noted that not every sequence is observed, as less stable primary radical atoms could undergo rapid depolymerization.

The results of the fragmentation of the primary polymer chains are shown in Figure 4.23. In this case only the following sequences were observed: ω-$D_1S_n^{\bullet}$; ω-$D_1S_{n\text{-}CH2}^{\bullet}$ and α-$D_2S_n^{\bullet}$. The sequences of chains corresponding to ω-$D_1S_n^{\bullet}$ dominate throughout the entire spectrum confirming the hypothesis that the second DPE-OSi unit is indeed predominantly located at the end of the chain. The hypothesis is particularly supported by the signals corresponding to ω-$D_1S_{1\text{-}CH2}^{\bullet}$, ω-$D_1S_{2\text{-}CH2}^{\bullet}$ and ω-$D_1S_2^{\bullet}$ because these signals show that there is still a DPE-OSi unit present when the chain is fragmented near the end of the chain. The signals corresponding to α-$D_2S_n^{\bullet}$ indicate that in some cases that DPE-OSi has been incorporated prior to the terminal unit suggesting the formation of telechelic polymers is not perfect. This is not particularly surprising since it is already known that DPE-OSi can be incorporated before the full consumption of styrene. Furthermore these sequences are only observed when there are over 16 units of styrene; hence showing that DPE-OSi does not become incorporated until the later stages of the polymerization. To further emphasize that the majority of chains are the intended telechelic copolymer, Figure 4.23 shows an expansion of the *m*/*z* = 850 – 1,500 g mol^{-1} region and the red arrows indicate where the sequences corresponding to ω-$S_n^{\bullet}$ and ω-$S_{n\text{-}CH2}^{\bullet}$ (i.e. signals arising from fragments containing no DPE-OSi units at the ω-chain end) would be expected to appear. It can therefore be concluded that the hypothesis is indeed correct and that the overwhelming majority of chains were the intended telechelic copolymers.

4.3.2. Synthesis of Telechelic Polybutadiene by the Copolymerization of Butadiene and 1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene in Benzene

Attempts were made to prepare telechelic polybutadiene by the simultaneous copolymerization of butadiene with DPE-OSi in an analogous fashion to that described above for telechelic polystyrene. Previous results suggest that the likelihood of DPE-OSi undergoing copolymerization with butadiene in a non-polar solvent such as benzene is extremely low. The reactivity ratio r_1 is 54 for the copolymerization of butadiene (M_1) and DPE (M_2) and the effect of the electron donating substituent on DPE-OSi has been shown to deactivate the monomer and will increase the value of r_1. Hence it was expected that if butadiene and DPE-OSi were copolymerized DPE-OSi would be completely excluded until complete consumption of butadiene; two copolymerizations were carried out to test this hypothesis.

An initial reaction was performed using only 1.85 mole equivalents of DPE-OSi with respect to the initiator (P(Bd-*co*-D_{OSi})-5). This ensures that only a maximum of 85 % of chains could be end-capped and thus the MALDI-ToF mass spectrum of the final copolymer could contain sequences corresponding to both end-capped and non-end-capped chains. It should therefore be possible to identify the telechelic sequence. DPE-OSi was initiated with *sec*-butyllithium and allowed to react for 1 hour at room temperature prior to the addition of butadiene. After the reaction had been stirred for 17 hours at room temperature a sample was withdrawn (P(Bd-*co*-D_{OSi})-5a) for characterization and TMEDA (5.0 equivalents with respect to lithium) injected. The

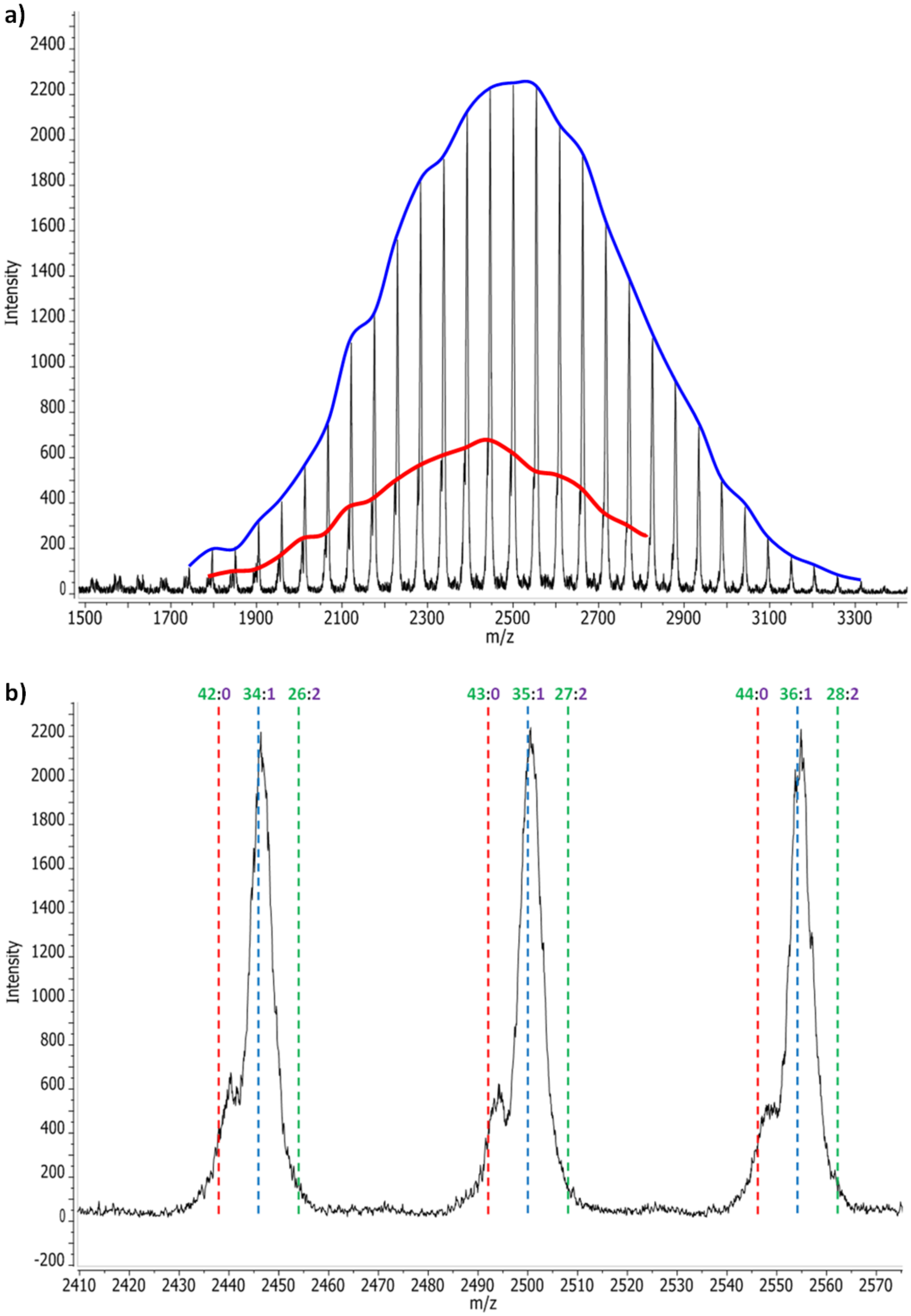

Figure 4.161: (a) MALDI-ToF spectrum of a sample (P(Bd-*co*-D_{OSi})-5a) collected after 17 hours of the anionic copolymerization of butadiene and DPE-OSi, in benzene with a molar feed ratio of Bd : DPE-OSi = 18.5 : 1.0 and (b) expansion showing the range m/z = 2410 – 2570 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

Table 4.26: DPE-OSi content and molecular weight analysis of Poly(Butadiene-*co*-DPE-OSi) copolymers.

Bd : DPE-OSi molar feed ratio	Total Reaction Time/ hours	Time with TMEDA/ hours	M_n/ g mol^{-1} (SEC)	Modal Molecular Weight (MALDI-ToF)	Đ	Bd:DPE-OSi by ^{1}H NMR	DPE-OSi per chain
18.5 : 1.0	17	0	2,300	2,500	1.04	36 : 1	1.0 ± 0.1
18.5 : 1.0	32	15	2,700	2,500	1.12	36 : 1	1.0 ± 0.1
18.5 : 1.0	151	134	2,800	2,500	1.10	22 : 1	1.4 ± 0.1

reaction was allowed to proceed and was sampled after a further 15 hours (P(Bd-*co*-D$_{OSi}$)-5b), and then terminated after 5 days (P(Bd-*co*-D$_{OSi}$)-5c). The resulting polymers were analysed by ^{1}H NMR spectroscopy, SEC and MALDI-ToF MS and characterization data for this experiment are contained in Table 4.2.

MALDI-ToF MS data for P(Bd-*co*-D$_{OSi}$)-5a, the sample extracted after 17 hours and prior to the addition of TMEDA, is shown in Figure 4.24. Although determining the sequence using the *m*/*z* values is potentially inaccurate (as the difference between 1 unit of DPE-OSi and 8 units of butadiene is only 8.0 g mol^{-1} which shown in Figure 24b), it does appear as if the main species present only contains a single unit of DPE-OSi and that the residual DPE-OSi has not been incorporated into the polymerization at all. This would be consistent with our expectations. There may however, be some sequences (represented by the red line) which could correspond to some polybutadiene initiated with butyl lithium and thus containing no DPE-OSi. This would suggest that the reaction between butyl lithium and DPE-OSi was incomplete (despite the strong red colour of the DPELi adduct) prior to the addition of the butadiene monomer. Although this is not ideal for the synthesis of telechelic polymers, the production of polybutadiene chains with no DPE-OSi units does confirm that in benzene and the absence of TMEDA, DPE-OSi is excluded from the polymerization. From the modal molecular mass (obtained from the MALDI-ToF mass spectrum) and the value of butadiene/DPE-OSi = 36 (obtained from the ^{1}H NMR spectrum) it is calculated that there is an average of 1.0 ± 0.1 units of DPE-OSi per chain (Table 4.2) which is consistent with predominant signals in the MALDI-ToF spectrum corresponding to chains containing 1 unit of DPE-OSi.

The sequence for P(Bd-*co*-D_{OSi})-5b, the sample collected 15 hours after the addition of TMEDA, (Figure 4.25) is difficult to analyse due to the weak signals. However, there only appears to be a single sequence and no noticeable increase in molecular weight. This is consistent with the value calculated for the number of DPE-OSi units per chain which was calculated as 1.0 ± 0.1. The MALDI-ToF mass spectrum of the final sample, P(Bd-*co*-D_{OSi})-5c, (5.5 days with TMEDA) (Figure 4.26) clearly contains two distributions of chains, although the resolution is not very good, and shows the presence of chains with 2 units of DPE-OSi indicating end-capping has occurred. Furthermore the number of units of DPE-OSi per chain was calculated as 1.4 ± 0.1, this value is lower than expected as there was enough DPE-OSi monomer to end-cap 85 % of the chains. This therefore suggests that end-capping is only 40 % complete and not as high as was expected. Although it was not possible to obtain a signal of these copolymers by MSMS, the fact that both P(Bd-*co*-D_{OSi})-5a and 5b only contain 1 unit of DPE-OSi and that there does not appear to be any increase in the number of butadiene units prove that the extra unit of DPE-OSi in P(Bd-*co*-D_{OSi})-5c must be at the chain end.

The reaction described above was repeated with 2.5 mole equivalents of DPE-OSi with respect to the initiator (P(Bd-*co*-D_{OSi})-6) and this time, DPE-OSi was allowed to react with *sec*-butyllithium for 24 hours at room temperature before the addition of butadiene. DPE-OSi and butadiene were copolymerized for 3 days at room temperature before a sample was withdrawn for characterization (P(Bd-*co*-D_{OSi})-6a) and the remaining reaction mixture was separated into two equal portions (P(Bd-*co*-D_{OSi})-6b and 6c) and TMEDA (2 moles with respect to lithium) injected into one portion P(Bd-*co*-D_{OSi})-6c). Both portions were allowed to react for a further 6 days before being terminated. The resulting polymers were analysed by ^{1}H NMR spectroscopy, SEC and MALDI-ToF MS and characterization data for this experiment are contained in Table 4.3. The MALDI-ToF mass spectra for both samples and the final copolymer are shown in Figures 4.27 – 4.29.

These results indicate in the absence of TMEDA, DPE-OSi is completely excluded from the polymerization, even after 9 days. Furthermore the polymerization of butadiene was complete after 3 days as the degree of polymerization, N_{Bd}, does not increase

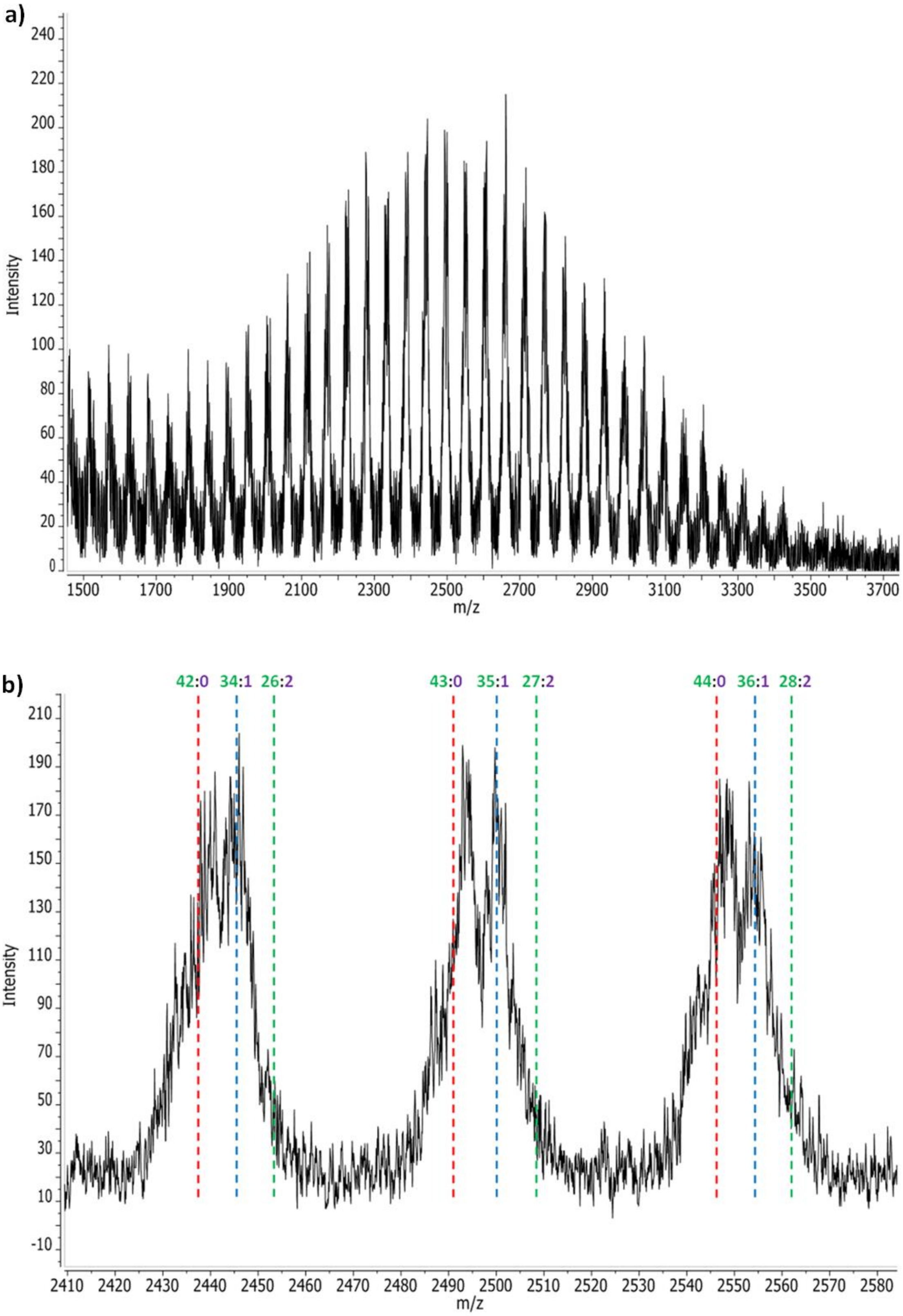

Figure 4.162: (a) MALDI-ToF spectrum of a sample (P(Bd-*co*-$\mathrm{D_{OSi}}$)-5b) collected after 32 hours (15 hours with TMEDA) of the anionic copolymerization of butadiene and DPE-OSi, in benzene with a molar feed ratio of Bd : DPE-OSi = 18.5 : 1.0 and (b) expansion showing the range m/z = 2410 – 2580 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

