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**How to cite:**

KEMPE, FABIAN (2013) *Synthesis of Branched Polybutadienes by Anionic Polymerisation with a Divinyl Crosslinker*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/10529/

# Synthesis of Branched polybutadienes by Anionic Polymerisation with a divinyl crosslinker

by

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A Thesis submitted for the degree
of Master of Science

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July 2013

# Abstract

The facile synthesis of branched polymers in high yields without gelation is a current challenge in polymer chemistry. The ”Strathclyde route” by Sherrington et al. successfully used a divinyl crosslinker during free radical polymerisation in presence of a chain transfer agent and was the inspiration to use the same approach in anionic polymerisation.

In this work soluble polybutadienes with a branched architecture were synthesised by anionic copolymerisation of butadiene with divinylbenzene. Potassium *tert*-butoxide served as an additive to alter the copolymerisation behaviour and to induce chain transfer to toluene in order to avoid gelation.

The highest fraction of branched polymer was derived for a sample of a molecular weight of $M_n = 23{,}000\,g{\cdot}mol^{-1}$, a polydispersity of PDI = 8.5, an estimated content of linear (non-crosslinked) chains of less than 23 wt-% in a high yield of 92 % with deliberate termination of the reaction after 20 min. The reaction was carried out as a one-pot batch reaction at 60 °C with toluene as the solvent.

Lower molecular weight branched polybutadienes ($M_n \approx 10{,}000\,g{\cdot}mol^{-1}$) were derived with apparently more linear (non-crosslinked) chains in batch reactions. Lower molecular weight branched polybutadienes were also prepared in a controlled feed reactor. Analysis with triple detection (with refractive index, viscosity and light scattering detectors) size exclusion chromatography strongly indicated a branched structured of the samples prepared in presence of the crosslinker compared to a sample prepared in absence of the crosslinker.

The vinyl content (1,2-enchainment of polybutadiene backbone) was up to 37 % for the most promising reactions and was in good agreement with literature regarding polar additives (potassium *tert*-butoxide in this work).

# Contents

# List of Abbreviations

| | |
|---|---|
| ASCVP | Anionic self-condensing vinyl polymerisation |
| ATRP | Atom transfer radical polymerisation |
| BD | butadiene |
| Bipy | 2,2'-Bipyridine |
| BHT | 2,6-di-*tert*-butyl-4-methylphenol |
| BuLi | butyllithium |
| DEB | diethylebenzene |
| DVB | divinylbenzene |
| EVB | ethylvinylbenzene |
| HB | hyperbranched |
| HPLC | High pressure liquid chromatography |
| INIMER | Initiator-monomer |
| KOtBu | Potassium *tert*-butoxide |
| LDPE | Low density polyethylene |
| NMR | nuclear magnetic resonance |
| MeOH | Methanol |
| MMA | Methylmethacrylate |
| PBD | polybutadiene |
| PDI | Polydispersity |
| PMMA | Poly(methylmethacrylate) |
| SCVP | Self-condensing vinyl polymerisation |
| SEC | size exclusion chromatography |
| THF | tetrahydrofuran |

# Statement of Copyright

# Acknowledgements

I am indebted to my supervisor Dr Lian Hutchings for his support, guidance and insight throughout my degree. I also thank Dr Neil Cameron as my co-supervisor for consultancy during absences of Lian.

I gratefully acknowledge the financial support of Synthomer Ltd. and the good cooperation with Dr Peter Shaw and Dr Paul Ross-Gardner. The cooperation enabled me to carry out my work with the necessary equipment and gave me valuable insight into chemical industry. I also warmly appreciate the assistance of Christian Wisbar during my industrial placement in Harlow.

I would like to thank the German National Academic Foundation for financial support and guidance previous to my year abroad.

I thank all the graduate students I worked with for the many productive hours in the lab, endless discussions in the desk room and enjoyable tea breaks. I especially thank my lab mates Paul, Serena and Tatiana for their friendship and so many happy moments inside and outside university. I cannot stress enough how grateful I am for the fantastic integration and the help with everyday troubles any foreign student experiences.

I thoroughly enjoyed being a member of Hatfield College and I am grateful for the warm welcome and many formal dinners. I especially thank Dr Anthony Bash for his friendship and the evenings with his wonderful family.

I am grateful for the company of my friends from Germany, who also spend some time in England, and for the great time we had visiting each other in these beautiful English towns.

Finally, I would thank my whole family for their lasting support of my studies and their continuing encouragement. I thank these persons and many others not mentioned here for a terrific year in Durham and everlasting memories of a very happy time.

# 1 Introduction

In this project a method was developed to synthesise branched polybutadienes by anionic copolymerisation of butadiene and divinylbenzene (to generate branch points) which included a chain transfer process to inhibit gelation. The aim was to prepare highly (hyper)branched polymers of polybutadiene, i.e. highly branched polymers with macromolecular spacers between branching points. The properties of branched polymers differ from their linear counterparts. Depending on the chain length between branches, they increase or decrease properties such as $T_g$ (glass transition temperature) and modulus, leading to a variety of applications in chemical engineering, such as coating applications.[1] The synthetic challenge is to achieve a high degree of branching without gelation of the product at high conversions. The incorporation of a difunctional comonomer introduces chain branching but can also lead to crosslinking. However the introduction of a chain transfer step into this process results in termination of growing chains and initiation of new chains and in doing so reduces the molecular weight and therefore helps to overcome the problem of gelation. This approach was originally developed by Sherrington et. al.[2] for a free radical polymerisation process and was consequently called the ”Strathclyde route”. Applying this concept to living anionic polymerisation has both advantages and disadvantages. A very important advantage of anionic polymerisation is the ability to control the molecular weight of the linear chains, as opposed to standard free radical polymerisation, where chain recombination occurs. Even if chain transfer takes place during the reaction and the polydispersity increases, the maximum molecular weight of any linear chain is determined by the ratio of initiator to monomer, because there is no chain recombination in anionic polymerisation. In order to exceed the maximum molecular weight, a linear chain has to have at least a single branch point which connects it to another chain, at which moment it no longer can be regarded as a linear chain. Therefore the linear chains, as well as the branched species derived from them, can be prepared with a desired molecular weight. The control of molecular weight is the most important advantage compared to the preparation of branched polymers by free radical polymerisation and because polybutadiene used in industrial processes often possess a low molecular weight, the preparation of branched polymers by anionic polymerisation is a suitable approach due to the control of molecular weight.

A disadvantage of anionic polymerisation in the preparation of branched polymers is the absence of termination reactions. Although anionic polymerisation is very sensitive to protic species and even carbon dioxide, which could lead to chain termination, much effort was directed at excluding these contaminants, as they could terminate the entire polymerisation even in trace amounts. Due to the experimental efforts undertaken to exclude all contaminants, undesired chain termination can be considered negligibly. In contrast to free radical polymerisation, in anionic polymerisation polymer chains remain active after complete monomer consumption and the chains can still react with any unreacted branching agent, causing more branching or even gelation. Hence, the absence of termination reactions makes it much more important to control the polymerisation variables, especially reaction time, in order to achieve reproducible results.