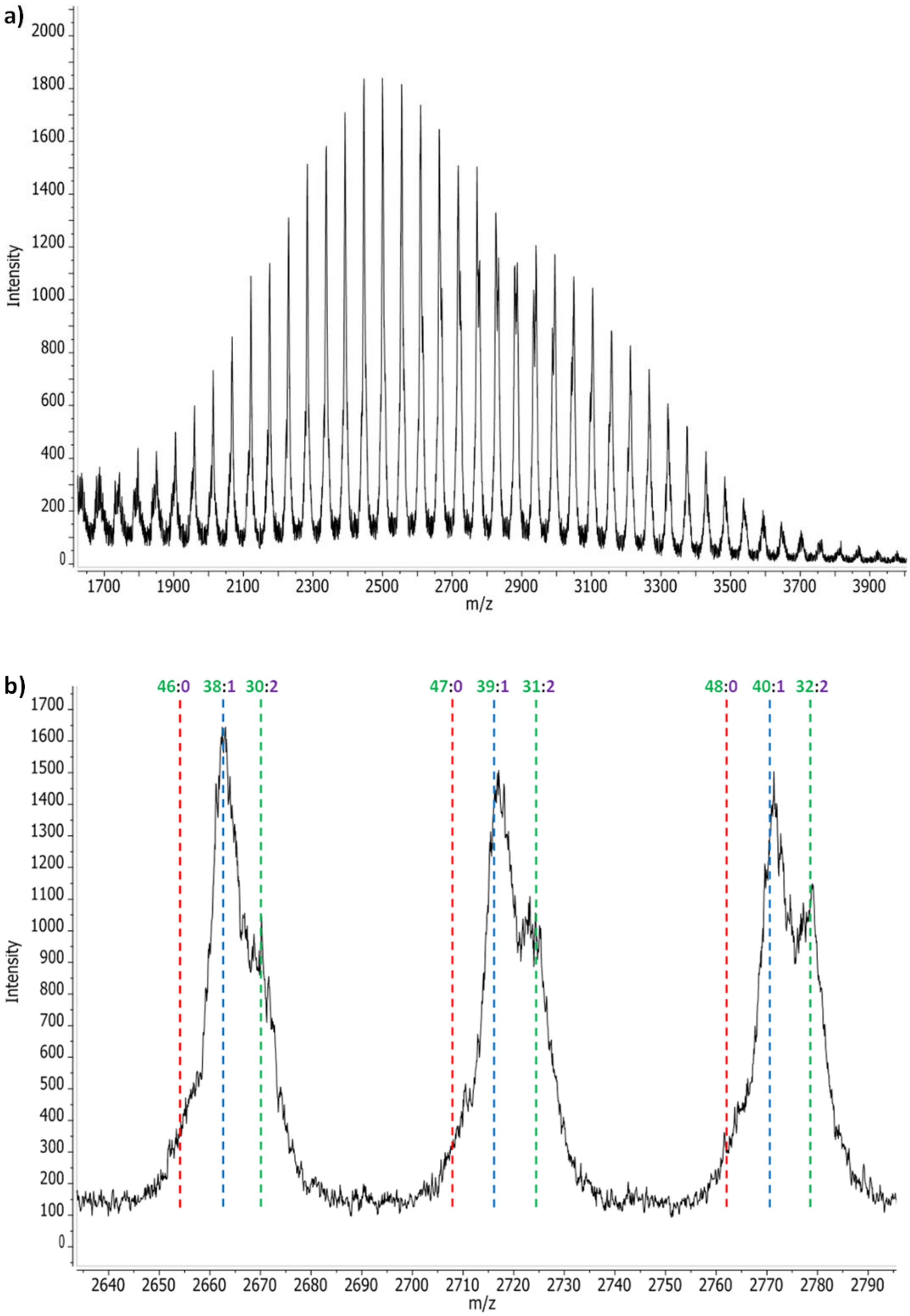

Figure 4.163: (a) MALDI-ToF spectrum of a sample (P(Bd-*co*-$\mathrm{D}_{\mathrm{OSi}}$)-5c) collected after 151 hours (127 hours with TMEDA) of the anionic copolymerization of butadiene and DPE-OSi, in benzene with a molar feed ratio of Bd : DPE-OSi = 18.5 : 1.0 and (b) expansion showing the range m/z = 2640 – 2790 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

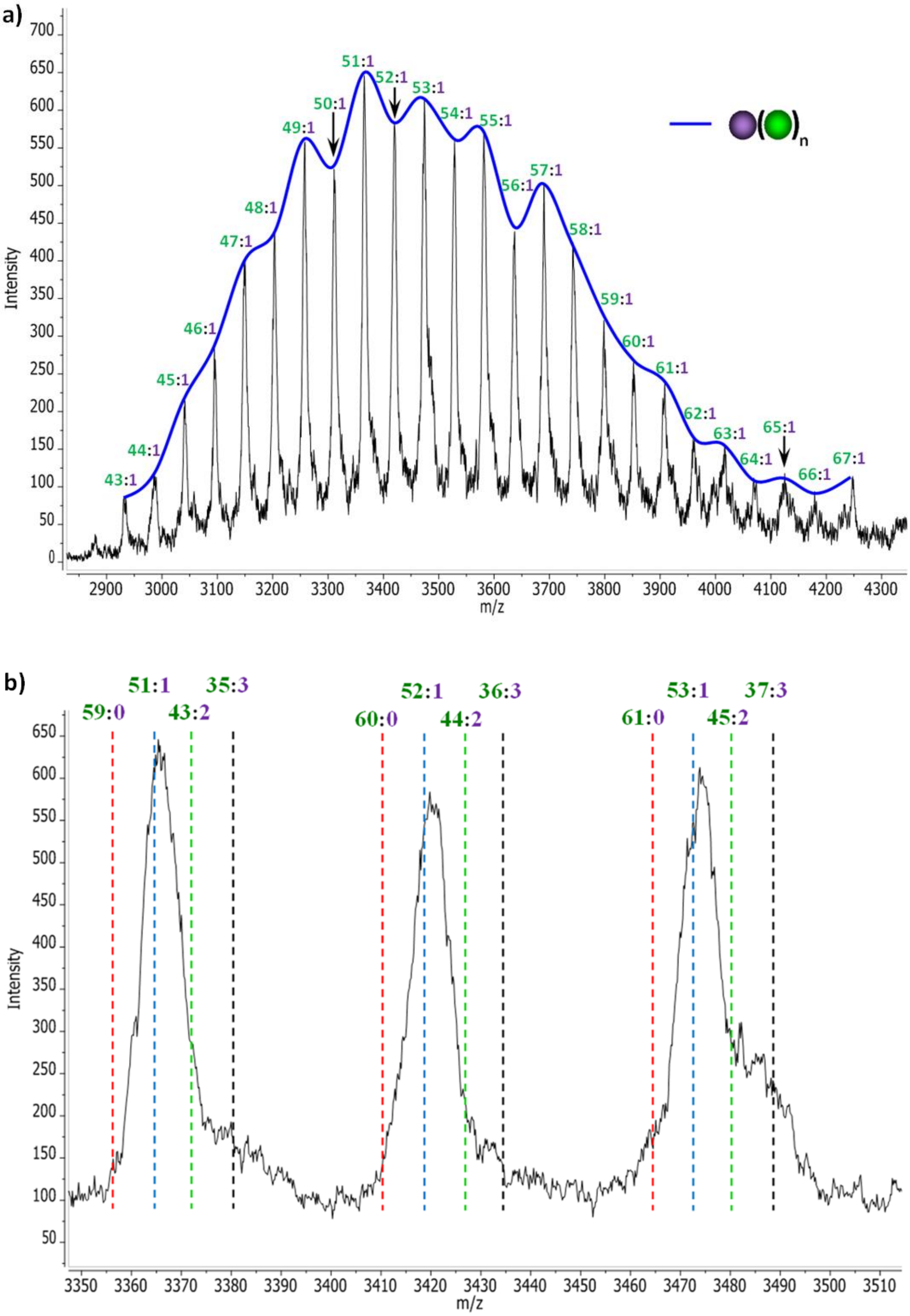

Figure 4.164: (a) MALDI-ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 3 days, P(Bd-*co*-D_{OSi})-6a, with a molar feed ratio of Bd : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range m/z = 3350 – 3510 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

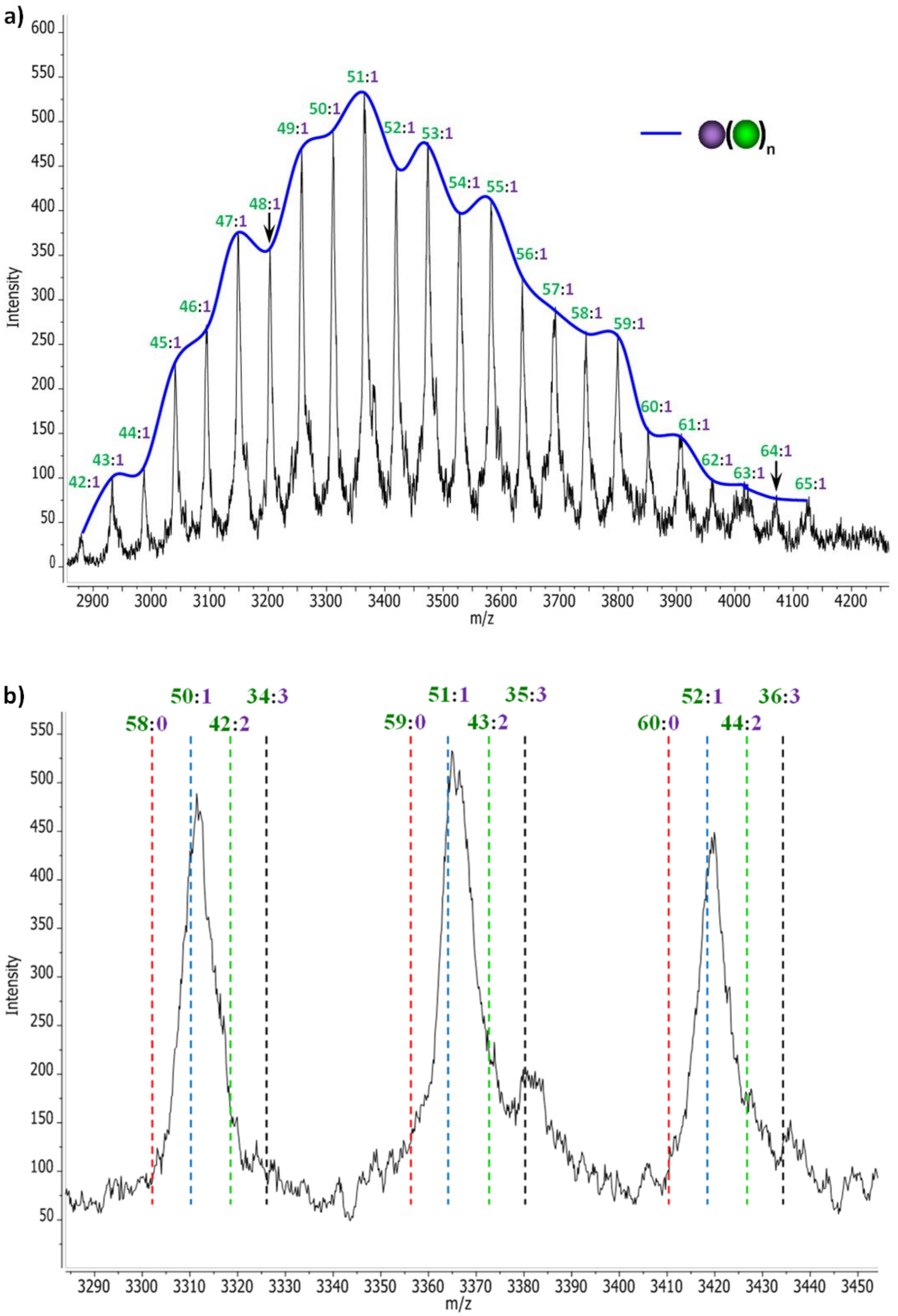

Figure 4.165: (a) MALDI-ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 9 days, P(Bd-*co*-D_{OSi})-6b, with a molar feed ratio of Bd : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range m/z = 3290 – 3450 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

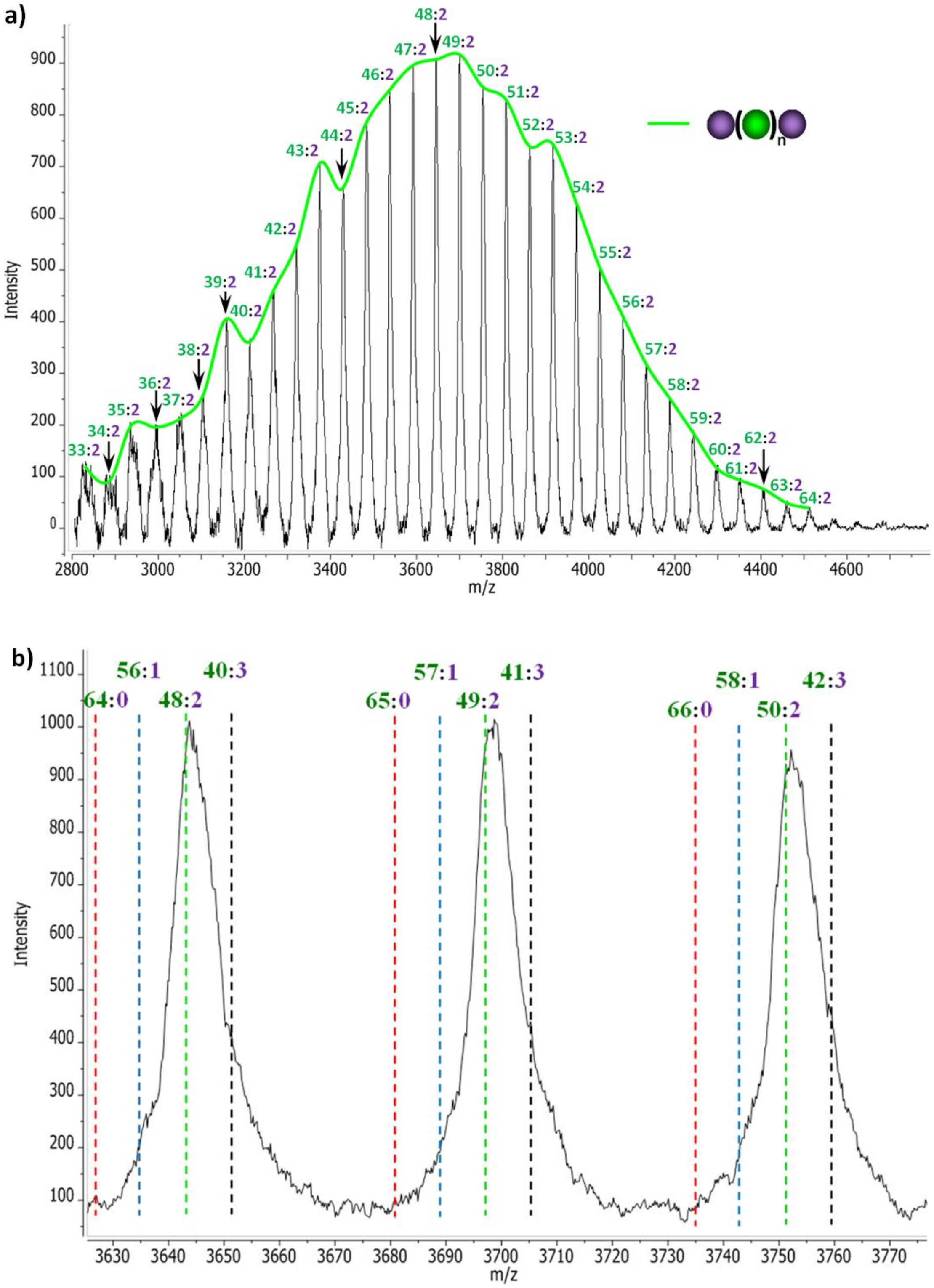

Figure 4.166: (a) MALDI-ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 3 days without TMEDA and 6 days with TMEDA, P(Bd-*co*-D_{OSi})-6c, with a molar feed ratio of Bd : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range m/z = 3630 – 3770 with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

Table 4.27: DPE-OSi content and molecular weight analysis of Poly(Butadiene-*co*-DPE-OSi) copolymers.

Bd : DPE-OSi feed ratio	Total Reaction Time/ days	TMEDA	M_n/ g mol^{-1}	Modal Molecular Weight (MALDI-ToF)	Đ	Bd : DPE-OSi by ^{1}H NMR	DPE-OSi per chain
13.0 : 1.0	3	No	3,700	3,500	1.06	48 : 1.0	1.1 ± 0.1
13.0 : 1.0	9	No	4,200	3,500	1.19	47 : 1.0	1.1 ± 0.1
13.0 : 1.0	9	Yes	4,300	3,700	1.08	28 : 1.0	1.8 ± 0.2

between 3 and 9 days. The average number of DPE-OSi units per chain was calculated as 1.1 ± 0.1 for both samples that were obtained in the absence of TMEDA (P(Bd-*co*-D_{OSi})-6a and P(Bd-*co*-D_{OSi})-6b).

The MALDI-ToF mass spectrum of the final sample (Figure 4.29) shows that after 6 days with TMEDA all the peaks correspond to chains with 2 units of DPE-OSi and the average number of DPE-OSi units per chain was calculated as 1.8 ± 0.2. These results imply that end-capping of butadiene with DPE-OSi either does not occur or is an extremely slow process in the absence of TMEDA; however, this is ideal for preparing telechelic copolymers as this prevents the incorporation of DPE-OSi units into the middle of the chains. Again, it was not possible to obtain a signal of these copolymers by MSMS, however, the increase in DPE-OSi units whilst N_{Bd} remains constant, in both the copolymerization with and that without TMEDA, indicates that DPE-OSi is only incorporated after butadiene has been consumed and the MALDI-ToF mass spectrum of the final copolymer shows there is only a single sequence corresponding to chains containing two units of DPE-OSi. Hence this 'fire and forget' method of simultaneously copolymerizing two monomers can be used to synthesize perfect telechelic copolymers.

4.4. References

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CHAPTER 5

Experimental

5. Experimental

5.1. Materials

Benzene (Aldrich, HPLC grade > 99.9%), toluene (Fisher, HPLC grade > 99.9%), styrene (Aldrich, 99%) and methyl methacrylate (Aldrich, 99%) were dried with calcium hydride (97%, Aldrich) and degassed by a series of freeze-pump-thaw cycles. Tetrahydrofuran (THF) (Fisher, HPLC grade) was dried and degassed over sodium (Aldrich) wire and benzophenone (Aldrich) by freeze-pump-thaw cycles until the solution turned purple, and was freshly distilled prior to use. Butadiene (Aldrich, 99%) was dried and purified by passing the monomer successively through columns of Carbosorb (Aldrich), to remove any inhibitor, and molecular sieves. Hexane (Fisher, GPR grade), diethyl ether (Fisher, GPR grade), methanol (Fisher, AR grade), silica (Aldrich), *n*-butyllithium (Aldrich, 2.5 M in hexanes), sand (Aldrich), dichlorodimethylsilane (Aldrich, 99.5%), *sec*-butyllithium (Aldrich, 1.4 M in cyclohexane; Acros, 1.3 M in cyclohexane), 2,6-di-*tert*-butyl-4-methyl phenol (BHT) (Aldrich, 99%), lithium chloride (Aldrich), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (Aldrich, 99.5%) and polystyrene-*block*-polybutadiene-*block*-polystyrene (Aldrich, styrene 30 wt.%, M_n = 47,000 g mol^{-1}; M_w = 52,800 g mol^{-1}, Đ = 1.12 calculated by triple detection SEC using a *dn*/*dc* value of 0.185) were all used as received. Diphenylethylene (DPE) (Aldrich, 97%) was degassed by freeze-pump-thaw cycles and purified by the dropwise addition of *sec*-butyllithium until a red colour persisted and freshly distilled prior to use. *Sec*-lithium butoxide was synthesized by reacting *sec*-butanol (Aldrich, anhydrous, 99.5%) with *sec*-butyllithium using 1,10-phenanthroline (Aldrich, 99%) as an indicator according to the previously described procedure.[1] 1,3-*Bis*(1-phenylvinyl)benzene was synthesized from 1,3-dibenzoylbenzene (Aldrich, 98 %) via the Wittig reagent generated from methyltriphenylphosphonium bromide (Aldrich, 98 %) and methyllithium (Aldrich, 1.6 M in diethyl ether) using an analogous procedure to the one reported by Schulz and Höcker.[2] The dilithium initiator was generated from reacting 1,3-*Bis*(1-phenylvinyl)benzene with 2.15 equivalents of *sec*-butyllithium according to the previously described procedure.[1a, 3] 1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) was synthesized according to the procedure of Quirk and Wang.[4] Cyanodiphenylethylene (DPE-CN) was synthesized from 4-cyanobenzophenone

(Aldrich, 97%) and methyl magnesium bromide (Aldrich, 3M in diethyl ether) according to the previously described procedure.[5]

5.2. Measurements

Molecular weight analysis was carried out by size exclusion chromatography (SEC) using a Viscotek TDA 302 with a refractive index, viscosity and light scattering detectors. 2 x 300 mm PLgel 5 µm mixed C-columns (with a linear range of molecular weight from 200 to 2,000,000 g mol^{-1}) were used and THF was the eluent with a flow rate of 1.0 ml/min at a temperature of 35 °C. Molecular weights were typically obtained by triple detection SEC with light scattering. The calibration was carried out with a narrow molecular weight polystyrene standard (Polymer Laboratories). A value of 0.185 for polystyrene, 0.124 for polybutadiene, 0.130 for polyisoprene and 0.085 for poly(methyl methacrylate) (obtained from Viscotek) were used for the *dn*/*dc* of the respective polymers. A *dn*/*dc* value of 0.196 (calculated from a known concentration of PSD-8 and PSD-9) was used for the poly(styrene-*co*-DPE) copolymers, a *dn*/*dc* value of 0.189 (calculated from a known concentration of PBdD-1) was used for the poly(butadiene-*co*-DPE) copolymers and a *dn*/*dc* value of 0.109 (calculated from a known concentration of PBd-1) was used for polybutadiene with a high 1,2-enchainment. Other copolymers were measured relative to polystyrene using a *dn*/*dc* value of 0.185. When the signal could not be detected by light scattering detection, a conventional calibration was used. The conventional calibration was generated using the RI detector and a calibration curve constructed using nine reference polystyrene standards (Polymer Laboratories, M_p between 580 – 3,114,000 g mol^{-1}, Đ ≤ 1.11).

^{1}H NMR, ^{13}C NMR, HSQCAD and COSY spectra were recorded on a Bruker-400 MHz, a Varian-600 MHz or a Varian VNMRS-700 MHz spectrometer using either $CDCl_3$ or CD_2Cl_2 as a solvent. Spectra were referenced to the trace of $CHCl_3$ (7.26 ppm) present in $CDCl_3$ or $CDHCl_2$ (5.32 ppm) present in CD_2Cl_2.

MALDI-ToF mass spectrometry analysis was carried out on an Autoflex II TOF/TOF mass spectrometer (Bruker Daltonik GmBH). The instrument is equipped with a 337 nm nitrogen laser (Bruker Daltonics Ltd., Coventry, UK) and a reflectron to enhance performance below, typically, *m*/*z* 10,000. This was calibrated for MS experiments with the sodium adducts of poly(ethylene glycol) 2.0 K. A ground-steel target plate was cleaned with methanol and acetone prior to use. Positive ion MSMS experiments using the LIFT^{TM} capability were conducted in the absence of a collision gas at a source pressure of approximately 2.5 x 10^{-7} mbar. The LIFT^{TM} device accelerates product ions allowing them passage through the reflectron improving sensitivity, resolution and mass accuracy.[6] Samples were dissolved in a solution of THF or chloroform (~1 mg/ml) and mixed with a matrix solution (~50 mg/ml) in a ratio of 1:9. 1 µL of this mixture was spotted on to a metal target and placed into the MALDI ion source. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) and a dopant of Ag^+ was added.

Differential Scanning Calorimetry (DSC) was performed under an inert atmosphere on a TA Q1000 instrument from room temperature to 493 K at 10 K/min, 20 K/min and 40 K/min; with 5 minute isothermal periods between each temperature ramp. Glass transition temperatures were analysed using TA instruments Universal Analysis 2000 version 4.5A.

Dynamic Mechanical Analysis (DMA) was performed on a TA Q800 DMA instrument with a 20 mm cantilever and samples with a length of 20.0 mm, width of 10.0 mm and thickness of 1.1 mm were used. Samples were pressed in a mould using a weight of 10 Kg, degassed, purged with dry nitrogen and put under vacuum. This process was repeated three times before being heated to 220 °C for 24 hours and cooled before being raised to atmospheric pressure to ensure no degradation of the polybutadiene block. The samples were then placed in the DMA; equilibrated at 30 °C; cooled to -150 °C at 5 °C/min; equilibrated at -150 °C and heated to 250 °C at 5 °C/min. The thermal properties were analysed using TA instruments Universal Analysis 2000 version 4.5A and the glass transition temperatures calculated by looking at the peaks of tan delta.

The density of the poly(styrene-*co*-DPE) copolymer was found for a sample of cast film (cast from a 30 wt. % solution in toluene) of PSD-3c. A sample of polymer was submerged in water to determine whether the density was greater or less than that of water (1.00 g cm^{-3}). As the sample sank it was therefore concluded that the density was greater than that of 1.00 g cm^{-3}. The sample was removed and subsequently submerged in different aqueous solutions of calcium chloride until a solution (with a known concentration of calcium chloride) was found in which the sample had a neutral buoyancy. It was found that neutral buoyancy was obtained for a calcium chloride solution of 11.9 % w/w. It was found (from Mettler Toledo) that a solution of 11.9 % w/w calcium chloride in water had a density of 1.10 g cm^{-3}, and it was therefore concluded that the density of PSD-3c was 1.10 g cm^{-3}.

Samples for Transmission Electron Microscopy (TEM) analysis were prepared by cryo-ultramicrotomy using a Leica EM UC6 Ultramicrotome and Leica EM FC6 cryochamber (Milton Keynes, UK) on a solvent cast film (cast from a 30 wt. % solution in toluene). Cryosections of 50 – 70 nm thickness were cut using a cryo 35° diamond knife (Diatome, Switzerland) at a temperature between –120 °C and –140 °C and then manipulated from the knife edge onto formvar coated grids. Sections were stained for 2 – 4 hours with osmium tetroxide (OsO_4) vapour then viewed with a Hitachi H7600 transmission electron microscope (Hitachi High Technologies Europe) using an accelerating voltage of 100 KV.

5.3. Polymer Synthesis

All polymers were synthesized by living anionic polymerizations using standard high vacuum techniques, highly purified (dried and degassed) solvents and monomers and trap to trap distillation. The reaction vessel used for these polymerizations is shown in Figure 5.1.

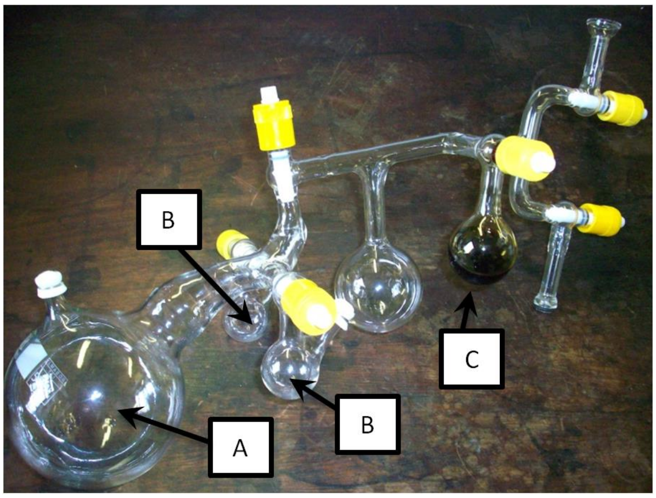

Figure 5.167: Reaction vessel used for polymerizations, showing (A) main reaction vessel (B) side flasks and (C) living polystyrene cleaning solution.

5.3.1. Synthesis of Poly(Styrene-*co*-1,1-Diphenylethylene) - PSD-1

The synthesis of poly(styrene-*co*-DPE) was typically carried out according to the following procedure: benzene (90 ml) and styrene (2.36 g, 23 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (2.72 g, 15 mmol) was injected *via* a rubber septum. For a target molecular weight of 7,500 g mol^{-1}, *sec*-butyllithium (BuLi) (0.45 ml of 1.4 M solution, 0.63 mmol) was added by injection *via* a rubber septum, resulting in the red colour indicative of a mixture of diphenylethyl lithium and styryl lithium. The solution was stirred at room temperature for 21 hours before a sample was extracted and terminated by the injection of nitrogen sparged methanol. The red colour of the living polymer solution dissipated instantly. The polymer sample was recovered by precipitation into methanol, collected by filtration, washed with further methanol and dried *in vacuo*.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 4.8 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 9,000 g mol^{-1}; M_w = 9,900 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn*/*dc* = 0.196).

The remaining reaction mixture was used in the synthesis of P(SD)-PBd-1 (below).

5.3.2. Synthesis of PSD-2

Poly(styrene-*co*-DPE) with a target molecular weight of 14,500 g mol^{-1}, was prepared by the procedure described above except that 100 ml of benzene, 2.10 g styrene (20 mmol), 3.75 g DPE (21 mmol) and 0.28 ml of 1.4 M BuLi (0.39 mmol) were used and the reaction was stirred at 50 °C for 21 hours before a sample was extracted and terminated.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 4.8 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 10,700 g mol^{-1}; M_w = 12,200 g mol^{-1}; Đ = 1.14 (triple detection SEC with *dn*/*dc* = 0.196).

The remaining reaction mixture was used in the synthesis of P(SD)-PBd-2 (below).

5.3.3. Synthesis of PSD-3a to 3c

Poly(styrene-*co*-DPE) with a target molecular weight of 40,000 g mol^{-1}, was prepared by the procedure described above except that 50 ml of benzene, 2.38 g styrene (23 mmol), 6.37 g DPE (35 mmol) and 0.12 ml of 1.4 M BuLi (0.17 mmol) were used and the reaction was stirred at 30 °C and sampled after 4 hours and after 18 hours to yield PSD-3a and PSD-3b respectively. The remaining reaction mixture was stirred at 30 °C for a further 30 hours before being terminated with degassed methanol to yield PSD-3c.

PSD-3a to 3c ^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.0 – 2.5 (5H –C$\mathbf{H_2}$CPh**H**-C$\mathbf{H_2}$CPh$_2$), 4.8 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C$\mathbf{Ph_2}$).

PSD-3a M_n = 7,800 g mol^{-1}; M_w = 9,000 g mol^{-1}; Đ = 1.16 (conventional calibration, PS standards)

PSD-3b M_n = 21,400 g mol^{-1}; M_w = 25,600 g mol^{-1}; Đ = 1.20 (conventional calibration, PS standards)

PSD-3c Yield = 90 %.

M_n = 91,800 g mol^{-1}; M_w = 105,500 g mol^{-1}; Đ = 1.15 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.4. Synthesis of PSD-4

Poly(styrene-*co*-DPE) with a target molecular weight of 35,600 g mol^{-1}, was prepared by the procedure described above except that 70 ml of benzene, 2.23 g styrene (21 mmol), 5.97 g DPE (33 mmol) and 0.13 ml of 1.4 M BuLi (0.18 mmol) were used and the reaction was stirred at room temperature for 4 days before a sample was extracted and terminated.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.0 – 2.5 (5H –C$\mathbf{H_2}$CPh**H**-C$\mathbf{H_2}$CPh$_2$), 4.8 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C$\mathbf{Ph_2}$).

M_n = 40,100 g mol^{-1}; M_w = 43,800 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.196).

The remaining reaction mixture was used in the synthesis of P(SD)-PBd-3 (below).

5.3.5. Synthesis of PSD-5

Poly(styrene-*co*-DPE) with a target molecular weight of 1,500 g mol^{-1}, was prepared by the procedure described above except that 50 ml of benzene, 1.94 g styrene (19 mmol), 3.46 g DPE (19 mmol) and 2.5 ml of 1.4 M BuLi (3.5 mmol) were used and the reaction was stirred at 50 °C for 20.5 hours before a sample was extracted and terminated.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C$\mathbf{H_2}$CPh$\mathbf{H}$-C$\mathbf{H_2}$CPh$_2$), 4.8 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C$\mathbf{Ph_2}$).

M_n = 1,900 g mol^{-1}; M_w = 2,100 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn*/*dc* = 0.196).

The remaining reaction mixture was used in the synthesis of P(SD)-PBd-4 (below).

5.3.6. Synthesis of PSD-6

Poly(styrene-*co*-DPE) with a target molecular weight of 1,500 g mol^{-1}, was prepared by the procedure described above except that 65 ml of benzene, 2.22 g styrene (21 mmol), 5.93 g DPE (33 mmol) and 2.9 ml of 1.4 M BuLi (4.1 mmol) were used and the reaction was stirred at 50 °C for 18 hours before a sample was extracted and terminated.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C$\mathbf{H_2}$CPh$\mathbf{H}$-C$\mathbf{H_2}$CPh$_2$), 4.8 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C$\mathbf{Ph_2}$).

M_n = 1,900 g mol^{-1}; M_w = 2,100 g mol^{-1}; Đ = 1.11 (triple detection SEC with *dn*/*dc* = 0.196).

The remaining reaction mixture was used in the synthesis of P(SD)-PBd-5 (below).

5.3.7. Synthesis of PSD-7

Poly(styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that toluene (50 ml) was used as the solvent; 2.00 g styrene (19 mmol), 3.65 g DPE (20 mmol) and 0.078 ml of 1.4 M BuLi (0.11 mmol) were used and the reaction was stirred at 25 °C for 6.2 days before being terminated with degassed methanol.

Yield = 75 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 4.8 – 7.4 (15H – CH₂C**Ph**H-CH₂C**Ph₂**).

M$_n$ = 57,200 g mol^{-1}; *M*$_w$ = 62,300 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.8. Synthesis of PSD-8

Poly(styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that 55 ml of toluene, 1.72 g styrene (17 mmol), 4.70 g DPE (26 mmol) and 0.065 ml of 1.4 BuLi (0.091 mmol) were used and the reaction was stirred at 25 °C for 5.5 days before being terminated with degassed methanol.

Yield = 71 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 4.8 – 7.4 (15H – CH₂C**Ph**H-CH₂C**Ph₂**).