## 1.1 Anionic Polymerisation

### 1.1.1 General Aspects

Anionic polymerisation remains the most important technique to prepare well-defined macromolecules with a high compositional homogeneity. The earliest observations of anionic polymerisation were made as early as 1910[3] and Ziegler proposed a mechanism of propagation by monomer insertion in the early 1930s.[4]
Although other research groups reported anionic polymerisation of vinyl monomers, Szwarc was the first to investigate the polymerisation of styrene in tetrahydrofuran, coining the term *living* and to prepare block copolymers.[5]
Anionic polymerisation is a chain-growth polymerisation mechanism, in which the propagating species is anionically charged. Anionic polymerisation is termed a living polymerisation and for a polymerisation to be called living, the following criteria must be met:[4–8]

- **Absence of termination**. Even after complete consumption of the monomer all the propagating species remain active.
- **No uncontrolled chain transfer**. Chain transfer only occurs when intended and if so, to a specific reaction partner.
- **Instantaneous initiation**. All initiating molecules trigger the polymerisation at the same time.
- **Equal propagation rate**. All propagating species polymerise with the same speed at any given time. This explicitly does not mean a constant rate of polymerisation throughout the reaction, only that a change of reaction speed occurs uniformly for all propagating species.

From these criteria, some significant *conclusions* can be deduced, as long as no chain transfer has been induced:[4–8]

1. The number of active centres is constant at all times.
2. Upon addition of monomer, the polymerisation would restart even when the initial charge was completely consumed.
3. By sequential addition of a different monomer, block-copolymers can be prepared.

4. The number average molecular weight, $M_n$, is a linear function of conversion.
5. The polydispersity is very low and a Poisson distribution of molecular weight should be observed.
6. The molecular weight is directly dependent on the [monomer]/[initiator] ratio.
7. Quantitative preparation of chain-end functionalised polymers is achievable.

In the current work, chain transfer to solvent has been exploited in order to reduce the amount of initiator. The system can still be regarded as living, because the number of active sites stays constant at all times. Nonetheless by design, many of the resulting reaction parameters differ from those stated in the above list, in this case conclusion 1 and 2 are still true.

The mechanism of anionic polymerisation is relatively straightforward and well understood. Chain growth is started by the nucleophilic addition of the initiator (usually butyllithium) to the double bond of a monomer. From that point, the propagation proceeds for as long as monomer is available (by addition of monomer to the reactive chain end). Termination only occurs when an electrophile is added to the reaction, resulting in the termination of all living chain ends by protonation:

$$Initiation: \quad I:^{\ominus} + M \longrightarrow P_n:^{\ominus} \tag{1a}$$

$$Propagation: \quad P_n:^{\ominus} + M \longrightarrow P_{n+1}:^{\ominus} \tag{1b}$$

$$Termination: \quad P_n:^{\ominus} + MeOH \longrightarrow P_n - H \tag{1c}$$

## 1.2 Copolymerisation

The current work will describe the synthesis of branched polymers by the copolymerisation of butadiene with divinylbenzene as a crosslinking agent. As such the crosslinker is a second monomer which gets incorporated into the propagating chains. This results in a copolymer with a composition that can be described by the Mayo-Lewis equation.[9] This equation enables the calculation of the composition of the resulting copolymer by taking into account the initial monomer concentrations and their reactivity ratios (defined below). When two kinds of monomers are polymerised simultaneously, the following four propagation reaction steps can take place at the living chain ends:[8]

$$P_n - M_1^{\ominus} \quad + \quad M_1 \quad \xrightarrow{k_{11}} \quad P_{n+1} - M_1^{\ominus} \tag{2a}$$

$$P_n - M_1^{\ominus} \quad + \quad M_2 \quad \xrightarrow{k_{12}} \quad P_{n+1} - M_2^{\ominus} \tag{2b}$$

$$P_n - M_2^{\ominus} \quad + \quad M_2 \quad \xrightarrow{k_{22}} \quad P_{n+1} - M_2^{\ominus} \tag{2c}$$

$$P_n - M_2^{\ominus} \quad + \quad M_1 \quad \xrightarrow{k_{21}} \quad P_{n+1} - M_1^{\ominus} \tag{2d}$$

The consumption rate for each monomer is given as:

$$\frac{-dM_1}{dt} = k_{11}[P_1^{\ominus}][m_1] + k_{21}[P_2^{\ominus}][m_1] \tag{3a}$$

$$\frac{-dM_2}{dt} = k_{22}[P_2^{\ominus}][m_2] + k_{12}[P_1^{\ominus}][m_2] \tag{3b}$$

Here, M refers to the amount of the respective monomer incorporated into the polymer at any given time and m refers to the concentration of the respective unreacted monomer. To obtain a compositional ratio for the current copolymerisation of these monomers equation 3a is being divided by equation 3b to give equation 4.

$$\frac{dM_1}{dM_2} = \frac{k_{11}[P_1^{\ominus}][m_1] + k_{21}[P_2^{\ominus}][m_1]}{k_{22}[P_2^{\ominus}][m_2] + k_{12}[P_1^{\ominus}][m_2]} \tag{4}$$

This equation can be further simplified by the introduction of a reactivity ratio for each monomer. The reactivity ratio is defined as the fraction of two rate constants, namely the rate constant for self propagation divided by the rate constant for cross propagation (see equation 5a and 5b).

$$r_1 = \frac{k_{11}}{k_{12}} \tag{5a}$$

$$r_2 = \frac{k_{22}}{k_{21}} \tag{5b}$$

However, in this case the concentration of living chain ends cannot be determined directly. This difficulty can be resolved by adopting the approximation of a steady state of living chain ends because by definition, the total number of living chain ends in an anionic polymerisation does not change (see section 1.1.1 on page 2). Additionally, it is assumed that the rate of interconversion of the two types of living chain ends is equal:

$$k_{21}[P_2^{\ominus}][m_1] = k_{12}[P_1^{\ominus}][m_2] \tag{6}$$

Rearrangement of equation 6 shows the direct dependency of $[P_2^{\ominus}]$ on $[P_1^{\ominus}]$:

$$[P_2^{\ominus}] = \frac{k_{12}[P_1^{\ominus}][m_2]}{k_{21}[m_1]} \tag{7}$$

From this relation the Mayo-Lewis equation can be derived:

$$\frac{dM_1}{dM_2} = \frac{[m_1]\,(r_1 \frac{[m_1]}{[m_2]} + 1\,)}{[m_2]\,(\;\frac{[m_1]}{[m_2]} + r_2)} \tag{8}$$

Equation 8 can be simplified by extending the fraction by an artificial 1:

$$\frac{dM_1}{dM_2} = \frac{[m_1]\,(r_1 \frac{[m_1]}{[m_2]} + 1\,)}{[m_2]\,(\;\frac{[m_1]}{[m_2]} + r_2)} \underbrace{\frac{[m_1][m_2]}{[m_1][m_2]}}_{=1} \tag{9}$$

Rearrangement gives the Mayo-Lewis equation in its familiar form:[10]

$$\frac{dM_1}{dM_2} = \frac{[m_1](r_1[m_1]+[m_2])}{[m_2](r_2[m_2]+[m_1])} \tag{10}$$

When $r_1 \approx r_2 \approx 0$ an alternating polymer will be synthesised, whereas when $r_1 \approx r_2 \approx 1$ a random copolymer is obtained. For $r_1,\ r_2 >> 1$ the monomers will be distributed in blocks because for both monomers self propagation is strongly favoured over cross propagation.