M$_n$ = 71,600 g mol^{-1}; *M*$_w$ = 84,900 g mol^{-1}; Đ = 1.19 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.9. Synthesis of PSD-9

Poly(styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that THF (60 ml) was used as the solvent; 2.51 g styrene (24 mmol), 4.57 g DPE (25 mmol) and 0.098 ml of 1.4 M BuLi (0.14 mmol) were used and the reaction was stirred at 0 °C for 16.5 hours before being terminated with degassed methanol.

Yield = 88 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 4.8 – 7.4 (15H – CH₂C**Ph**H-CH₂C**Ph₂**).

M$_n$ = 60,000 g mol^{-1}; *M*$_w$ = 66,000 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.10. Synthesis of PSD-10

Poly(styrene-*co*-DPE) with a target molecular weight of 1,500 g mol^{-1}, was prepared by the procedure described above except that 25 ml of THF, 2.37 g styrene (23 mmol), 4.32 g DPE (24 mmol) and 3.1 ml of 1.4 M BuLi (2.2 mmol) were used and the reaction was stirred at 0 °C for 16.5 hours before being terminated with degassed methanol.

Yield = 93 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.5 (5H –$C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$), 4.8 – 7.4 (15H –$CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

M_n = 1,800 g mol^{-1}; M_w = 2,200 g mol^{-1}; Đ = 1.24 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.11. Synthesis of PSD-11

Poly(styrene-*co*-DPE) with a target molecular weight of 1,500 g mol^{-1}, was prepared by the procedure described above except that toluene (20 ml) was used as the solvent, TMEDA (1.17 ml, 7.83 mmol) was used as an additive and 2.15 g styrene (21 mmol), 3.94 g DPE (22 mmol) and 2.8 ml of 1.4 M BuLi (3.9 mmol) were used and the reaction was stirred at room temperature (22 °C) for 25 hours before being terminated with degassed methanol.

Yield = 94 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = -0.1 – 2.7 (5H –$C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$), 5.0 – 7.5 (15H –$CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

M_n = 1,900 g mol^{-1}; M_w = 2,100 g mol^{-1}; Đ = 1.11 (triple detection SEC with *dn*/*dc* = 0.196).

5.3.12. Synthesis of PSD-12

Poly(styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that 50 ml of toluene, TMEDA (0.044 ml, 0.29 mmol), 2.45 g styrene (24 mmol), 4.24 g DPE (24 mmol) and 0.104 ml of 1.4 M BuLi (0.15 mmol) were used and the reaction was stirred at room temperature (22 °C) for 25 hours before being terminated with degassed methanol.

Yield = 10 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = -0.1 – 2.6 (5H –$C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$), 4.9 – 7.5 (15H –$CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

5.3.13. Synthesis of Poly(Butadiene-*co*-1,1-Diphenylethylene) – PBdD-1

The synthesis of poly(butadiene-*co*-DPE) was typically carried out as follows: THF (60 ml) and butadiene (1.89 g, 35 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (6.07 g, 34 mmol) was injected *via* a rubber septum. The solution was cooled to 0 °C with an ice bath and for a target molecular weight of 50,000 g mol^{-1}, *sec*-butyllithium (0.11 ml of 1.4 M solution, 0.16 mmol) was added by injection *via* a rubber septum, resulting in the red colour indicative of a mixture of diphenylethyl lithium and butadienyl lithium. The solution was stirred at 0 °C for 4 days after which time the reaction was terminated by the injection of nitrogen sparged methanol. The red colour of the living polymer solution dissipated instantly. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*.

Yield > 70%.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 1.0 – 2.9 (2H –C$\mathbf{H_2}$CPh_2); (3H –C$\mathbf{H_2}$C**H**CH=CH_2) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$), 3.7 – 5.7 (3H – CH_2CHC**H**=C$\mathbf{H_2}$) and (2H –CH_2C**H**=C**H**CH_2), 6.5 – 7.4 (10H –CH_2C$\mathbf{Ph_2}$).

M_n = 40,600 g mol^{-1}; M_w = 43,400 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.189).

5.3.14. Synthesis of PBdD-2

Poly(butadiene-*co*-DPE) with a target molecular weight of 1,100 g mol^{-1} was prepared by the procedure described above except that 50 ml of THF, 1.30 g butadiene (24 mmol), 4.46 g DPE (25 mmol) and 3.6 ml of 1.4 M BuLi (5.0 mmol) were used and the reaction was stirred at 0 °C for 3 days before being terminated with degassed methanol.

Yield > 50 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 1.0 – 2.9 (2H –C$\mathbf{H_2}$CPh_2); (3H –C$\mathbf{H_2}$C**H**CH=CH_2) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$), 3.7 – 5.7 (3H – CH_2CHC**H**=C$\mathbf{H_2}$) and (2H –CH_2C**H**=C**H**CH_2), 6.5 – 7.4 (10H –CH_2C$\mathbf{Ph_2}$).

M_n = 2,100 g mol^{-1}; M_w = 2,300 g mol^{-1}; Đ = 1.11 (triple detection SEC with *dn*/*dc* = 0.189).

5.3.15. Synthesis of PBdD-3a and 3b

Poly(butadiene-*co*-DPE) with a target molecular weight of 1,500 g mol^{-1} was prepared by the procedure described above except that benzene (40 ml) was used as the solvent; 3.96 g butadiene (73 mmol), 4.05 g DPE (22 mol) and 2.0 ml of 1.3 M BuLi (2.6 mmol) were used. Upon initiation the reaction mixture became a yellow colour which faded to a pale yellow colour within one minute. The reaction was stirred at room temperature and sampled after 2 hours to yield PBdD-3a. Between 17 and 19 hours the reaction mixture darkened to the same yellow colour as seen upon first initiating the reaction. The remaining reaction mixture was stirred at room temperature for a further 40 minutes before being terminated with degassed methanol to yield PBdD-3b.

PBdD-3a and 3b ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (2H –$C\mathbf{H_2}CPh_2$); (3H – $C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 5.2 – 5.5 (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}{=}CH_2$), 7.0 – 7.4 (10H –$CH_2C\mathbf{Ph_2}$).

PBdD-3b Yield = 38 %.

M_n = 1,400 g mol^{-1}; M_w = 1,500 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn/dc* = 0.185).

5.3.16. Synthesis of PBdD-4a and 4b

Poly(butadiene-*co*-DPE) with a target molecular weight of 58,400 g mol^{-1} was prepared by the procedure described above except that toluene (20 ml) was initially used as the solvent; 0.92 g butadiene (17 mmol), 2.92 g DPE (16 mmol) and 50 µL of 1.3 M BuLi (0.065 mmol) were used. Upon initiation the reaction mixture became a pale yellow colour indicative of propagating butadienyl anions. After stirring at room temperature for 2.5 hours the reaction mixture was sampled to yield PBdD-4a, cooled to 0 °C and dry THF (20 ml) was added by distillation into a side flask and decanted into the main reaction flask. Upon addition of THF the colour of the reaction mixture became pale orange but after 16 hours of stirring at 0 °C the reaction mixture colour faded to pale yellow and then to colourless after a further 24 hours. The reaction was stirred at 0 °C for a further 5 hours before being terminated with degassed methanol to yield PBdD-4b. No polymer was obtained for sample PBdD-4a.

PBdD-4b Yield = 16 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.5 – 2.9 (2H –C**H₂**CPh_2); (3H –C**H₂**C**H**CH=CH_2) and (4H –C**H₂**CH=CHC**H₂**), 3.8 – 5.6 (3H – CH_2CHC**H**=C**H₂**) and (2H –CH_2C**H**=C**H**CH_2), 6.5 – 7.5 (10H –CH_2C**Ph₂**).

M_n = 103,000 g mol^{-1}; M_w = 275,300 g mol^{-1}; Đ = 2.67 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.17. Synthesis of PBdD-5a and 5b

Poly(butadiene-*co*-DPE) with a target molecular weight of 89,200 g mol^{-1} was prepared by the procedure described above except that 46 ml of toluene, 2.24 g butadiene (41 mmol) and 7.75 g DPE (43 mmol) were used and upon addition of 86 µL of 1.3 M *sec*-BuLi (0.11 mmol) no colour change was observed so an additional 50 µL of 1.3 M *sec*-BuLi (0.065 mmol) was added at which point the reaction mixture became a pale yellow colour indicative of propagating butadienyl anions. After stirring at 40 °C for 3.5 hours the reaction mixture was sampled to yield PBdD-5a, cooled to 0 °C and dry THF (50 ml) was added by distillation into a side arm and decanted into the main reaction vessel. Upon addition of THF the colour of the reaction mixture became orange-red but after 16 hours of stirring at 0 °C the reaction mixture colour faded to pale orange and then to pale yellow after a further 24 hours. The reaction was stirred at 0 °C for a further 4 hours before being terminated with degassed methanol to yield PBdD-5b.

PBdD-5a ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh_2); (3H –C**H₂**C**H**CH=CH_2) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH_2CHCH=C**H₂**), 5.1 – 5.5 (2H – CH_2C**H**=C**H**CH_2), 5.5 – 5.7 (1H – CH_2CHC**H**=CH_2), 7.0 – 7.4 (10H –CH_2C**Ph₂**).

M_n = 14,300 g mol^{-1}; M_w = 15,000 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

PBdD-5b Yield = 22 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (2H –C**H₂**CPh_2); (3H –C**H₂**C**H**CH=CH_2) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH_2CHCH=C**H₂**), 5.1 – 5.5 (2H –CH_2C**H**=C**H**CH_2), 5.5 – 5.7 (1H – CH_2CHC**H**=CH_2), 6.8 – 7.4 (10H –CH_2C**Ph₂**).

M_n = 17,200 g mol^{-1}; M_w = 19,100 g mol^{-1}; Đ = 1.11 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.18. Synthesis of PBdD-6a and 6b

Poly(butadiene-*co*-DPE) with a target molecular weight of 89,200 g mol^{-1} was prepared by the procedure described above except that 52 ml of toluene; 2.18 g butadiene (40 mmol), 7.55 g DPE (42 mmol) and 85 µL of 1.3 M BuLi (0.11 mmol) were used. Upon initiation the reaction mixture became a pale yellow colour indicative of propagating butadienyl anions. After stirring at 40 °C for 56 minutes the reaction mixture was sampled to yield PBdD-6a, cooled to 0 °C and dry THF (50 ml) was added by distillation into a side arm and decanted into the main reaction vessel. Upon addition of THF the colour of the reaction mixture became red. The reaction was stirred at 0 °C for a further 48 hours before being terminated with degassed methanol to yield PBdD-6b.

PBdD-6a ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.3 (2H $–C\mathbf{H_2}CPh_2$); (3H $–C\mathbf{H_2}C\mathbf{H}CH=CH_2$) and (4H $–C\mathbf{H_2}CH=CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH=C\mathbf{H_2}$), 5.1 – 5.5 (2H – $CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.5 – 5.7 (1H – $CH_2CHC\mathbf{H}=CH_2$), 7.1 – 7.4 (10H $–CH_2C\mathbf{Ph_2}$).

M_n = 10,600 g mol^{-1}; M_w = 11,400 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

PBdD-6b Yield = 48 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.5 – 2.9 (2H $–C\mathbf{H_2}CPh_2$); (3H $–C\mathbf{H_2}C\mathbf{H}CH=CH_2$) and (4H $–C\mathbf{H_2}CH=CHC\mathbf{H_2}$), 3.8 – 5.7 (3H – $CH_2CHC\mathbf{H}=C\mathbf{H_2}$) and (2H $–CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.3 – 5.5 (2H $–CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.5 – 5.7 (1H – $CH_2CHC\mathbf{H}=CH_2$), 6.6 – 7.4 (10H $–CH_2C\mathbf{Ph_2}$).

M_n = 130,600 g mol^{-1}; M_w = 157,000 g mol^{-1}; Đ = 1.20 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.19. Synthesis of PBdD-7a and 7b

Poly(butadiene-*co*-DPE) with a target molecular weight of 50,700 g mol^{-1} was prepared by the procedure described above except that THF (75 ml) was used as the solvent; 3.60 g butadiene (67 mmol), 4.21 g DPE (23 mmol) and 0.11 ml of 1.4 M BuLi (0.15 mmol) were used. Upon initiation the colour of the reaction mixture became red. The reaction was stirred at 0 °C for 1.5 hours before the reaction was sampled to yield PBdD-7a. After stirring at 0 °C for a further 1 hour the reaction mixture colour became purple. The reaction was stirred at 0 °C for a further 21 hours before being terminated with degassed methanol to yield PBdD-7b.

PBdD-7a ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.2 – 2.9 (2H –$C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 3.6 – 5.5 (3H – $CH_2CHC\mathbf{H}{=}C\mathbf{H_2}$) and (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 6.4 – 7.4 (10H –$CH_2C\mathbf{Ph_2}$).

M_n =66,300 g mol^{-1}; M_w = 69,800 g mol^{-1}; Đ = 1.05 (triple detection SEC with dn/dc = 0.185).

PBdD-7b Yield = 93 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.4 – 2.9 (2H –$C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 3.6 – 5.9 (3H – $CH_2CHC\mathbf{H}{=}C\mathbf{H_2}$) and (2H –$CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 6.5 – 7.4 (10H –$CH_2C\mathbf{Ph_2}$).

M_n = 83,300 g mol^{-1}; M_w = 92,000 g mol^{-1}; Đ = 1.10 (triple detection SEC with dn/dc = 0.185).

5.3.20. Synthesis of PBdD-8

Poly(butadiene-*co*-DPE) with a target molecular weight of 51,500 g mol^{-1} was prepared by the procedure described above except that 50 ml of THF; 2.66 g butadiene (49 mmol), 3.10 g DPE (0.17 mmol) and 80 µl of 1.4 M BuLi (0.11 mmol) were used. Upon initiation the reaction mixture colour became red. After stirring at 0 °C for 1 hour the reaction mixture colour became purple. After stirring at 0 °C for a further 1.5 hours the reaction mixture colour reverted back to red. The reaction was stirred at 0 °C for a further 12.5 hours before being terminated with degassed methanol.

Yield = 96 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.4 – 2.9 (2H –$C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 3.6 – 5.9 (3H – $CH_2CHC\mathbf{H}{=}C\mathbf{H_2}$) and (2H –$CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 6.5 – 7.4 (10H –$CH_2C\mathbf{Ph_2}$).

M_n = 71,600 g mol^{-1}; M_w = 76,200 g mol^{-1}; Đ = 1.07 (triple detection SEC with dn/dc = 0.185).

5.3.21. Synthesis of Poly(Styrene-*co*-1,1-Diphenylethylene)-*block*-Polybutadiene - P(SD)-PBd-1

The poly(styrene-*co*-DPE) block was synthesized according to the procedure previously described for the synthesis of PSD-1 (5.3.1), after the reaction was sampled, the solution of living polymer was cooled with a cold water bath and butadiene (5.38 g, 99 mmol) was added by distillation for a target block molecular weight of 8,600 g mol^{-1}. Upon addition of butadiene the red colour indicative of a mixture of diphenylethyl lithium and styryl lithium, dissipated instantly to a pale yellow. The reaction was stirred at room temperature for 22 hours before being terminated by the injection of nitrogen sparged methanol. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*.

Yield = 83 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.2 – 2.4 (5H –C$\mathbf{H_2}$CPh$\mathbf{H}$-C$\mathbf{H_2}$CPh$_2$); (3H – C$\mathbf{H_2}$C$\mathbf{H}$CH=CH$_2$) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$), 4.9 – 5.0 (2H – CH$_2$CHCH=C$\mathbf{H_2}$), 5.1 – 5.5 (2H – CH$_2$C$\mathbf{H}$=C$\mathbf{H}$CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC$\mathbf{H}$=CH$_2$), 5.6 – 7.3 (15H –CH$_2$C$\mathbf{Ph}$H-CH$_2$C$\mathbf{Ph_2}$).

M_n = 16,800 g mol^{-1}; M_w = 17,800 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.22. Synthesis of P(SD)-PBd-2

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 5,500 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that the poly(styrene-*co*-DPE) block was synthesized according to the procedure previously described for the synthesis of PSD-2 (5.3.2); 1.85 g of butadiene (34 mmol) was used and the reaction was stirred at 50 °C. Between 25 and 41 hours of stirring at 50 °C the reaction reverted back to a red colour. The reaction was stirred for a further 6 hours before being terminated with degassed methanol.

Yield = 85 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.0 – 2.5 (5H –C$\mathbf{H_2}$CPh$\mathbf{H}$-C$\mathbf{H_2}$CPh$_2$); (3H – C$\mathbf{H_2}$C$\mathbf{H}$CH=CH$_2$) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$), 4.9 – 5.0 (2H – CH$_2$CHCH=C$\mathbf{H_2}$), 5.1 – 5.5 (2H – CH$_2$C$\mathbf{H}$=C$\mathbf{H}$CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC$\mathbf{H}$=CH$_2$), 5.6 – 7.4 (15H –CH$_2$C$\mathbf{Ph}$H-CH$_2$C$\mathbf{Ph_2}$).