### 1.2.1 Structural classification

The different physical and mechanical properties exhibited by branched polymers compared to their linear analogues can be explained by the topology of the macromolecules. In particular the rheological behaviour in the melt is strongly influenced by branching and makes branched polymers extremely useful in applications (see section 1.2.3).[11,12] Hence, different topologies of a macromolecule of similar chemical composition and molecular weight affect mechanical properties in different ways. Generally, all polymers can be classified as linear, cyclic, branched or networks. The decisive distinction between branched polymers and a network is the number of molecules in the system. A network itself is essentially a single molecule, in which every chain is connected to every other chain *via* crosslinking. Therefore, networks are insoluble and merely swell in a good solvent, a state in which they are also called a gel. Furthermore, the molecular weight of a network is practically infinite. Despite this precise definition of networks, there is an undefined area between branched polymers and networks where the molecular weight of branched polymers is extremely high (maybe millions of $g{\cdot}mol^{-1}$), leading to insoluble, macroscopic particles that can be seen with the naked eye. These macroscopic particles do not fulfil the definition of a network because they still have a definite molecular weight and are not crosslinked with each other. Particles which are insoluble but do not fulfil the definition of a network (i.e. gel) will subsequently be called microgel throughout this work. They are not defined as hyperbranched polymers because they are not solvent soluble.

Further sub-classification of the nature of branching is more complex, because exact definitions and criteria have yet not been established in literature.[13]

In this study branched polymers have been divided into two categories; *long-chain branched* polymers and *dendritic* polymers.

Long-chain branched molecules are polymers which contain branch points and include materials both with a specific number of branch points (e.g. star- and H-shaped polymers, see figure 1.2.1) and with a more random nature of branching (e.g. comb-shaped polymers or linear low density polyethylene).

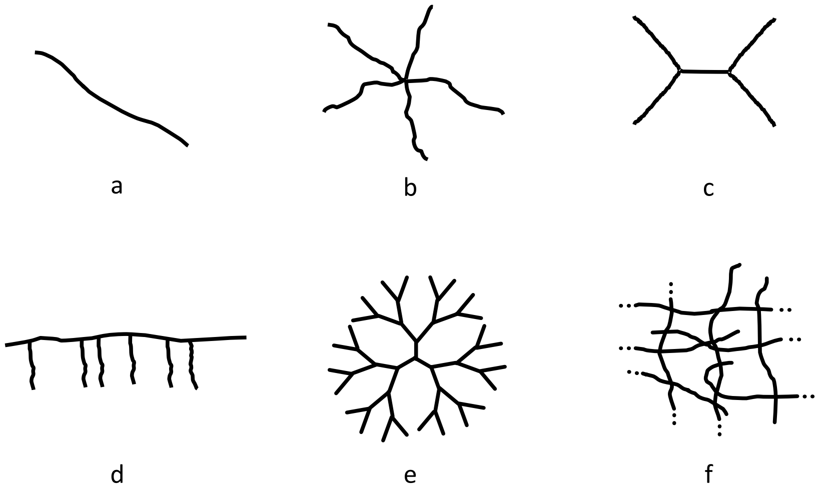

**Figure 1.2.1:** Polymer structures: (a) linear, (b) star-shaped, (c) H-shaped, (d) comb-shaped, (e) dendrimer, (f) network.

Dendritic polymers are branched polymers with hierarchical branching, i.e. branches on branches. It must be clarified that the use of the term dendritic varies dramatically in literature.[1,12,14–28]

Dendritic molecules can be differentiated into monodisperse and polydisperse systems, both in terms of molecular weight and degree of branching.[16] Either of these systems can be short-chain or long-chain branched. Here, short-chain branching describes a polymer which is made up of monomer units which all contain a branching geometry. Hence it follows that the counterpart, long-chain analogues, are defined by having more than one monomer unit between branching points.

Dendrimers are short chain branched polymers which are designed to be perfectly monodisperse. They have also been called arborols[29] or cascade polymers; their oligomers being starburst polymers.[30] Their imperfectly branched polydisperse analogues are hyperbranched polymers, a term first used in this context by Kim and Webster.[31]

For these polymers the degree of branching (DB) constitutes a relatively well defined parameter to quantify the polydispersity of such systems. Equation 11 shows the definition of the DB for an $AB_2$ type polymer.[11]

$$DB = \frac{B+T}{B+L+T} \tag{11}$$

Here, DB is derived from the ratio of branched (B), terminal (T) and linear (L) units. For dendrimers DB is 1, for linear polymers DB is 0 and hyperbranched polymers are all species in between ($0 < \text{DB} < 1$).

The long-chain branched analogues of dendrimers have been called DendriMac,[32] Cayley tree[33] or Comb-burst®[34] polymers. The names often refer not only to the topology but to the method of preparation as well. The pivotal characteristic of long-chain analogues of dendrimers is the uniform distribution of branch points and the highly defined molecular weight of the spacers between them. Depending upon the method of preparation, the desire to create ideal monodisperse molecules is achieved with a varying degree of success.

The long-chain analogues of hyperbranched polymers are called HyperMac[17] or polymers prepared by chain walking,[14] again names that refer to the method of preparation as well. Long-chain analogues of hyperbranched polymers can be imperfect in several ways compared to long-chain analogues of dendrimers. Actual HyperMacs are prepared from macromonomers which are randomly branched. Hence, HyperMacs have highly defined spacers, i.e. $\text{PDI}_{\text{spacer}} \leq 1.1$, but a random number of spacers per molecule, i.e. $\text{PDI}_{\text{molecule}} > 1.1$ and can be very high. Other HyperMac-like polymers exist, which are randomly branched and are made up from polydisperse spacers with a $\text{PDI}_{\text{spacer}}$ and $\text{PDI}_{\text{molecule}}$ much greater than 1. Such topologies include polymers like LDPE, polymers prepared by chain walking as well as polymers prepared with a divinyl crosslinker.[2] Unfortunately no definite term exists in the literature which describes polymers which are long-chain branched analogues of hyperbranched polymers and are polydisperse both in terms of the spacers between branch points as well as their molecular weight. In this work they will be called highly (hyper)branched polymers in order to distinguish them from clearly defined HyperMacs.

There also exist numerous hybrid structures of dendritic polymers. Dendronised polymers are hybrid structures with dendrons attached to the linear backbone (see figure 1.2.2).[25] While the dendrons themselves are monodisperse and highly symmetrical, the distribution of dendrons along the linear backbone is usually not well defined. A more random hybrid structure are hypergrafted polymers with hyperbranched polymers attached to a linear backbone. Also linear-dendritic block-copolymers (hybrids) have been synthesised.[35]

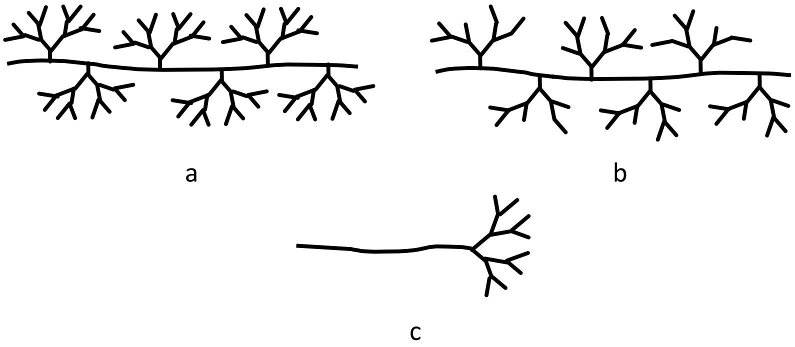

**Figure 1.2.2:** Hybrid polymers: (a) dendronised polymer, (b) hypergrafted polymer, (c) linear-dendritic hybrid.

The physical properties of branched polymers are highly dependent upon their molecular architecture.[1] Apart from molecular weight and polydispersity their properties are dependent on the degree of branching. For instance, the branched low density polyethylene shows a lower $T_g$ and melting point, and a lower degree of crystallinity than high density polyethylene, its linear analogue. Generally branching is known to influence not only thermal properties but rheological and solution properties as well. In the melt, branching hinders chain entanglement and thereby reduces melt viscosity. In solution, higher solubility was observed for branched polymers due to their higher surface area compared to linear polymers of the same molecular weight.[26]

### 1.2.2 Theory of Gelation

Generally the copolymerisation of any monomer in the presence of a crosslinker can cause gelation. Therefore in this section we outline the variables which influence gelation. Because the main aim of this work is to prepare branched polymers by a mechanism that can lead to gelation, it would seem useful to be able to predict the point of gelation. Hence, a model for controlled radical polymerisation[36] (ATRP) was adapted to calculate the conversion at the point of gelation for polymers when using a difunctional comonomer in anionic polymerisation. It is based on the Flory-Stockmayer theory for gelation.[37,38]

In the model for ATRP it is assumed that all chains are initiated simultaneously and propagate with the same rate. For both ATRP and anionic polymerisation these are valid approximations. Furthermore the model assumes ideal copolymerisation for both monomers ($r_1 = r_2 = 1$), a fact that adds an inherent inaccuracy to the calculation. Chain transfer is also not included in this model. As the chain transfer reaction step is pivotal for the aim of this work, the model had to be adjusted to take this matter into account. This has been achieved by changing the parameter $M_{n,linear}$ to $M_{w,linear}$ . $M_{n,linear}$ represents the number average molecular weight of an analogous ATRP reaction carried out in absence of a branching agent. For this approximation the weighted average molecular weight of an analogous reaction is more appropriate, because the chain transfer causes a significant increase in polydispersity. Since longer chains are more likely to crosslink, $M_{w,linear}$ gives more accurate results. The model also assumes that all incorporated crosslinking monomers immediately turn into a branching point (i.e. the pendent vinyl group immediately gets incorporated into another chain). Therefore the model gives better values for high conversions, where the conversions of the pendent vinyl groups are also relatively high. Despite the inherent inaccuracies the model was found to be sufficiently accurate for the purpose of avoiding the conditions which lead to gelation even at low yields.

The degree of polymerisation $\overline{DP}$ in this work has been defined as the product of the conversion of all monomer units present, $x$, and the maximum degree of polymerisation, $\overline{DP}_{max}$. Essentially, this directly follows from the characteristics of all anionic polymerisations, where the number of active centres is constant at all times. Hence, the degree of polymerisation is a linear function of the monomer conversion:

$$\overline{DP} = x \times \overline{DP}_{max} \tag{12}$$

$\overline{DP}_{max}$ itself has been defined as the fraction of $M_{w,linear}$ over the molecular weight of the monomer, $M_{monomer}$. By using $M_{w,linear}$ instead of $M_{n,linear}$ the longer chains of the polydisperse system, which are more likely to cause gelation, are favoured in the calculation. For low crosslinker concentrations the molecular weight of the main monomer can be used as $M_{monomer}$:

$$\overline{DP}_{max} = \frac{M_{w,linear}}{M_{monomer}} \tag{13}$$

The average number of crosslinking molecules per linear chain, $n_b$, is given as the product of $\overline{DP}_{max}$ and the concentration of crosslinker, $[x - linker]$. The latter was defined as decimal molar fraction with regard to the main monomer. It should be noted at this point that the definition $n_b$ treats every crosslinking molecule as belonging to precisely one linear chain rather than to both chains it cross links.

$$n_b = \overline{DP}_{max} \times [x - linker] \tag{14}$$

The branching density, $\rho$, is defined as the number fraction of the total number of branching points compared to the total number of repeating units. This can be safely approximated referring to a single linear chain:

$$\rho = \frac{n_b \times M_{monomer}}{M_{w,linear}} \tag{15}$$

The critical condition for the formation of an infinite network is given as:[36]

$$\rho \times \overline{DP} = 1 \tag{16}$$

For polydisperse systems the weight average chain length has to be used for the definition of $\overline{DP}$, as has been done for this work (see equation 13). Now equations 12 and 15 can be inserted into equation 16:

$$x \times \frac{M_{w,linear}}{M_{monomer}} \times [x - linker] = 1 \tag{17}$$

This can now be rearranged to solve for $x$:

$$x = \frac{M_{monomer}}{M_{w,linear} \times [x - linker]} \tag{18}$$

For a series of experiments, $M_{monomer}$ is a constant parameter. Therefore the point of gelation depends equally on $M_{w,linear}$ and $[x - linker]$. Both variables are in the denominator. Hence, a lower molecular weight and a lower concentration of crosslinker lead to a higher conversion at which gelation occurs, as would be generally expected.[37]

If the chain length of the linear chains is increased, the reaction is more likely to crosslink at the very same concentration of crosslinking agent. This relationship is plausible, because longer chains can incorporate more crosslinking molecules and the higher functionality per chain leads to more crosslinking and eventually to gelation. This fact has an important consequence for this work: there is no ideal concentration of crosslinker for all molecular weight ranges. On the contrary any change of the molecular weight of the linear chains makes an adjustment of the crosslinker concentration reasonable.

### 1.2.3 Applications

In the same way as linear polymers are used widely in all aspects of life, branched polymers have found their way into a wide variety of applications. Either they are being used in the same area as their linear analogues because of a higher performance or they are being used in entirely new fields due to unique chemical and physical properties. In general, dendrimers and DendriMacs are exclusively used as model polymers, for instance for the development of theories for the prediction of rheological behaviour. Hyperbranched polymers and HyperMacs are inherently polydisperse but are much easier (and cheaper) to synthesise and are therefore of higher industrial importance.[22,26] Because of the wide range of applications for branched polymers, the examples given focuses on cases where they show outstanding performances compared to their linear analogues.