M_n = 16,100 g mol^{-1}; M_w = 17,800 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.23. Synthesis of P(SD)-PBd-3

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 18,800 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that the poly(styrene-*co*-DPE) block was synthesized according to the procedure previously described for the synthesis of PSD-4 (5.3.4); 2.73 g of butadiene (50 mmol) was used and the reaction was stirred at room temperature. After 52 hours of stirring at 50 °C the reaction reverted back to a red colour, at which point the reaction was terminated with degassed methanol.

Yield = 87 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.2 – 2.9 (5H –C**H$_2$**CPh**H**-C**H$_2$**CPh$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.9 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.1 – 5.5 (2H – CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 5.6 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C**Ph$_2$**).

M_n = 66,600 g mol^{-1}; M_w = 71,100 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.24. Synthesis of P(SD)-PBd-4

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 1,700 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that the poly(styrene-*co*-DPE) block was synthesized according to the procedure previously described for the synthesis of PSD-5 (5.3.5); 5.36 g of butadiene (99 mmol) was used and the reaction was stirred at 50 °C for 24.5 hours before being terminated with degassed methanol.

Yield = 89 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.9 (5H –C**H$_2$**CPh**H**-C**H$_2$**CPh$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.9 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.1 – 5.5 (2H – CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 5.6 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C**Ph$_2$**).

M_n = 3,300 g mol^{-1}; M_w = 3,500 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.25. Synthesis of P(SD)-PBd-5

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 1,500 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that the poly(styrene-*co*-DPE) block was synthesized according to the procedure previously described for the synthesis of PSD-6 (5.3.6); 5.09 g of butadiene (94 mmol) was used and the reaction was stirred at 50 °C. After 5 hours of stirring at 50 °C the reaction reverted back to a red colour, at which point the reaction was terminated with degassed methanol.

Yield = 57 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.0 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 3,600 g mol^{-1}; M_w = 4,400 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.26. Synthesis of P(SD)-PBd-6

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 41,000 g mol^{-1} for the poly(styrene-*co*-DPE) block and 113,600 g mol^{-1} for the polybutadiene block was carried out as follows: benzene (300 ml) and styrene (3.74 g, 36 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (10.15 g, 56 mmol) was injected *via* a rubber septum. 50 µl of 1.3 M *sec*-butyllithium (0.065 mmol) was added dropwise until a red colour indicative of a mixture of diphenylethyl lithium and styryl lithium persisted at which point a final addition of 0.19 ml of 1.3 M BuLi solution (0.25 mmol) was added by injection *via* a rubber septum. The solution was stirred at 25 °C for 41 hours before 22.80 g of butadiene (0.422 mol) was added by distillation using a cold water bath and the red colour dissipated to a pale yellow colour. After 50 hours of stirring at 25 °C the reaction had reverted back to a red colour, at which point the reaction was terminated by the injection of nitrogen sparged methanol. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*. 8.37 g of crude poly(styrene-*co*-DPE)-*b*-polybutadiene was retained for analysis and 21.33 g was further purified by fractionation using a toluene/methanol solvent/non-solvent system.

Yield = 90 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 97,900 g mol^{-1}; M_w = 102,000 g mol^{-1}; Đ = 1.04 (triple detection SEC with *dn*/*dc* = 0.185).

Fractionated M_n = 106,200, M_w = 109,300, Đ = 1.03 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.27. Synthesis of P(SD)-PBd-7

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 19,400 g mol^{-1} for the poly(styrene-*co*-DPE) block and 40,600 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that 3.84 g styrene (37 mmol), 10.49 g DPE (58 mmol), 40 µl of 1.4 M BuLi (0.056 mmol) to titrate impurities and 0.38 ml of 1.4 M BuLi (0.53 mmol) as initiator were used and the reaction was stirred at 25 °C for 62 hours before 22.50 g of butadiene (0.416 mol) was added by distillation and the reaction stirred at 25 °C for a further 3 days, by which time the reaction had reverted back to a red colour, at which point the reaction was terminated with degassed methanol.

Yield = 90 %.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 49,500 g mol^{-1}; M_w = 53,400 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.28. Synthesis of P(SD)-PBd-8

Poly(styrene-*co*-DPE)-*b*-polybutadiene with a target molecular weight of 39,900 g mol^{-1} for the poly(styrene-*co*-DPE) block and 60,900 g mol^{-1} for the polybutadiene block was prepared by the procedure described above except that 1.29 g styrene (12 mmol), 3.58 g DPE (20 mmol) and 63 µl of 1.4 M BuLi (0.088 mmol) were used and the reaction was stirred at 25 °C for 4.5 days before 5.37 g of butadiene (99 mmol) was added via distillation and the reaction stirred at 25 °C for a further 2 days, by which time the reaction had reverted back to a red colour and the reaction was subsequently terminated with degassed methanol.

Yield = 89 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.9 (5H $–\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H $–\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $–\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 5.6 – 7.4 (15H $–\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).

M_n = 135,500 g mol^{-1}; M_w = 142,200 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.29. Synthesis of Poly(Butadiene-*co*-Styrene-*co*-1,1-Diphenylethylene) - PBdSD-1a to 1d

The synthesis of poly(butadiene-*co*-styrene-*co*-DPE) terpolymer was carried out as follows: benzene (80 ml) and styrene (2.42 g, 23 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (2.80 g, 16 mol) was injected *via* a rubber septum and 6.75 g butadiene (0.12 mol) added by distillation. For a target molecular weight of 18,000 g mol^{-1}, *sec*-butyllithium (BuLi) (0.46 ml of 1.4 M solution, 0.65 mmol) was added by injection *via* a rubber septum, resulting in the pale yellow colour indicative of butadienyl lithium. The solution was stirred at room temperature for 8 hours before a sample was extracted and terminated by the injection of nitrogen sparged methanol to yield PBdSD-1a. The remaining solution was stirred at room temperature for a further 17 hours before a second sample was extracted to yield PBdSD-1b and the remaining solution was heated to 50 °C. The pale yellow colour of the reaction mixture began to darken to a red colour indicative of a mixture of diphenylethyl lithium and styryl lithium over the next 45 minutes when another sample was extracted to yield PBdSD-1c. The reaction was then stirred at 50 °C for a further 22.5 hours before being terminated by the injection of nitrogen sparged methanol to yield PBdSD-1d. The final polymer and polymer samples were recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*.

PBdSD-1a and 1b ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (5H $–\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H $–\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $–\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.2 – 5.5 (2H $–\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 7.0 – 7.4 (15H $–\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).

PBdSD-1a M_n = 13,800 g mol^{-1}; M_w = 14,600 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-1b M_n = 19,300 g mol^{-1}; M_w = 20,400 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-1c ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.2 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 6.2 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 22,600 g mol^{-1}; M_w = 23,800 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-1d Yield = 78 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 36,900 g mol^{-1}; M_w = 39,100 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.30. Synthesis of PBdSD-2a to 2c

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 10,000 g mol^{-1} was prepared by the procedure described above except that 70 ml benzene, 2.18 g styrene (21 mmol), 2.18 g DPE (12 mmol), 3.71 g butadiene (68 mmol) and 0.58 ml of 1.4 M BuLi (0.81 mmol) were used and the reaction was stirred at 50 °C for 1.5 hours before the pale yellow colour of the reaction mixture began to darken when a sample was extracted to yield PBdSD-2a. After stirring at 50 °C for a further 30 minutes the colour of the reaction mixture had become red and another sample was extracted to yield PBdSD-2b. The reaction was stirred at 50 °C for a further 21 hours before being terminated with degassed methanol to yield PBdSD-2c).

PBdSD-2a ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.7 – 3.0 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.8 – 5.1 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.7 (1H – CH₂CHC**H**=CH₂), 6.9 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 5,100 g mol^{-1}; M_w = 5,300 g mol^{-1}; Đ = 1.04 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-2b ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.6 – 3.1 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.8 – 5.1 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.8 (1H – CH₂CHC**H**=CH₂), 6.3 – 7.5 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 6,400 g mol^{-1}; M_w = 7,000 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-2c Yield = 76 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.3 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 11,100 g mol^{-1}; M_w = 11,800 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.31. Synthesis of PBdSD-3a to 3e

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 5,500 g mol^{-1} was prepared by the procedure described above except that 200 ml benzene, 4.91 g styrene (47 mmol), 13.15 g DPE (73 mmol), 5.08 g butadiene (94 mmol) and 2.6 ml of 1.3 M BuLi (3.6 mmol) were used and the reaction was stirred at room temperature. Samples were extracted for analysis after 35 minutes, 75 minutes, 7.5 hours and 11.5 hours. The first and second samples were extracted when the colour of the reaction mixture was pale yellow (PBdSD-3a and PBdSD-3b respectively); the third sample was extracted when the pale yellow colour of the reaction mixture had just begun to darken (PBdSD-3c) and the forth sample was taken when the reaction mixture was a more intense yellow colour (PBdSD-3d). Between 11.5 and 16 hours the reaction mixture darkened to a red colour. The remaining reaction mixture was stirred at room temperature for a further 26 hours before being terminated with degassed methanol to yield PBdSD-3e. No polymer was obtained for sample PBdSD-3a.

PBdSD-3b to 3d ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.5 – 2.9 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.2 – 5.5 (2H –CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 7.0 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

PBdSD-3c M_n = 1,300 g mol^{-1}; M_w = 1,400 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-3d M_n = 1,500 g mol^{-1}; M_w = 1,700 g mol^{-1}; Đ = 1.12 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-3e Yield = 54 %.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.0 – 3.0 (5H –C**H$_2$**CPh**H**-C**H$_2$**CPh$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.7 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.1 – 5.5 (2H – CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 5.6 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C**Ph$_2$**).
M_n = 4,900 g mol^{-1}; M_w = 5,400 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn/dc* = 0.185).

5.3.32. Synthesis of PBdSD-4a to 4d

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 54,900 g mol^{-1} was prepared by the procedure described above except that 150 ml benzene, 3.62 g styrene (35 mmol), 9.69 g DPE (54 mmol), 5.10 g butadiene (94 mmol) and 0.21 ml of 1.3 M BuLi (0.27 mmol) were used and the reaction was stirred at room temperature and samples extracted after 4 hours, 23 hours and 26 hours. Samples 1 and 2 were extracted when the colour of the reaction mixture was pale yellow to yield PBdSD-4a and PBdSD-4b and sample 3 was extracted when the colour of the reaction mixture was dark yellow to yield PBdSD-4c. The remaining reaction mixture continued to darken and after a further 4 hours was a red colour. The reaction was stirred at room temperature for a further 3.5 days before being terminated with degassed methanol to yield PBdSD-4d.

PBdSD-4a and 4b ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (5H –C**H$_2$**CPh**H**-C**H$_2$**CPh$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.9 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.2 – 5.5 (2H –CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 7.0 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C**Ph$_2$**).

PBdSD-4a M_n = 8,700 g mol^{-1}; M_w = 9,300 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn/dc* = 0.185).

PBdSD-4b M_n = 22,200 g mol^{-1}; M_w = 23,000 g mol^{-1}; Đ = 1.04 (triple detection SEC with *dn/dc* = 0.185).

PBdSD-4c ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.8 – 2.9 (5H –C**H$_2$**CPh**H**-C**H$_2$**CPh$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.9 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.2 – 5.5 (2H – CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 6.9 – 7.4 (15H –CH$_2$C**Ph**H-CH$_2$C**Ph$_2$**).
M_n = 23,600 g mol^{-1}; M_w = 24,400 g mol^{-1}; Đ = 1.04 (triple detection SEC with *dn/dc* = 0.185).

PBdSD-4d Yield = 77 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.3 – 3.0 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H – $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 5.6 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H}\text{-}\mathrm{CH_2C}\mathbf{Ph_2}$).

M_n = 58,500 g mol^{-1}; M_w = 62,700 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.33. Synthesis of PBdSD-5

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 100,000 g mol^{-1} was prepared by the procedure described above except that 300 ml benzene, 3.85 g styrene (37 mmol), 10.25 g DPE (57 mmol), 21.91 g butadiene (0.405 mol) and 0.25 ml of 1.3 M BuLi (0.33 mmol) were used and the reaction was stirred at 25 °C. Between 2 and 3.5 days the reaction mixture darkened from a pale yellow colour to a red colour. The reaction was stirred at 25 °C for a further 2 days before being terminated with degassed methanol.

Yield = 86 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.8 – 2.9 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H – $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 5.6 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H}\text{-}\mathrm{CH_2C}\mathbf{Ph_2}$).

M_n = 111,900 g mol^{-1}; M_w = 119,600 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.34. Synthesis of PBdSD-6

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 60,000 g mol^{-1} was prepared by the procedure described above except that 3.53 g styrene (34 mmol), 9.45 g DPE (52 mmol), 20.14 g butadiene (0.372 mol) and 0.38 ml of 1.3 M BuLi (0.49 mmol) were used and the reaction was stirred at 25 °C. Between 22 and 38 hours the reaction darkened from a pale yellow colour to a red colour. The reaction was stirred at 25 °C for a further 48.5 hours before being terminated with degassed methanol.

Yield = 85 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.8 – 3.0 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H – $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 5.6 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H}\text{-}\mathrm{CH_2C}\mathbf{Ph_2}$).

M_n = 50,700 g mol^{-1}; M_w = 53,100 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.35. Synthesis of PBdSD-7

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 100,000 g mol^{-1} was prepared by the procedure described above except that 130 ml benzene, 1.64 g styrene (16 mmol), 4.54 g DPE (25 mmol), 8.55 g butadiene (0.16 mol) and 93 µl of 1.4 M BuLi (0.13 mmol) were used and the reaction was stirred at 25 °C. Between 48 and 64.5 hours the reaction darkened from a pale yellow colour to a red colour. The reaction was stirred at 25 °C for a further 3 days before being terminated with degassed methanol.

Yield = 87 %.

^{1}H NMR (700 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.8 – 2.9 (5H –$\mathrm{C\mathbf{H_2}CPh\mathbf{H}\text{-}C\mathbf{H_2}CPh_2}$); (3H –$\mathrm{C\mathbf{H_2}C\mathbf{H}CH{=}CH_2}$) and (4H –$\mathrm{C\mathbf{H_2}CH{=}CHC\mathbf{H_2}}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C\mathbf{H_2}}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C\mathbf{H}{=}C\mathbf{H}CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC\mathbf{H}{=}CH_2}$), 5.6 – 7.4 (15H –$\mathrm{CH_2C\mathbf{Ph}H\text{-}CH_2C\mathbf{Ph_2}}$).

M_n = 96,900 g mol^{-1}; M_w = 99,500 g mol^{-1}; Đ = 1.03 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.36. Synthesis of PBdSD-8

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 100,000 g mol^{-1} was prepared by the procedure described above except that 100 ml benzene, 1.39 g styrene (13 mmol), 3.61 g DPE (20 mmol), 5.55 g butadiene (0.10 mol) and 67 µl of 1.4 M BuLi (0.094 mmol) were used and the reaction was stirred at 25 °C. Between 22.5 and 38.5 hours the reaction darkened from a pale yellow colour to a red colour. The reaction was stirred at 25 °C for a further 6 days before being terminated with degassed methanol.

Yield = 87 %.

^{1}H NMR (700 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.3 – 2.9 (5H –$\mathrm{C\mathbf{H_2}CPh\mathbf{H}\text{-}C\mathbf{H_2}CPh_2}$); (3H –$\mathrm{C\mathbf{H_2}C\mathbf{H}CH{=}CH_2}$) and (4H –$\mathrm{C\mathbf{H_2}CH{=}CHC\mathbf{H_2}}$), 4.8 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C\mathbf{H_2}}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C\mathbf{H}{=}C\mathbf{H}CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC\mathbf{H}{=}CH_2}$), 5.6 – 7.4 (15H –$\mathrm{CH_2C\mathbf{Ph}H\text{-}CH_2C\mathbf{Ph_2}}$).

M_n = 117,100 g mol^{-1}; M_w = 122,500 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.37. Synthesis of PBdSD-9

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that toluene (80 ml) was used as the solvent; 2.47 g styrene (24 mmol), 4.51 g DPE (25 mmol), 2.18 g butadiene (40 mmol) and 0.13 ml of 1.4 M BuLi (0.18 mmol) were used and the reaction was stirred at room temperature. Between 14 and 25 hours the reaction mixture darkened from a pale yellow colour to a red colour. The reaction was stirred at room temperature for a further 26 hours before being terminated with degassed methanol.

Yield = 65 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.3 – 3.0 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.8 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 48,700 g mol^{-1}; M_w = 51,100 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.38. Synthesis of PBdSD-10a to 10e

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 60,000 g mol^{-1}, was prepared by the procedure described above except that THF (190 ml) was used as the solvent; 3.55 g styrene (34 mmol), 12.68 g DPE (70 mmol), 1.84 g butadiene (34 mmol) and 0.20 ml of 1.4 M BuLi (0.28 mmol) were used and the reaction was stirred at 0 °C and samples extracted after 1 hour, 4 hours, 8 hours and 22 hours to yield PBdSD-10a, PBdSD-10b, PBdSD-10c and PBdSD-10d respectively. The reaction mixture remained red throughout and was stirred at 0 °C for a further 4 days before being terminated with degassed methanol to yield PBdSD-10-e.