Industrially LDPE (low density polyethylene) is of very high importance and is primarily used for films and carrier bags.[39] Branched polymers also give a prospect for biomedical applications because of their globular shapes similar to many proteins such as haemoglobin or to hormones, for instance insulin. The encapsulation properties often enable the use as nanocarriers. These can generally improve drug delivery by influencing water solubility, pharmakokinetics and bioavailability of drugs in vivo.[40]

In chemical engineering and polymer processing branched polymers can be used in small quantities (as additive) to adjust polymer properties for production purposes or for the final material itself.[13] Furthermore the viscosity of a mixture can be reduced in the same way, enhancing the effectiveness of molding processes.[41] Branched polymers are also widely used in coating and resin applications as they allow tuning of melt and solution viscosity.[13] The use of branched polymers in catalysis, microelectronics, sensors and membrane technology is also increasing.[13,26] Hyperbranched PEGs have been used as ion-conducting materials for lithium.[16] The encapsulation effect used in biomedical applications can also be employed to load dyes into amphiphilic core-shell hyperbranched polymers.[25] Hyperbranched polymers are also used as non-volatile entrainers in extractive distillation, leading to large separation efficiencies. The high density of functional groups enables a high solubility of the entrainer, while the solution viscosity is comparatively low due to the branched topology.[26] Even more importantly, these systems are non-corrosive, easy to recover and can be adjusted in their physical and chemical properties depending on the nature of the distillation process.[26,42]

### 1.2.4 Synthetic routes towards highly (hyper)branched polymers with long-chain spacers between branching points

A large number of synthetic routes have been developed to produce branched polymers and no one single approach provides a generic solution for all branched polymer topologies. Depending on the desired nature of the branching and the monomer comonomer system, various strategies can proof useful. The principal aim of this work is the synthesis of highly (hyper)branched polymers by a facile, scalable route. The synthesis of highly ordered structures will only be discussed in passing in this section to give some wider context. Furthermore, many excellent, recently published reviews describe synthetic routes to well defined polymers extensively.

Well defined structures like stars, mikto-arm stars and H-shaped polymers have been prepared by coupling of living chain ends with chlorosilanes or divinylbenzene.[43–46] For the preparation of long-chain analogues of Dendrimers, which have a much higher complexity in architecture, divergent and convergent approaches have been used. In the divergent approach, the structure is build ”core-out”, i.e. the core is used as initiator for the first generation. With iterative deprotection/polymerisation steps, more generations are build up, always using the endgroup of the last generation as initiator. The divergent approach has been used in the synthesis of long-chain dendrimers of styrene employing 4,4-dibromodiphenylethylene as TERMINI reagent,[47] of $\varepsilon$-caprolactone using living ring-opening polymerisation[48] and of PMMA using anionic polymerisation.[49] In the convergent approach, a series of iterative reactions is carried out to couple macromonomers. The macromonomers themselves are prepared from living chains coupled into $AB_2$ type macromonomers. Dendrimers derived in a convergent approach have been called many different names, the most intuitive being DendriMac.[50]

Since the initial paper by Sherrington’s group in 2000, countless routes have been developed to prepare highly (hyper)branched polymers by using divinyl crosslinkers in connection with a chain transfer process.[2] Previously only few practical methods have been available, with self-condensing vinyl polymerisation (SCVP) being the most promising one. The range of publications covers all known polymerisation mechanisms, with varying success and versatility.[19] To give this overview more structure, it was tried to focus on key criteria to present the different approaches. The most obvious are the mode of polymerisation and chain transfer (if present). Additionally, the range of molecular weights, polydispersities, temperatures and yields for an outstanding product of every publication are given. Despite a very important criterion, the branching fraction in the sample is often not stated in the respective papers, usually because of the lack of reliable characterisation methods.

Self-condensing vinyl polymerisation (SCVP) was first demonstrated by Fréchet et al. in 1995 as a ”living” radical process.[21] Here, the monomer is both initiator and monomer at the same time and is therefore being called *inimer*. In this paper, the inimer consisted of a living styrene radical in a dormant state with tetramethylpiperidine-1-oxy radical (TEMPO). Furthermore Fréchet synthesised either linear or hyperbranched polymers from 4-(chloromethyl)-styrene by SCVP.[51] The combination of the two routes lead to the synthesis of highly (hyper)branched polymers. The polymerisation was a ”living” radical process carried out with $Cu^I$-bipy.

The inherent disadvantage of SCVP is the need for special monomers such as 4-(chloromethyl)styrene, which are usually not widely available. Therefore SCVP is not a facile method and in some cases must be considered a two stage process if the monomer has to be prepared or modified specifically before the actual polymerisation. Thus this is of less industrial interest.

A synthesis of polystyrene *via* cationic polymerisation including chain transfer to monomer was shown by the Sherrington group in 2006.[52] DVB was used as crosslinking co-monomer. Sufficient chain transfer was surprisingly achieved by chain transfer to styrene, making an extra chain transfer agent or additive as support for this redundant. The reactions have been carried out at 0 °C and have been very fast with a typical reaction time of 15 min. Initiation was achieved by $SnCl_4$ in dichloromethane. One of the polymers was prepared with styrene/DVB ratio of 100/5 with a molecular weight of $M_w = 480{,}000\,g{\cdot}mol^{-1}$ and a PDI = 13 at a yield of 87 %. Though no estimate for the branched fraction could be made, the samples are undoubtedly branched in some way. Conclusively, despite being limited to polystyrene, this route is very elegant and simple at the same time.

Radical polymerisation with chain transfer to branching monomer has been shown by Jiang et. al.[53] for styrene in toluene. The branching co-monomer was 3-mercaptohexyl methacrylate, synthesised by esterification from the corresponding alcohol and acid. The chain transfer monomer can either be incorporated into polymer chains *via* the vinyl or the mercapto group, generating macromolecular chain transfer agents or macromonomers, respectively. While a concentration of co-monomer of about 5 % produced a gel at 60 °C, no gelation occurred at 80 °C. This suggests that chain transfer only occurs at elevated temperatures in sufficiently high degrees. One of the products had a molecular weight of $M_w = 211{,}000\,g{\cdot}mol^{-1}$ and a PDI = 13 at a yield of 99 % at 80 °C. This sample has been hydrolysed, cleaving the ester bond of the crosslinking monomer and revealing the branched nature of the product, as shown in the supporting information. While no precise fraction of branched polymer is given, the SEC data suggest it to be at least 50%. Branched polymers of MMA and vinylacetate have also been prepared. Overall, the most central criteria for preparing branched polymers have been met with a reasonable fraction of branched polymer at a high yield. Therefore this approach seems to be a versatile route to branched polymers at moderate reaction times and polymerisation conditions. Compared to this work, no chain transfer additive needs to be separated from the crude product, while an additional preparation step is necessary to prepare the unusual co-monomer.

Anionic self-condensing vinyl polymerisation (ASCVP) has been reported by Baskaran[54] for DVB and 1,3-diisopropenylbenzene. The corresponding inimer have been synthesised using equimolar ratios of n-BuLi and the monomer. This led to hyperbranched polymers of DVB and 1,3-diisopropenylbenzene, but gel formation could not be suppressed entirely. While the chemicals employed are commercially available, the high amount of the effective initiator (n-BuLi) makes this approach expensive. Furthermore this approach is restricted to very few monomers, reducing the range of polymers which can be produced significantly.

Sherrington et al. developed the synthesis of highly (hyper)branched polymers by using a divinyl crosslinking agent and a chain transfer agent at the same time. This approach was successfully used in their initial paper for the preparation of highly (hyper)branched PMMA in a free radical process.[2] Hereby gelation was successfully prevented by the chain transfer agent, which reduced the molecular weight of the linear chain sections. Only readily available chemicals had been used and the approach can be transferred to many other systems using different monomers, branching agents and chain transfer processes. Sherrington et al. demonstrated their approach also with divinylbenzene as branching agent.[55] More importantly they demonstrated the synthesis of branched polystyrene in a cationic polymerisation, using chain transfer to monomer to prevent gelation.[52] Using a different polymerisation mechanism, monomer and chain transfer process impressively showed the versatility of this approach. The Sherrington approach, sometimes called ”Strathclyde route”, has been used to prepare branched polystyrene *via* a free radical process.[53] Interestingly in this approach was the use of the branching agent as chain transfer agent as well, i.e. chain transfer to branching monomer.

The aim for the current work was to synthesise highly branched polybutadiene without microgelation in a high yield/conversion from readily available chemicals in a cheap and scalable anionic polymerisation process. Attempts were made to prepare both high molecular weight branched polymers (ca. 100,000 $g{\cdot}mol^{-1}$) and lower molecular weight polymers (less than 20,000 $g{\cdot}mol^{-1}$). The reactions have been carried out both as lab scale batch reactions under vacuum and in a larger scale continuous monomer feed reactor under nitrogen at atmospheric pressure.

# 2 Results and Discussion

The aim of this work was to develop a synthetic route towards hyperbranched polybutadiene from readily available chemicals, in high yield and without microgelation of the product, i.e. to produce a fully soluble product. Therefore butadiene has been copolymerised with a divinyl crosslinking agent in the presence of a chain transfer process. The divinyl crosslinking agent introduces branching points into the polymer backbone, while the chain transfer process reduces the molecular weight of the polymer backbone. Because the point of the gelation is dependent on chain length and crosslink density (see section 1.2.2), the chain transfer process can help prevent gelation by terminating chains prior to gelation. This approach was adapted from the ”Strathclyde route” first reported by the Sherrington group,[2] which used a radical polymerisation process. In this work, anionic polymerisation was used. It should be stressed that anionic polymerisation allows direct control of the molecular weight by the initiator concentration. Hence, a chain transfer process can be used as an additional feature (for instance for the reduction of the required initiator concentration), but is not essential to produce hyperbranched polybutadiene. Divinylbenzene was chosen as branching/crosslinking agent due to its ready availability and low cost. Chain transfer to solvent has been chosen as chain transfer process (mechanism see figure 2.0.1). DVB was used in 80 % purity with monofunctional isomers present (see section 3.1.2 for details). The amount of DVB used in the polymerisation reactions was always calculated in the way that the DVB concentration represents the concentration of difunctional monomers in the mixture. Therefore, all DVB concentration values given represent fully the amount of difuntional monomer and do not include the monofunctional impurities.

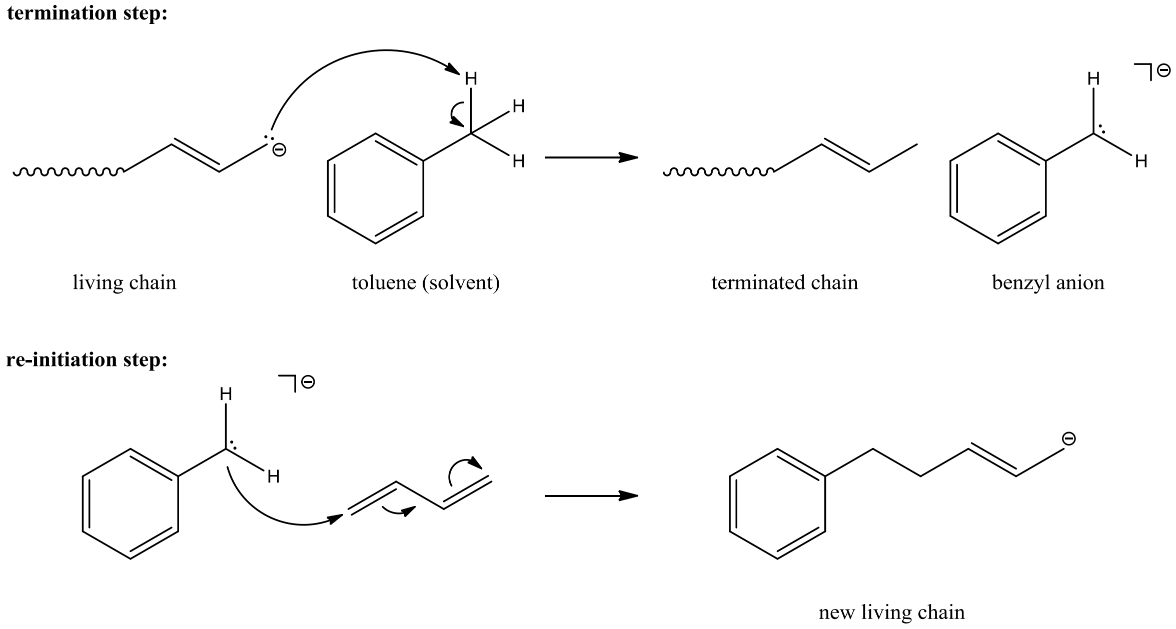

**Figure 2.0.1:** Chain transfer of polybutadiene to solvent is shown with toluene as the chain transfer agent.

Fortunately, the anionic polymerisation of dienes including butadiene in toluene is known to undergo chain transfer to solvent (Figure 2.0.1) and Lewis bases are generally known to promote chain transfer to toluene.[8] Typical Lewis bases used in this context are N,N,N',N'-tetramethylethylenediamine and potassium *tert*-butoxide. Where chain transfer to solvent occurs it does so in two steps: termination followed by re-initiation (see figure 2.0.1).
Hence, toluene was used as solvent in combination with potassium *tert*-butoxide (KOtBu) as an additive, because this chain transfer system was already demonstrated to work well. The *tert*-butoxide can deprotonate toluene in the benzylic position in order to create a new living chain, while the resulting *tert*-butanol protonates another living chain end. Therefore, the rate of chain transfer to toluene is greatly enhanced.[8]

The challenges associated with the preparation of branched polymers may not be obvious at first sight and hence shall be discussed in further detail.

1. **Discrepancy between chemical feed ratio and product composition.** The branched polymers described in this work have been prepared by the copolymerisation of vinyl monomers with a difunctional crosslinking/branching agent. While all the chemicals used have been introduced into the reaction vessel in defined quantities, there is no guarantee all of them have been fully consumed in the resulting polymer. This may produce differences between the composition of the feed and the composition of the

resulting polymer. Unfortunately, a reliable analysis of the product composition was not possible due to the chemical nature of the crosslinker and its very low concentration. Other workers avoided this problem by using crosslinkers which are easier to detect.[2,55] Usually these compounds are relatively exotic and the present work was focussed on widely available chemicals.

2. **Gelation point is influenced by both crosslinker concentration and chain length.**
   The gelation point (and avoiding gelation) is crucial to any work in this area, because gels (better known in their dry state as networks) are insoluble and as such their synthesis must be avoided when aiming to synthesise soluble and processable branched polymers. The challenge is to optimise chain branching of the polymer without producing a gel. The complication is that the point of gelation depends not on a single, but on many interrelated parameters including the crosslinker concentration, the ratio of initiator to monomer and the polymerisation mechanism. In a living anionic copolymerisation involving a crosslinking agent, gelation can occur even at moderate chain lengths because the living nature of the polymerisation causes high crosslinking efficiencies if the reaction is not terminated deliberately early. Gelation can be avoided by using a chain transfer polymerisation but it should be realised that modifications to the synthetic procedure should be considered with care and it is rarely possible to change one parameter, for example the quantity of crosslinking agent, without modifying other parameters to maintain a branched structure and prevent gelation.