PBdSD-10a to 10e ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.5 (2H –C**H₂**CPh₂); (3H – C**H₂**CPh**H**); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 3.3 – 6.1 (3H – CH₂CHC**H**=C**H₂**) and (2H –CH₂C**H**=C**H**CH₂), 6.1 – 7.4 (10H –CH₂C**Ph**H) and (5H –CH₂C**Ph₂**).

PBdSD-10a M_n = 14,300 g mol^{-1}; M_w = 16,400 g mol^{-1}; Đ = 1.15 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-10b M_n = 44,100 g mol^{-1}; M_w = 47,000 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-10c M_n = 60,500 g mol^{-1}; M_w = 64,800 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-10d M_n = 67,700 g mol^{-1}; M_w = 73,400 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-10e Yield = 93 %.

M_n = 67,700 g mol^{-1}; M_w = 74,000 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.39. Synthesis of PBdSD-11

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 73,000 g mol^{-1} was prepared by the procedure described above except that 160 ml THF, 3.20 g styrene (31 mmol), 11.12 g DPE (62 mmol), 1.53 g butadiene (28 mmol) and 0.15 ml of 1.4 M BuLi (0.21 mmol) were used and the reaction was stirred at 0 °C for 3 days before being terminated with degassed methanol.

Yield = 96 %.

^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.3 – 2.8 (2H –C**H$_2$**CPh$_2$); (3H –C**H$_2$**CPh**H**); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 3.3 – 6.0 (3H – CH$_2$CHC**H**=C**H$_2$**) and (2H – CH$_2$C**H**=C**H**CH$_2$), 6.0 – 7.4 (10H –CH$_2$C**Ph**H) and (5H –CH$_2$C**Ph$_2$**).

M_n = 106,400 g mol^{-1}; M_w = 112,400 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.40. Synthesis of PBdSD-12a and 12b

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1} was prepared by the procedure described above except that 135 ml THF, 4.16 g styrene (40 mmol), 7.67 g DPE (43 mmol), 2.20 g butadiene (41 mmol) and 0.23 ml of 1.4 M BuLi (0.32 mmol) were used and the reaction was stirred at 0 °C and sampled after 24 hours to yield PBdSD-12a. The reaction mixture remained red throughout and was stirred at 0 °C for a further 3 days before being terminated with degassed methanol to yield PBdSD-12b.

PBdSD-12a and 12b ^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.2 – 2.7 (2H –C**H$_2$**CPh$_2$); (3H – C**H$_2$**CPh**H**); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 3.3 – 5.9 (3H – CH$_2$CHC**H**=C**H$_2$**) and (2H –CH$_2$C**H**=C**H**CH$_2$), 5.9 – 7.4 (10H –CH$_2$C**Ph**H) and (5H –CH$_2$C**Ph$_2$**).

PBdSD-12a M_n = 56,900 g mol^{-1}; M_w = 60,300 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-12b Yield = 90 %.

M_n = 57,000 g mol^{-1}; M_w = 61,100 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.41. Synthesis of PBdSD-13a to 13e

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that 150 ml THF, 4.34 g styrene (42 mmol), 7.90 g DPE (44 mmol), 2.57 g butadiene (48 mmol) and 0.21 ml of 1.4 M BuLi (0.29 mmol) were used and the reaction was stirred at 0 °C and samples extracted after 30 minutes, 45 minutes, 1 hour and 2 hours to yield PBdSD-13a, PBdSD-13b, PBdSD-13c and PBdSD-13d respectively. The colour of the reaction mixture remained red throughout and was stirred at 0 °C for a further 17.5 hours before being terminated with degassed methanol to yield PBdSD-13e.

PBdSD-13a to 13e ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.7 (2H –$C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}CPh\mathbf{H}$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 3.3 – 5.8 (3H –$CH_2CHC\mathbf{H}{=}C\mathbf{H_2}$) and (2H –$CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.8 – 7.4 (10H –$CH_2C\mathbf{Ph}H$) and (5H –$CH_2C\mathbf{Ph_2}$).

PBdSD-13a M_n = 13,800 g mol^{-1}; M_w = 16,200 g mol^{-1}; Đ = 1.18 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-13b M_n = 20,400 g mol^{-1}; M_w = 23,400 g mol^{-1}; Đ = 1.15 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-13c M_n = 25,300 g mol^{-1}; M_w = 28,500 g mol^{-1}; Đ = 1.13 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-13d M_n = 42,000 g mol^{-1}; M_w = 46,300 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn*/*dc* = 0.185).

PBdSD-13e Yield > 67 %.

M_n = 78,600 g mol^{-1}; M_w = 90,200 g mol^{-1}; Đ = 1.15 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.42. Synthesis of PBdSD-14a to 14d

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 60,000 g mol^{-1}, was prepared by the procedure described above except that 100 ml THF, 1.45 g styrene (14 mmol), 4.88 g DPE (27 mmol), 0.71 g butadiene (0.13 mmol) and 84 µl of 1.4 M BuLi (0.12 mmol) were used and the reaction was stirred at -78 °C. The colour of the reaction mixture faded from red to colourless after 2 hours and the reaction was reinitiated with a further 84 µl of 1.4 M BuLi. A sample was extracted 2, 4 and 22 hours after re-initiation to yield PBdSD-14a; PBdSD-14b and PBdSD-14c. The remaining red reaction mixture was stirred at -78 °C for a further 10 days before being terminated with degassed methanol to yield PBdSD-14d. No polymer was obtained for samples PBdSD-14a to 14c.

PBdSD-14d Yield = 17 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.6 (2H –C$\mathbf{H_2}$CPh$_2$); (3H –C$\mathbf{H_2}$CPh**H**); (3H –C$\mathbf{H_2}$**CH**CH=CH$_2$) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$), 3.3 – 5.9 (3H – CH$_2$CHC**H**=C$\mathbf{H_2}$) and (2H – CH$_2$C**H**=C**H**CH$_2$), 5.9 – 7.6 (10H –CH$_2$C**Ph**H) and (5H –CH$_2$C$\mathbf{Ph_2}$).

M_n = 8,200 g mol^{-1}; M_w = 10,700 g mol^{-1}; Đ = 1.31 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.43. Synthesis of PBdSD-15

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that toluene (70 ml) was used as the solvent; 2.15 g styrene (21 mmol), 3.80 g DPE (21 mmol), 2.03 g butadiene (38 mmol) and 0.11 ml of 1.4 M BuLi (0.15 mmol) were used and the reaction was stirred at room temperature (~18 °C). Upon initiation the colour of the reaction mixture became pale yellow. After 24.5 hours the colour of the reaction mixture began to slightly darken, at which point 48 µL of TMEDA (0.32 mmol) was added. The colour of the reaction mixture instantly darkened to red. The reaction was stirred at room temperature for a further 62.5 hours before being terminated with degassed methanol.

Yield = 34 %.

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.4 – 2.9 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H – $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.8 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}{=}\mathrm{C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}{=}\mathrm{CH_2}$), 5.6 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).
M_n = 22,700 g mol^{-1}; M_w = 24,800 g mol^{-1}; Đ = 1.09 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.44. Synthesis of PBdSD-16

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that 94 ml of toluene, 3.04 g styrene (29 mmol), 5.56 g DPE (31 mmol), 2.52 g butadiene (47 mmol) and 0.15 ml of 1.4 M BuLi (0.21 mmol) were used. Upon initiation the reaction colour became pale yellow. After stirring at room temperature for 24 hours the colour of the reaction mixture had become dark yellow, at which point 65 µL of TMEDA (0.43 mmol) was added. The colour of the reaction mixture instantly darkened to red. The reaction was stirred at room temperature for a further 67 hours before being terminated with degassed methanol.
Yield = 39 %.
^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ = 0.3 – 3.0 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H – $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.8 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H – $\mathrm{CH_2C}\mathbf{H}{=}\mathrm{C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.7 (1H – $\mathrm{CH_2CHC}\mathbf{H}{=}\mathrm{CH_2}$), 5.7 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).
M_n = 19,500 g mol^{-1}; M_w = 20,400 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.45. Synthesis of PBdSD-17

Poly(butadiene-*co*-styrene-*co*-DPE) with a target molecular weight of 50,000 g mol^{-1}, was prepared by the procedure described above except that 70 ml of toluene, 1.98 g styrene (19 mmol), 3.43 g DPE (19 mmol), 1.92 g butadiene (35 mmol) and 0.11 ml of 1.4 M BuLi (0.15 mmol) were used. Upon initiation the colour of the reaction mixture became pale yellow. After stirring at room temperature (~20 °C) for 22 hours the colour of the reaction mixture became red, at which point 44 µL of TMEDA (0.29 mmol) was added. The reaction was stirred at room temperature for a further 4 days before being terminated with degassed methanol.

Yield = 43 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.4 – 3.0 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H – C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.8 – 5.0 (2H – CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H – CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 32,900 g mol^{-1}; M_w = 35,100 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.46. Synthesis of 1,2-Polybutadiene with a high 1,2 enchainment – PBd-1

The synthesis of high 1,2-polybutadiene was carried out as follows: THF (300 ml) and butadiene (32.7 g, 0.605 mol) were distilled, under vacuum, into the reaction apparatus. The solution was cooled to 0 °C, and for a target molecular weight of 2,000 g mol^{-1}, *sec*-butyllithium (11.7 ml of 1.4 M solution, 16.4 mmol) was added by injection *via* a rubber septum. The solution was stirred at 0 °C overnight, after which time the reaction was terminated by the injection of nitrogen sparged methanol. The polymer was recovered by precipitation into methanol that contained a small amount of antioxidant (BHT), collected, redissolved in THF and reprecipitated into methanol, recovered and dried *in vacuo*.

Yield = 98.1 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.60 – 2.61 (3H –C**H₂**C**H**(CH=CH₂)), 4.80 – 5.10 (2H – CH₂CH(CH=C**H₂**)), 5.22 – 5.90 (2H – CH₂C**H**=C**H**CH₂)) and (2H – CH₂CH(C**H**=CH₂)).

M_n = 2,100 g mol^{-1}; M_w = 2,300 g mol^{-1}; Đ = 1.07 (triple detection SEC with *dn*/*dc* = 0.109).

1,2-polybutadiene content: 84 % calculated by ^{1}H NMR.

5.3.47. Synthesis of Poly(Styrene-*co*-1,1-Diphenylethylene)-*co*-Polybutadiene-*co*-Poly(Styrene-*co*-1,1-Diphenylethylene) using a Difunctional Initiator – P(BdSD)₂-I

The synthesis of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) was carried out as follows: benzene (400 ml) and styrene (3.39 g, 33 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (9.39 g, 52 mmol) was added by injection into a side flask *via* a rubber septum before decanting into the main reaction flask and 21.82 g butadiene (0.403 mol) was added by distillation. *Sec*-butoxide (2.40 ml of 0.17 M solution, 0.41 mmol) was added by injection *via* a rubber septum into a side vessel and decanted in. For a target molecular weight of 150,000 g mol^{-1}, the dilithium initiator synthesized from 1,3-dibenzoylbenzene (0.67 ml of 0.31 M solution, 0.21 mmol) was added by injection *via* a rubber septum into a side vessel and decanted into the reaction flask. Upon initiation, the red colour of the dilithium initiator could be seen to slowly fade as butadiene began to propagate. The reaction was stirred at 40 °C, and between 48 and 63 hours the reaction mixture darkened from yellow to red and became so viscous that it could no longer be stirred. The reaction was kept at 40 °C for a further 4 days before being terminated with nitrogen sparged methanol. The polymer was recovered by precipitation into methanol that contained a small amount of antioxidant (BHT), collected, redissolved in THF and reprecipitated into methanol, recovered and dried *in vacuo*.

Yield = 87 %.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.1 – 2.6 (5H –$C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 5.1 – 5.5 (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}{=}CH_2$), 5.6 – 7.3 (15H –$CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

M_n = 317,700 g mol^{-1}; M_w = 339,700 g mol^{-1}; Đ = 1.07 (triple detection SEC with dn/dc = 0.185).

5.3.48. Synthesis of Poly(Styrene-*co*-1,1-Diphenylethylene)-*block*-Polybutadiene-*block*-Poly(Styrene-*co*-1,1-Diphenylethylene)

The synthesis of poly(styrene-*co*-DPE)-block-polybutadiene-block-poly(styrene-*co*-DPE) was attempted with various synthetic strategies including sequential addition to a difunctional initiator and by cross-coupling a copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene prepared by sequential addition of butadiene.

5.3.48.1. Synthesis of P(SD)-PBd-P(SD)-1 using a Difunctional Initiator

The attempted synthesis of poly(styrene-*co*-DPE)-*b*-polybutadiene-*b*-poly(styrene-*co*-DPE) was carried out as follows: benzene (400 ml) and butadiene (21.84 g, 0.404 mol) were distilled, under vacuum, into the reaction apparatus. *Sec*-butoxide (1.98 ml of 0.21 M solution, 0.41 mmol) was added by injection *via* a rubber septum into a side vessel and decanted in. For a target molecular weight of 150,000 g mol^{-1}, the dilithium initiator synthesized from 1,3-dibenzoylbenzene (1.15 ml of 0.18 M solution, 0.21

mmol) was added by injection *via* a rubber septum into a side vessel and decanted in. Upon initiation the red colour (caused by the dilithium initiator) could be seen to slowly fade as butadiene began to propagate. The reaction was stirred at room temperature for 3 days before being heated at 40 °C for a further 3 days, at which point a solution of DPE (10.06 g, 56 mmol) and, TMEDA (0.125 ml, 0.83 mmol) was titrated with *n*-butyllithium (12 µL, 2.5 M, 0.030 mmol) and decanted in. Upon addition of the DPE/TMEDA solution the reaction mixture could be seen to become less viscous and the colour changed to red. The reaction mixture was stirred at 40 °C for 25 hours before styrene (3.30 g, 32 mmol) was added by distillation. The mixture was stirred at 40 °C for a further 6 days before being terminated with nitrogen sparged methanol. The resulting polymer was recovered by precipitation into methanol that contained a small amount of antioxidant (BHT), collected, redissolved in THF and reprecipitated into methanol, recovered and dried *in vacuo*.

Yield = 70 %.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.2 – 2.3 (5H $–C\mathbf{H_2}CPh\mathbf{H}\text{-}C\mathbf{H_2}CPh_2$); (3H – $C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H $–C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 5.2 – 5.5 (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}{=}CH_2$), 6.1 – 7.3 (15H $–CH_2C\mathbf{Ph}H\text{-}CH_2C\mathbf{Ph_2}$).

M_n = 200,500 g mol^{-1}; M_w = 216,900 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.48.2. Synthesis of P(SD)-PBd-P(SD)-2 using a Difunctional Initiator

The attempted synthesis of poly(styrene-*co*-DPE)-*b*-polybutadiene-*b*-poly(styrene-*co*-DPE) with a target molecular weight of 150,000 g mol^{-1} was carried out according to the previously described procedure except that 21.02 g butadiene (0.389 mol), 1.59 ml of 0.25 M *sec*-butoxide (0.40 mmol), 1.64 ml of 0.12 M dilithium initiator (0.20 mmol), 3.25 g styrene (31 mmol), 9.04 g DPE (50 mmol), 0.124 ml TMEDA (0.83 mmol) and 14 µL 2.5 M *n*-butyllithium (0.035 mmol) were used and the reaction was stirred at 40 °C for 52 hours before the addition of DPE/TMEDA/*n*-BuLi and for a further 26 hours before the addition of styrene. The reaction was then stirred at 40 °C for 6 days before being terminated with degassed methanol.

Yield = 69 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.5 – 2.3 (5H $-C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$); (3H $-C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H $-C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 5.2 – 5.5 (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}{=}CH_2$), 6.1 – 7.4 (15H $-CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

M_n = 214,200 g mol^{-1}; M_w = 228,000 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.48.3. Synthesis of P(SD)-PBd-P(SD)-3 using a Difunctional Initiator

The attempted synthesis of poly(styrene-*co*-DPE)-*b*-polybutadiene-*b*-poly(styrene-*co*-DPE) with a target molecular weight of 150,000 g mol^{-1} was carried out according to the previously described procedure except that 21.68 g butadiene (0.401 mol), 1.64 ml of 0.25 M *sec*-butoxide (0.41 mmol), 1.69 ml of 0.12 M dilithium initiator (0.20 mmol), 3.37 g styrene (32 mmol) and 9.33 g DPE (52 mmol) were used. In this case TMEDA was not added into the reaction. The reaction mixture was stirred at 40 °C for 4 days before the addition of a mixture of DPE and styrene which had been purified by 14 µL 2.5 M *n*-butyllithium (0.035 mmol). Upon addition of the styrene/DPE/*n*-Buli mixture the colour of the reaction mixture could be seen to slowly turn red over the next 30 minutes. The reaction mixture was then stirred at 40 °C for 6 days before being terminated with degassed methanol.

Yield = 96 %.

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.3 (5H $-C\mathbf{H_2}CPh\mathbf{H}$-$C\mathbf{H_2}CPh_2$); (3H $-C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H $-C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH{=}C\mathbf{H_2}$), 5.1 – 5.5 (2H – $CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}{=}CH_2$), 5.6 – 7.4 (15H $-CH_2C\mathbf{Ph}H$-$CH_2C\mathbf{Ph_2}$).