3. **Relative kinetics of different reaction processes during branched polymer synthesis.**
   If more than one polymerisation process is ongoing in the reaction, they will influence each other to some degree. For instance the anionic chain transfer polymerisation of butadiene is straightforward to understand and predict, however, chain transfer accompanying a copolymerisation is more complex, since the different monomers at a chain-end will have a different rate of chain transfer. Moreover in the present case, the addition of potassium butoxide enhances the rate of chain transfer, but it also has a significant impact upon the reactivity ratios of the two monomers. Therefore it is very likely that the change of one experimental parameter is inadvertently affecting other factors as well.

As a result of the second complication stated above, the influence of multiple interrelated parameters on the point of gelation, was considered when planning the order of experiments. Therefore, an investigation of chain transfer was carried out independently of chain branching. Additionally the amount of crosslinker required to promote branching but not crosslinking was determined by considering both the concentration of crosslinker and the reactivity ratios of the copolymerisation of the vinyl monomer with the crosslinker. Therefore the copolymerisation behaviour was investigated in the absence of a chain transfer process, whereby the chain length is solely determined by the initiator concentration. With the preliminary data derived from these two initial studies it was possible to draw comparisons with the branching experiments conducted in the later stage of this work, where the full reaction system has been investigated.

This directly leads to the third issue discussed above, namely the interplay between the various reaction processes. Although the initial investigations into chain transfer and copolymerisation behaviour gave valuable information to direct the design of the full reaction system, the conclusions drawn from the first two parts do not translate directly to the full reaction system, where copolymerisation takes place in presence of chain transfer processes. From perspective, it becomes clear that the conclusions drawn from the first two parts are of a more general nature. The present investigation was carried out in four parts, each described in a single section.

1. Anionic copolymerisation of butadiene and divinylbenzene in the absence of chain transfer
2. The anionic polymerisation of butadiene in toluene - the impact of chain transfer to solvent
3. Anionic copolymerisation of butadiene and divinylbenzene with chain transfer
4. Adaption of reactions for use in a controlled feed reactor

The final part of this work (4 above) investigated not only the feasibility to carry out reactions on a larger scale with an industrial butadiene feed reactor but also the effect of continuous monomer feed upon the polymerisation. While it was expected that the reaction system would behave quite differently from the batch reactor used in the first three parts of this work, the knowledge and experience gained in the previous reactions allowed the process to be optimised with a relatively small number of experiments.

For clarification some remarks should be made to the definition of polymer chains between branching points, as explained in figure 2.0.2. Polymerisation in the presence of a divinyl crosslinker leads to connection of otherwise linear chains. In this process, the vinyl groups of a fully reacted crosslinker are incorporated into the respective chains and become part of the polymer backbone.

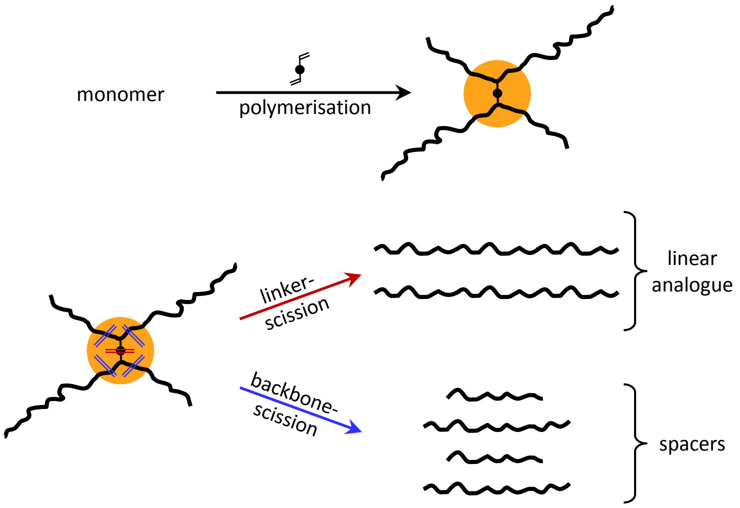

**Figure 2.0.2:** Explanation of the terms *linear analogue* and *spacer*.

The actual branch point, from a structural point of view, is highlighted by an orange-coloured circle (figure 2.0.2). It comprises of 4 adjoining chains, rather than 2. A theoretical scission of the crosslinker reveals the linear chains which would have been synthesised in the absence of crosslinking. Hence, they are called ”linear analogue” chains throughout this work. A theoretical scission of the backbone at the carbon atoms of the former crosslinker-vinyl groups reveals the macromolecular *spacers* between the branching points. The terms *linear analogue* and *spacer* are used consistently in this way throughout this work and should make it easier to follow the line of argument.

## 2.1 Anionic copolymerisation of butadiene and divinylbenzene in the absence of chain transfer

The most important objective of this preliminary study was to provide data to inform later reactions. If the copolymerisation behaviour without chain transfer is known, the results can be used to compare (and predict) with results obtained with chain transfer.

Although 1,3-butadiene (BD) is a divinyl monomer, polymers produced from BD are not branched and do not undergo crosslinking reactions during anionic polymerisation. This is due to both electronic and steric effects. An anion generated by the nucleophilic attack of a living chain-end on a vinyl group of a different chain is not stabilised by either mesomeric or inductive effects. Hence the residual double bonds found in the backbone of polybutadiene are generally unreactive towards attack by the propagating anion of other polymer chains.

In order to introduce branching, divinylbenzene (DVB) has been employed as comonomer. In anionic polymerisation DVB has long been used to introduce branching by its addition at the end of the polymerisation of linear chains, creating star branched polymers.[56–59]

Although the addition of DVB at the end of a polymerisation is known to produce star-like polymers, the objective of the present study is to produce randomly (hyper)branched polymers with branch points along the polymer backbone rather than exclusively at the chain-end. With this in mind we investigated the copolymerisation of BD and DVB under a variety of reaction conditions, always aiming to achieve high conversions (>85%).

There are no reactivity ratio data available from the literature for the copolymerisation of butadiene and DVB. However,in this study it was assumed that DVB behaves in a similar fashion to styrene with regard to its copolymerisation with butadiene and some general conclusions can be drawn. This assumption does not suggest that DVB and styrene have identical reactivities, because 1,4-divinyl benzene is more reactive towards nucleophilic attack due to its better mesomeric stabilisation of negativ charge in the benzylic position.[60] Despite this discrepancy, the behaviour of styrene in the copolymerisation towards butadiene should be discussed to get a general idea of reactivity ratios. For the copolymerisation of styrene and butadiene at 40 °C in toluene, the reactivity ratios have been found to be $r_{Bd} = 13$ and $r_{St} = 0.18$ .[61] Hence it follows that in the unlikely addition of styrene to the living chain-end, the next monomer added to the chain will be most likely be butadiene, which is then very unlikely to switch back. Therefore, the resulting copolymer will have a blocky structure with mainly butadiene monomer consumed at the beginning of the reaction. In the later stages of the reaction, the concentration of butadiene monomer decreases and therefore the incorporation of styrene becomes much more likely. Hence the resulting polymer will have a second block of mainly styrene monomer. The overall polymer can also be described as a tapered polymer, because with an increasing degree of polymerisation the incorporation of butadiene gets less likely, while the incorporation of styrene is more favoured. It is assumed that for a copolymerisation of BD and DVB the behaviour will be similar.