M_n = 371,000 g mol^{-1}; M_w = 595,600 g mol^{-1}; Đ = 1.61 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.48.4. Synthesis of P(SD)-PBd-P(SD)-4a to 4c using a Coupling Reagent

The attempted synthesis of poly(styrene-*co*-DPE)-*b*-polybutadiene-*b*-poly(styrene-*co*-DPE) with a target molecular weight of 400,000 g mol^{-1} was carried out as follows: benzene (325 ml) and styrene (3.41 g, 33 mmol) were distilled, under vacuum, into the reaction flask. DPE (9.44 g, 52 mmol) was added by injection into a side flask *via* a rubber septum and initiated with 0.11 ml of 1.4 M *sec*-butyllithium (0.15 mmol) before being decanted into the reaction flask. The reaction was heated at 40 °C for 3.5 days before a sample was extracted and butadiene (22.06 g, 0.408 mol) added by distillation. The reaction was reheated to 40 °C, after 1 hour the reaction mixture had faded to a pale yellow colour. Between 7 and 23 hours the reaction mixture reverted back to a red colour, the reaction was stirred at 40 °C for 1 hour before a sample was extracted for analysis. Dichlorodimethyl silane (8.7 µL, 0.072 mmol) was then added by distillation. The reaction mixture was stirred at 50 °C for 24 hours at which point the reaction mixture had faded to a pale orange colour at which point the reaction was terminated with nitrogen sparged methanol. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*.

P(SD)-PBd-P(SD)-4a ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.2 – 2.5 (5H –C**H₂**CPh**H**-C**H₂**CPh₂), 5.0 – 7.5 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

M_n = 61,300 g mol^{-1}; M_w = 71,700 g mol^{-1}; Đ = 1.17 (triple detection SEC with *dn*/*dc* = 0.185).

P(SD)-PBd-P(SD)-4b and 4c ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.3 – 2.3 (5H –C**H₂**CPh**H**-C**H₂**CPh₂); (3H –C**H₂**C**H**CH=CH₂) and (4H –C**H₂**CH=CHC**H₂**), 4.9 – 5.0 (2H –CH₂CHCH=C**H₂**), 5.1 – 5.5 (2H –CH₂C**H**=C**H**CH₂), 5.5 – 5.6 (1H – CH₂CHC**H**=CH₂), 5.6 – 7.4 (15H –CH₂C**Ph**H-CH₂C**Ph₂**).

P(SD)-PBd-P(SD)-4b M_n = 232,800 g mol^{-1}; M_w = 251,300 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn*/*dc* = 0.185).

P(SD)-PBd-P(SD)-4c Yield = 93 %.

M_n = 245,800 g mol^{-1}; M_w = 272,600 g mol^{-1}; Đ = 1.11 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.49. Synthesis of Poly(Methyl Methacrylate-*co*-4-Cyanodiphenylethylene) - P(MMA-*co*-D$_{CN}$)-1

Poly(methyl methacrylate-*co*-4-cyanodiphenylethylene) was synthesized by Karina Bley (in our group) and carried out as follows: lithium chloride (0.32 g, 7.6 mmol) was added into a side flask and evacuated. DPE-CN (0.51 g, 2.5 mmol) was dissolved in dry THF and added by injection into the main reaction vessel. The THF was then removed from the vessel by distillation and approximately 10 ml of dry benzene was added by distillation into the vessel, dissolving the DPE-OSi. The benzene was then removed from the vessel by distillation and replaced with a further 10 ml of dry benzene. This process was repeated twice more to azeotropically dry the DPE-OSi. THF (60 ml) was then distilled, under vacuum, into the reaction apparatus. A solution of lithium chloride in dry THF was decanted into the reaction flask from the side flask. The reaction vessel was raised to atmospheric pressure using dry nitrogen and then cooled to -78 °C using a dry ice/acetone bath. *Sec*-butyllithium was titrated in dropwise until a red colour indicative of diphenylethyl lithium persisted and a final addition of 1.08 ml of 1.4 M BuLi solution (1.5 mmol) was added by injection *via* a rubber septum for a target molecular weight of 2,000 g mol^{-1}. Methyl methacrylate (2.50 g, 25 mmol) was added dropwise by injection *via* a rubber septum. The reaction was stirred at -78 °C and sampled after 19 hours; 24 hours; 45 hours; 3 days and terminated by the injection of nitrogen sparged methanol after 4 days. The polymer sample was recovered by precipitation into hexane and collected by filtration.

Yield = 69 %.

^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 0.5 – 1.3 (3H –$CH_2C(C\mathbf{H_3})CO_2CH_3$); 1.3 – 2.0 (2H –$C\mathbf{H_2}C(CH_3)CO_2CH_3$); 3.5 – 3.7 (3H –$CH_2C(CH_3)CO_2C\mathbf{H_3}$); 7.0 – 7.6 (9H –C**PhAr**).

M_n = 3,200 g mol^{-1}; M_w = 3,300 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.3.50. Synthesis of P(MMA-*co*-D$_{CN}$)-2

Poly(methyl methacrylate-*co*-4-cyanodiphenylethylene) with a target molecular weight of 2,000 g mol^{-1} was synthesized by Karina Bley and prepared by the procedure described above except that 50 ml THF, 1.00 g DPE-CN (4.9 mmol), 0.49 g methyl methacrylate (4.9 mmol) and 0.53 ml of 1.4 M *sec*-BuLi (0.74 mmol) were used. The reaction was stirred at -78 °C and sampled after 10 minutes; 20 minutes; 45 minutes; 1.5 hours and 2 hours. The reaction was stirred for a further hour before being terminated with degassed methanol. The polymer sample was recovered by precipitation into hexane and collected by filtration.

Yield = 60 %.

^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 0.5 – 1.3 (3H –$CH_2C(C\mathbf{H_3})CO_2CH_3$); 1.3 – 2.0 (2H –$C\mathbf{H_2}C(CH_3)CO_2CH_3$); 3.5 – 3.7 (3H –$CH_2C(CH_3)CO_2C\mathbf{H_3}$); 7.0 – 7.6 (9H –C**PhAr**).

M_n = 2,500 g mol^{-1}; M_w = 2,800 g mol^{-1}; Đ = 1.12 (conventional calibration, PS standards).

5.3.51. Synthesis of Poly(Butadiene-*co*-1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)-ethylene) - P(Bd-*co*-D$_{OSi}$)-1

The synthesis of poly(butadiene-*co*-1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene) was assisted by Serkan Sevinc and attempted as follows: THF (20 ml) and butadiene (0.2 g, 3.7 mmol) were distilled, under vacuum, into the reaction apparatus. DPE-OSi (1.63 g, 3.7 mmol) was added to an ampoule sealed with a Youngs tap, degassed and dried azeotropically three times using benzene. THF (5 ml) was added by distillation into the ampoule to dissolve DPE-OSi, and then the ampoule was raised to atmospheric pressure with dry nitrogen. The DPE-OSi/THF solution was then added to the reaction vessel by injection *via* a rubber septum. The reaction mixture was freeze-pump-thawed for further purification. The reaction vessel was cooled to -78 °C using a dry ice/acetone bath and, for a target molecular weight of 1,900 g mol^{-1}, *sec*-butyllithium (0.73 ml of a 1.3 M solution, 0.95 mmol) was added by injection *via* a rubber septum, resulting in a red colour indicative of the presence of living DPE-OSi. The solution was stirred at -78 °C overnight but after 15 hours the colour of the reaction mixture had faded to colourless. The reaction mixture was stirred at -78 °C for a further 48 hours by which point the colour of the reaction mixture had become light orange. The reaction was stirred at -78 °C for a further 2.5 hours before being terminated by the injection of nitrogen sparged methanol. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = -0.2 – 3.0 (12H –OSi(C$\mathbf{H_3}$)$_2$C(CH$_3$)$_3$); (18H –OSi(CH$_3$)$_2$C(C$\mathbf{H_3}$)$_3$); (2H –C$\mathbf{H_2}$CAr$_2$); (3H –C$\mathbf{H_2}$C**H**CH=CH$_2$) and (4H –C$\mathbf{H_2}$CH=CHC$\mathbf{H_2}$); 4.1 – 5.9 (2H – CH$_2$CHCH=C$\mathbf{H_2}$); (2H –CH$_2$C**H**=C**H**CH$_2$) and (1H – CH$_2$CHC**H**=CH$_2$); 6.4 – 7.1 (8H –CH$_2$C$\mathbf{Ar_2}$).

M_n = 570 g mol^{-1}; M_w = 750 g mol^{-1}; Đ = 1.31 (conventional calibration, PS standards).

5.3.52. Synthesis of P(Bd-*co*-D_{OSi})-2a to 2c

The attempted synthesis of poly(butadiene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)-ethylene) with a target molecular weight of 2,500 g mol^{-1} was prepared by the procedure described above except that 1.65 g DPE-OSi (3.7 mmol), 0.2 g butadiene (3.7 mmol) and 0.57 ml of 1.3 M *sec*-butyllithium (0.74 mmol) were used and the reaction kept at 0 °C. Upon the addition of *sec*-butyllithium the colour of the reaction mixture became red but reverted back to colourless within 1 minute. The reaction was stirred at 0 °C for 22 hours before the reaction mixture was split into two portions and a further 0.20 ml of 1.3 M *sec*-butyllithium added by injection into one portion (P(Bd-*co*-D_{OSi})-2a). Upon addition the colour of the reaction mixture became red. Both reaction mixtures were stirred at 0 °C for 20.5 hours before another portion of the main reaction mixture was removed (P(Bd-*co*-D_{OSi})-2b) and 0.27 ml *sec*-butyllithium added to the main reaction mixture (P(Bd-*co*-D_{OSi})-2c). This time the colour of the reaction mixture faded to a light yellow after the initial red colour. All three reaction mixtures were stirred at 0 °C for a further 12 days before being terminated with degassed nitrogen. No polymer was obtained for sample P(Bd-co-D_{OSi})-2b and analysis revealed that it did not polymerize.

P(Bd-*co*-D_{OSi})-2a and 2c ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = -0.2 – 3.0 (12H –$OSi(C\mathbf{H_3})_2C(CH_3)_3$); (18H –$OSi(CH_3)_2C(C\mathbf{H_3})_3$); (2H –$C\mathbf{H_2}CAr_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH{=}CH_2$) and (4H –$C\mathbf{H_2}CH{=}CHC\mathbf{H_2}$); 3.7 – 5.8 (2H – $CH_2CHCH{=}C\mathbf{H_2}$); (2H –$CH_2C\mathbf{H}{=}C\mathbf{H}CH_2$) and (1H – $CH_2CHC\mathbf{H}{=}CH_2$); 6.4 – 7.1 (8H –$CH_2C\mathbf{Ar_2}$).

P(Bd-*co*-D_{OSi})-2a M_n = 480 g mol^{-1}; M_w = 940 g mol^{-1}; Đ = 1.94 (conventional calibration, PS standards).

P(Bd-*co*-D_{OSi})-2c M_n = 490 g mol^{-1}; M_w = 1,020 g mol^{-1}; Đ = 2.08 (conventional calibration, PS standards).

5.3.53. Synthesis of P(Bd-*co*-D_{OSi})-3

The attempted synthesis of poly(butadiene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)-ethylene) with a target molecular weight of 43,700 g mol^{-1} was prepared by the procedure described above except that 20 ml THF, 0.28 g butadiene (5.2 mmol) and 2.28 g DPE-OSi (5.2 mmol) were used. This time *sec*-butyllithium was added by injection into the reaction mixture prior to the addition of butadiene. *Sec*-butyllithium

(35 µL of 1.3 M solution, 0.046 mmol) was titrated into the DPE-OSi/THF mixture until a red colour persisted and a final addition of 25 µL of 1.3 M sec-butyllithium solution (0.033 mmol) was added by injection. Butadiene was then added by distillation into the reaction vessel however within seconds the colour of the reaction mixture changed to a bright blue colour. The reaction was stirred at 0 °C overnight and by 15.5 hours the colour of the reaction mixture had become pale yellow. The reaction was stirred at 0 °C for a further 4 days before the reaction was terminated with degassed nitrogen. However, no polymer was obtained and analysis revealed that the monomers did not polymerize.

5.3.54. Synthesis of P(Bd-*co*-D_{OSi})-4

The attempted synthesis of poly(butadiene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)-ethylene) with a target molecular weight of 100,000 g mol^{-1} was prepared by the procedure described above except that 0.31 g butadiene (5.7 mmol) and 2.31 g DPE-OSi (5.2 mmol) were used. *Sec*-butyllithium (45 µL of 1.3 M solution, 0.056 mmol) was titrated into the DPE-OSi/THF mixture until a red colour persisted and a final addition of 15 µL of 1.3 M sec-butyllithium solution (0.020 mmol) was added by injection. Butadiene was then added by distillation into the reaction vessel however, within seconds the colour of the reaction mixture changed to a bright blue colour. *Sec*-butyllithium (2.45 ml of 1.3 M solution, 3.2 mmol) was again titrated in until a red colour persisted. The reaction was stirred at 0 °C and remained red for 4 days before the reaction was terminated with degassed nitrogen.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = -0.2 – 2.9 (12H –OSi(C**H$_3$**)$_2$C(CH$_3$)$_3$); (18H –OSi(CH$_3$)$_2$C(C**H$_3$**)$_3$); (2H –C**H$_2$**CAr$_2$); (3H –C**H$_2$**C**H**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**); 3.9 – 5.7 (2H – CH$_2$CHCH=C**H$_2$**); (2H –CH$_2$C**H**=C**H**CH$_2$) and (1H – CH$_2$CHC**H**=CH$_2$); 6.5 – 7.1 (8H –CH$_2$C**Ar$_2$**).

M_n = 510 g mol^{-1}; M_w = 940 g mol^{-1}; Đ = 1.82 (conventional calibration, PS standards).

5.3.55. Synthesis of P(Bd-*co*-D_{OSi})-5a to 5c

The synthesis of poly(butadiene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene) was assisted by Serkan Sevinc and carried out as follows: Benzene (40 ml) was distilled, under vacuum, into the reaction apparatus. DPE-OSi (1.43 g, 3.2 mmol) was added to an ampoule sealed with a Youngs tap, degassed and dried azeotropically three times using benzene. Benzene (5 ml) was added by distillation into the ampoule to dissolve DPE-OSi, and then the ampoule was raised to atmospheric pressure with dry nitrogen. The DPE-OSi/benzene solution was then added to the reaction vessel by injection *via* a rubber septum. The reaction mixture was freeze-pump-thawed for further purification. 1.3 M *sec*-butyllithium (0.10 ml, 0.13 mmol) was added dropwise until a red colour persisted and a final addition of 1.35 ml (1.8 mmol) of BuLi was added by injection *via* a rubber septum for a target molecular weight of 2,500 g mol^{-1}. The solution was stirred at room temperature for 1 hour before butadiene (3.24 g, 60 mmol) was added by distillation into the reaction vessel. Upon addition of butadiene the colour of the reaction mixture faded to orange and after being stirred at room temperature overnight for 14.5 hours the colour had become dark yellow. The reaction was stirred at room temperature for a further 3 hours before a sample was extracted (P(Bd-*co*-D$_{OSi}$)-5a) and TMEDA (1.32 ml, 8.8 mmol; 5 mole equivalents with respect to *sec*-butyllithium) added into the reaction vessel. Within minutes of the addition of TMEDA the colour of the reaction mixture became red. The reaction was stirred at room temperature for 24.5 hours before the temperature was increased to 50 °C. The reaction was allowed to stir at 50 °C for a further 27 hours before a second sample was extracted (P(Bd-*co*-D$_{OSi}$)-5b). The reaction was stirred at 50 °C for 5 days before the being terminated with nitrogen sparged methanol. All the solutions were then precipitated into excess methanol that contained a small amount of antioxidant (BHT), collected and dried to constant mass *in vacuo*.

P(Bd-*co*-D$_{OSi}$)-5a to 5c ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 0.1 – 0.2 (12H – OSi(C**H$_3$**)$_2$C(CH$_3$)$_3$); 0.9 – 1.0 (18H –OSi(CH$_3$)$_2$C(C**H$_3$**)$_3$); 0.5 – 2.2 (2H –C**H$_2$**CAr$_2$); (3H – C**H$_2$CH**CH=CH$_2$) and (4H –C**H$_2$**CH=CHC**H$_2$**), 4.9 – 5.0 (2H – CH$_2$CHCH=C**H$_2$**), 5.1 – 5.5 (2H – CH$_2$C**H**=C**H**CH$_2$), 5.5 – 5.6 (1H – CH$_2$CHC**H**=CH$_2$), 6.6 – 7.1 (8H –CH$_2$C**Ar$_2$**).

P(Bd-*co*-D$_{OSi}$)-5a M_n = 2,500 g mol^{-1}; M_w = 2,600 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn/dc* = 0.124).

P(Bd-*co*-D$_{OSi}$)-5b M_n = 2,900 g mol^{-1}; M_w = 3,200 g mol^{-1}; Đ = 1.12 (triple detection SEC with *dn/dc* = 0.124).

P(Bd-*co*-D$_{OSi}$)-5c M_n = 2,900 g mol^{-1}; M_w = 3,200 g mol^{-1}; Đ = 1.10 (triple detection SEC with *dn/dc* = 0.124).

5.3.56. Synthesis of P(Bd-*co*-D_{OSi})-6a to 6c

The synthesis of poly(butadiene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene) with a target molecular weight of 2,600 g mol^{-1} was prepared by the procedure described above except that 50 ml benzene, 2.26 g butadiene (42 mmol), 1.42 g DPE-OSi (3.2 mmol) and 0.92 ml 1.3 M *sec*-butyllithium (1.20 mmol) were used and DPE-OSi and *sec*-butyllithium were allowed to react at room temperature for 24 hours to ensure complete reaction. Butadiene was then added and the reaction mixture was stirred at room temperature. The initial colour of the reaction mixture was red but 15 minutes after the addition of butadiene the colour of the reaction mixture had faded to orange, and by 19 hours had faded to dark yellow. After the reaction had proceeded for 66 hours, the reaction mixture was sampled (P(Bd-*co*-D_{OSi})-6a). The remaining reaction mixture was split into two portions. A small portion was separated into a side arm (P(Bd-*co*-D_{OSi})-6b) and to the remainder was added TMEDA (0.22 ml, 1.47 mmol; 2 mole equivalents with respect to *sec*-butyllithium) (P(Bd-*co*-D_{OSi})-6c). Within minutes of the addition of TMEDA, the reaction mixture had become a red colour. Both portions of living polymer were stirred at room temperature for a further 6.5 days before being terminated with nitrogen sparged methanol. All three samples were then recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected and dried to constant mass *in vacuo*.

P(Bd-*co*-D_{OSi})-6a to 6c ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.1 – 0.2 (12H –$OSi(C\mathbf{H_3})_2C(CH_3)_3$); 0.9 – 1.0 (18H –$OSi(CH_3)_2C(C\mathbf{H_3})_3$); 0.5 – 2.3 (2H –$C\mathbf{H_2}CAr_2$); (3H –$C\mathbf{H_2}\mathbf{CH}CH=CH_2$) and (4H –$C\mathbf{H_2}CH=CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH=C\mathbf{H_2}$), 5.2 – 5.5 (2H – $CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}=CH_2$), 6.6 – 7.1 (8H –$CH_2C\mathbf{Ar_2}$).

P(Bd-*co*-D_{OSi})-6a M_n = 3,700 g mol^{-1}; M_w = 3,900 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn/dc* = 0.124).

P(Bd-*co*-D_{OSi})-6b M_n = 4,200 g mol^{-1}; M_w = 5,000 g mol^{-1}; Đ = 1.19 (triple detection SEC with *dn/dc* = 0.124).

P(Bd-*co*-D_{OSi})-6c Yield = 62 %.

M_n = 4,300 g mol^{-1}; M_w = 4,600 g mol^{-1}; Đ = 1.08 (triple detection SEC with *dn/dc* = 0.124).

5.3.57. Synthesis of Poly(Styrene-*co*-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene) - P(S-*co*-D_{OSi})-1a and 1b

The synthesis of poly(styrene-*co*-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene) was assisted by Serkan Sevinc and carried out as follows: Benzene (40 ml) was distilled, under vacuum, into the reaction apparatus. DPE-OSi (0.99 g, 2.3 mmol) was added to an ampoule sealed with a Youngs tap, degassed and dried azeotropically three times using benzene. Benzene (20 ml) was added by distillation into the ampoule to dissolve DPE-OSi, and then the ampoule was raised to atmospheric pressure with dry nitrogen. The DPE-OSi/benzene solution was then added to the reaction vessel by injection *via* a rubber septum. The reaction mixture was freeze-pump-thawed for further purification. 1.3 M *sec*-butyllithium was added dropwise until a red colour persisted and a final addition of 0.69 ml (0.90 mmol) of 1.3 M *sec*-butyllithium was added by injection *via* a rubber septum for a target molecular weight of 2,500 g mol^{-1}. The solution was stirred at room temperature for 1 hour before styrene (2.25 g, 22 mmol) was added by injection into the reaction vessel and the red colour could be seen to turn orange, indicative of polystyryllithium. Within several minutes the orange colour had darkened a little, more closely resembling the red colour of living DPE-OSi. The reaction was allowed to stir at room temperature for one day, at which point part of the reaction mixture was separated into a side flask (P(S-*co*-D_{OSi})-1a) and TMEDA (0.269 ml, 1.8 mmol) added to the main reaction vessel (P(S-*co*-D_{OSi})-1b) and allowed to continue reacting. After one more day both solutions were terminated with nitrogen sparged methanol, precipitated into methanol, collected and dried to constant mass *in vacuo*.

P(S-*co*-D_{OSi})-1a and 1b ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.1 – 0.3 (12H – $OSi(C\mathbf{H_3})_2C(CH_3)_3$); 0.9 – 1.1 (18H –$OSi(CH_3)_2C(C\mathbf{H_3})_3$); 0.4 – 2.7 (2H –$C\mathbf{H_2}CAr_2$); (3H – $C\mathbf{H_2}C\mathbf{H}Ph$); 6.0 – 7.4 (8H –$CH_2C\mathbf{Ar_2}$) and (5H –$CH_2CH\mathbf{Ph}$).

P(S-*co*-D_{OSi})-1a M_n = 3,100 g mol^{-1}; M_w = 3,300 g mol^{-1}; Đ = 1.06 (triple detection SEC with *dn*/*dc* = 0.185).

P(S-*co*-D_{OSi})-1b Yield = 71 %.

M_n = 3,100 g mol^{-1}; M_w = 3,300 g mol^{-1}; Đ = 1.05 (triple detection SEC with *dn*/*dc* = 0.185).

5.4. References

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CHAPTER 6

Concluding Remarks

6. Concluding Remarks

6.1 Conclusions

The copolymerization of 1,1-diphenylethylene (DPE) with styrene and butadiene was carried out under various reaction conditions and the resulting monomer sequences were investigated and analysed by 1D and 2D NMR spectroscopy and MALDI-ToF mass spectrometry (MS). It was found that both styrene and butadiene can form nearly perfectly alternating copolymers with DPE in a polar solvent (THF), however, in non-polar solvents, such as benzene or toluene, it was found that the results were quite different. An alternating sequence did not result with styrene and DPE although a high degree of incorporation of DPE was observed with some level of alternation. The incorporation of DPE (with styrene) can also be enhanced by increasing the molar feed ratio of DPE with respect to styrene. However, the copolymerization of butadiene with DPE resulted in a strong preference for butadiene to undergo self-propagation, leaving DPE almost entirely excluded from the copolymerization. It was also found that MALDI-ToF MS was an extremely useful technique for analysing the resulting sequences of these copolymers. Indeed it was used to unequivocally prove the presence of perfectly alternating sequences. It has also been demonstrated that further information, such as the initiator reactivity ratio, can potentially be obtained by the computer simulation of these MALDI-ToF mass spectra.

The simultaneous terpolymerization of styrene, butadiene and DPE was investigated in benzene, toluene and THF and the term ‘fire and forget’ coined to describe the simultaneous polymerization. In benzene or toluene a tapered block copolymer of polybutadiene-*block*-poly(styrene-*co*-DPE) was formed which had similar thermal properties and phase separated morphology to an analogous copolymer prepared by the more common sequential addition of monomers (i.e. that of a well-defined block copolymer). It was found that the simultaneous terpolymerization of styrene, butadiene and DPE in THF with a molar feed ratio of styrene : butadiene : DPE = 1 : 1 : 2 resulted in an alternating tapered copolymer of poly(styrene-*co*-DPE)-*co*-poly(butadiene-*co*-DPE), that is the DPE was fully incorporated indicating a perfectly alternating copolymer but the styrene and butadiene were incorporated in a tapered sequence. The results herein strongly suggest that initially styrene is consumed in preference to butadiene thus forming a gradient from styrene-rich to butadiene-rich, however the extent of this gradient is currently uncertain.

A number of other techniques for influencing the monomer sequence were also demonstrated such as switching the polarity of the solvent during the copolymerization by the addition of THF resulting in the formation of block copolymer of polybutadiene-*block*-poly(butadiene-*co*-DPE). Copolymerizations with a reduced molar feed ratio of DPE were also investigated, such as the copolymerization of butadiene with DPE in THF using a molar feed ratio of butadiene : DPE = 3 : 1 to form a copolymer of poly(butadiene-*co*-DPE)-*co*-polybutadiene, or the copolymerization of styrene, butadiene and DPE in THF with a molar feed ratio of styrene : butadiene : DPE = 1 : 1 : 1 to form a copolymer of poly(styrene-*co*-DPE-*co*-butadiene)-*co*-polybutadiene.

It was also demonstrated that the ‘fire and forget’ terpolymerization of styrene, butadiene and DPE in benzene could be performed using a difunctional initiator to form a copolymer of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE). ABA tri-block copolymers where A consists of a glassy copolymer and B consists of a rubbery copolymer with a spherical or cylindrical morphology typically display good mechanical properties and are termed thermoplastic elastomers. Hence it was demonstrated that a ‘fire and forget’ terpolymerization could be used to prepare a copolymer of poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) with spherical morphology.

The synthesis of an analogous copolymer of poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) was attempted by sequential addition, however, the synthesis proved challenging and clearly demonstrates the synthetic simplicity of the ‘fire and forget’ approach of copolymerizing all three monomers simultaneously.

The ‘fire and forget’ approach is a much more facile technique for synthesizing copolymers with a controlled monomer sequence than the more common method of the sequential addition of monomers. The ‘fire and forget’ approach even allows more complicated sequences to be synthesized that are much more synthetically challenging when using a sequential addition approach. Furthermore, a clear advantage of the ‘fire and forget’ approach is that no premature termination occurs during the polymerization.

Functional derivatives of DPE were also investigated as a means of controlling the reactivity of the DPE monomer whilst also introducing functionality into the resulting copolymer. The copolymerization of methyl methacrylate (MMA) with a functionalized DPE monomer, 4-cyanodiphenylethylene (DPE-CN) was investigated using ^{1}H NMR spectroscopy and MALDI-ToF MS. Whilst MMA does not react with DPE, it was hoped that it would react with DPE-CN (which is a more reactive monomer than DPE), however, the copolymerization resulted in the preferential self-propagation of MMA. Current results are inconclusive whether a final unit of DPE-CN was incorporated upon consumption of MMA.

It was found that the copolymerization of styrene with the less reactive functionalized DPE monomer, 1,1-bis(4-tert-butyldimethylsiloxyphenyl)ethylene (DPE-OSi), in benzene resulted in the formation of telechelic copolymers, with only a small minority of chains corresponding to sequences containing one or three units of DPE-OSi. The sequence of these copolymers was determined using ^{1}H NMR spectroscopy, MALDI-ToF MS and a positive ion MSMS experiment, and demonstrated that it is possible to prepare telechelic copolymers by a ‘fire and forget’ approach.

In the copolymerization of butadiene with DPE-OSi it was found that DPE-OSi was completely excluded from the copolymerization. Hence by the addition of TMEDA to promote the end-capping reaction of polybutadienyllithium with DPE-OSi, the polybutadiene chains could be end-capped to form a perfect telechelic copolymer.

DPE is therefore a very useful and versatile monomer for the synthesis of a wide variety of polymeric materials using anionic polymerization, especially in terms of controlling the monomer sequence. Functional derivatives of DPE can also be used to control the monomer sequence whilst simultaneously introducing functionality into the resulting copolymer.

6.2. Future Work

The following list relates to experiments and areas of work that, due to time constraints, were not able to be completed during this project:

- To prepare poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) copolymer by sequential addition for comparison (thermal, morphological and mechanical properties) with the analogous copolymer synthesized by simultaneous terpolymerization.
- To characterise the mechanical properties of the copolymers which have potential application as thermoplastic elastomers, namely poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) and poly(styrene-*co*-DPE)-*block*-polybutadiene-*block*-poly(styrene-*co*-DPE) prepared by simultaneous terpolymerization and sequential monomer addition respectively. This would allow a comparison between polymers prepared by the 'fire and forget' approach and by the more common sequential addition of monomers approach.
- To prepare copolymers of polystyrene-*block*-polybutadiene-*block*-polystyrene with an analogous structure (i.e. similar molecular weight and similar wt. % of the glassy block) to the prepared poly(styrene-*co*-DPE)-*co*-polybutadiene-*co*-poly(styrene-*co*-DPE) copolymer.
- To investigate the mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene and determine whether the thermoplastic elastomers containing DPE have improved mechanical properties in comparison to the commercially available copolymers of polystyrene-*block*-polybutadiene-*block*-polystyrene.
- To prepare a series of poly(butadiene-*co*-DPE) copolymers with varying wt. % of DPE and to determine the correlation between the glass transition temperature and the wt. % DPE.
- To further examine the phase diagram of polybutadiene-*block*-poly(styrene-*co*-DPE) to determine the phase boundaries and compare the phase diagram to that of polybutadiene-*block*-polystyrene.

- To investigate the copolymerization of butadiene and DPE with a molar feed ratio of butadiene : DPE = 3 : 1 (initially in toluene) and switching the polarity of the solvent during the reaction by the addition of THF. It is hypothesized that this would result in the formation of a copolymer of polybutadiene-*block*-poly(butadiene-*co*-DPE)-*co*-polybutadiene.
- As DPE is an expensive monomer, it would be beneficial if the terpolymerization of styrene, butadiene and DPE did not require an excess of DPE to prepare a copolymer of polybutadiene-*co*-poly(styrene-*co*-DPE) with a high incorporation of DPE. Whilst it was found that TMEDA inhibits the incorporation of DPE, it is possible that either an increased concentration of TMEDA, or the addition of another polar additive such as THF may be able to increase the incorporation of DPE and will therefore be investigated.
- To further investigate the poly(MMA-*co*-DPE-CN) copolymers and determine whether the copolymer is telechelic. This can be done by the addition of DPE-CN to a living solution of PMMA and thereby determining by ^{1}H NMR whether any DPE-CN has been incorporated.
- The synthesis of poly(butadiene-*co*-DPE-OSi) copolymers in THF will be further investigated to determine whether it is possible to prepare higher molecular weight copolymers. If, as it was hypothesized, the low molecular weights and termination problems were a result of impurities present in the DPE-OSi monomer, further monomer purification may be required.
- The copolymerization of butadiene and DPE-OSi in THF, with 2.5 equivalents of DPE-OSi with respect to the initiator, could be investigated as a method of preparing telechelic copolymers without requiring the addition of TMEDA. However, it should be noted that with THF as the solvent the copolymerization will result in a high 1,2-polybutadiene content.

With regards to future work in this area, the following concepts would be both beneficial and interesting:

- Copolymers of poly(styrene-*co*-DPE-OSi) and poly(butadiene-*co*-DPE-OSi) will be deprotected and the thermal properties investigated prior to deprotection and post deprotection.

- Once the copolymers of poly(styrene-*co*-DPE-OSi) and poly(butadiene-*co*-DPE-OSi) have been deprotected, Normal Phase TGIC could be used to further characterize the functionalized telechelic polymers.
- The terpolymerization of styrene, butadiene and DPE in THF could be further characterized by monitoring with real time ^{1}H NMR spectroscopy.
- Stilbene (1,2-diphenylethylene) is another monomer that cannot homopolymerize and is economically more viable than DPE (1,1-diphenylethylene). However, it has been reported that the reactivity ratio, r_1, for the copolymerization of styrene (M_1) with *trans*-stilbene (M_2) in benzene is 18, and therefore will not form an alternating copolymer with styrene.[1] Furthermore, chain transfer to the *trans*-stilbene monomer occurred in THF which would prevent the formation of the desired sequences (i.e. tapered copolymers).[2] However, butadiene and *trans*-stilbene copolymerized in THF to form an alternating copolymer, and, due to the fast propagation this copolymerization occurred without any termination reactions.[3] Hence other copolymerizations involving butadiene and *trans*-stilbene could be investigated.
- The copolymerization of DPE in cationic polymerization has largely been unsuccessful. In 2012 the copolymerization of DPE with *p*-substituted styrenes was reported. However, it was found that the resulting molecular weight was low and/or the extent of incorporation of DPE was low.[4] The likely reason for the low molecular weight is the slow cross-propagation reaction of DPE to the co-monomer. High molecular weights were obtained when DPE was copolymerized with a reactive co-monomer but this resulted in a low incorporation of DPE.[4] It would therefore be interesting to study the use of functionalized DPE in living cationic polymerization as a more reactive propagating species of DPE could allow high molecular weight polymers with a high incorporation of functionalized DPE to be synthesized.

6.3. References

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[2] Y. Okamoto, M. Kato and H. Yuki, *Bulletin of the Chemical Society of Japan* **1969**, *42*, 760-765.
[3] H. Yuki, Y. Okamoto, K. Tsubota and K. Kosai, *Polym J* **1970**, *1*, 147-154.
[4] K. Yasuoka, S. Kanaoka and S. Aoshima, *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 2758-2761.