Initially hexane was used as a solvent to allow the copolymerisation to proceed in the absence of chain transfer processes. Unlike toluene, hexane has no benzylic proton and therefore has a lower acidity than styrene. Hence, chain transfer to hexane isconsiderably less likely than it is to toluene. Because hexane is a non-polar solvent like toluene (which will be used in the subsequent sections), the trends derived from the results should be comparable. Both the mole ratio of DVB monomer and the reaction temperature have been investigated. The target molecular weight ($M_{target}$) was kept constant and describes the molecular weight which would be produced in the absence of a crosslinking agent or a chain transfer process. It should be noted that $M_{target}$ is essentially a different expression for initiator concentration, but $M_{target}$ allows a more intuitive comparison with the obtained molecular weights. $M_{target}$ was calculated from the mass of monomer divided by the molar amount of initiator used. With $M_{target}$ constant, any increase in molecular weight has to be caused by branching, because branching is only dependent on crosslinker concentration and chain length of the linear analogues. Table 2.1.1 and figure 2.1.1 show the results of a series of three polymerisations of butadiene carried out with two different concentrations of DVB and at two different temperatures.

**Table 2.1.1:** Molecular weight data for HB-BD-01, HB-BD-02 and HB-BD-03 derived from the SEC traces in figure 2.1.1.
The influence of DVB upon the molecular weight was investigated in the absence of any additives. Additionally, the temperature was varied between HB-BD-01 and HB-BD-03 at the same DVB concentration.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-01-1 | 14.6 | 13,500 | 14,100 | 1.04 |
| HB-BD-01-2 | 14.0 | 32,000 | 37,000 | 1.16 |
| HB-BD-02-1 | 14.4 | 14,500 | 15,200 | 1.05 |
| HB-BD-02-2 | 13.8 | 38,000 | 50,000 | 1.3 |
| HB-BD-03-1 | 14.4 | 16,200 | 16,900 | 1.04 |
| HB-BD-03-2 | 13.9 | 30,500 | 31,300 | 1.03 |
| HB-BD-03-3 | 13.5 | 92,000 | 143,000 | 1.6 |

HB-BD-01: hexane, 30 °C, 0.5 mol-% DVB, 21 h, $M_{target}$ = 9,700 g·mol$^{-1}$.
HB-BD-02: hexane, 30 °C, 1.0 mol-% DVB, 24 h, $M_{target}$ = 9,400 g·mol$^{-1}$.
HB-BD-03: hexane, 60 °C, 0.5 mol-% DVB, 21 h, $M_{target}$ = 9,700 g·mol$^{-1}$.

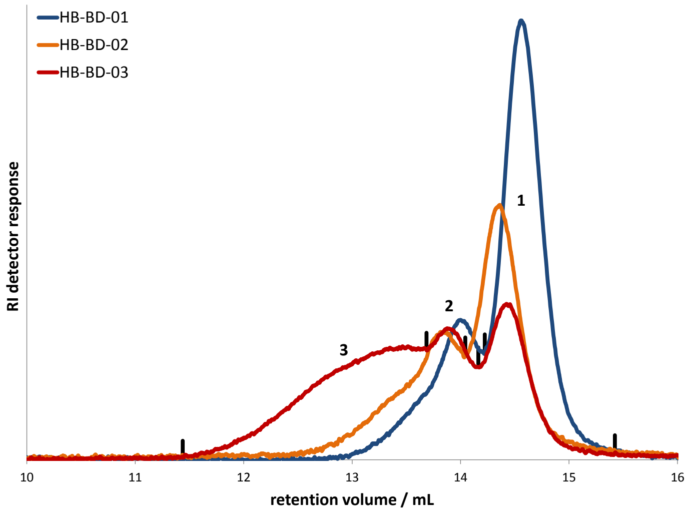

**Figure 2.1.1:** SEC analysis of HB-BD-01, HB-BD-02 and HB-BD-03.
See table 2.1.1 for molecular weight data. Vertical lines indicate integration limits.
HB-BD-01: hexane, 30 °C, 0.5 mol-% DVB, 21 h, $M_{target}$ = 9,700 g·mol$^{-1}$.
HB-BD-02: hexane, 30 °C, 1.0 mol-% DVB, 24 h, $M_{target}$ = 9,400 g·mol$^{-1}$.
HB-BD-03: hexane, 60 °C, 0.5 mol-% DVB, 21 h, $M_{target}$ = 9,700 g·mol$^{-1}$.

HB-BD-01 was carried out at 30 °C with 0.5 mol-% DVB with respect to butadiene and resulted in a very low degree of crosslinking. The size exclusion chromatography (SEC) trace in figure 2.1.1 is bimodal with two peaks at 14.6 and 14.0 ml retention volume with one peak having a molecular weight a little more than double the other ($M_n = 13{,}500$ vs. $32{,}000\,g{\cdot}mol^{-1}$), indicating that the chains of the higher molecular weight peak HB-BD-01-2 (lower retention volume) derived from coupling of the lower molecular weight chains of peak 1. Additionally, peak 1 (14.6 ml retention volume in figure 2.1.1) has a molecular weight of $M_n = 13{,}500\,g{\cdot}mol^{-1}$, which is about 1.4-times the target molecular weight of $M_{target} = 9{,}700\,g{\cdot}mol^{-1}$. This maybe suggests that there is some evidence of chain branching because in the absence of chain transfer, any chain coupling has to cause an increase in molecular weight. At the same time it may also be possible that there were some impurities in the reaction mixture, leading to some deactivation of the initiator. The deactivation of the initiator would result in a higher molecular weight of the linear chains. Therefore it is possible that peak 1 consists of linear chains. Therefore it was proposed that peak 2 has been derived from coupling reactions of two or more chains from peak 1, the chains represented in peak 2 are likely to be lightly branched. There is also evidence of a shoulder on peak 2, which suggests that there are species present arising from a higher degree of coupling.

Doubling the mole ratio of DVB to 1.0 mol-% in reaction HB-BD-02 resulted in an increase in the extent of crosslinking as has been expected for an increase in DVB mole ratio at the same target molecular weight. The SEC trace in figure 2.1.1 shows two peaks with peak 2 having roughly double the molecular weight of peak 1 ($M_n = 14{,}500$ vs. $38{,}000\,g{\cdot}mol^{-1}$), similar to the SEC trace of reaction HB-BD-01. Therefore it can be assumed that the chains of peak 2 have been derived from coupling reactions of two or more chains from peak 1. Peak 1 of HB-BD-02 has a molecular weight of $M_n = 14{,}500\,g{\cdot}mol^{-1}$, which was about 1.5-times its target molecular weight of $M_{target} = 9{,}700\,g{\cdot}mol^{-1}$. Again, this can be interpreted as either a low degree of branching or some deactivation of the initiator, most likely the latter. The second peak in the SEC trace of HB-BD-02 also shows a clear shoulder suggesting the presence of more highly branched polymers. Although the molecular weights of the two peaks in both HB-BD 01 and 02 are similar the relative intensity (peak heights) of the two peaks in each case is very different. In HB-BD-02 far more of the primary linear chain has undergone coupling - as evidenced by the reduced relative peak height and peak area - even if the degree of crosslinking (as evidenced by molecular weight) is not much different.
The increase in chain coupling as a result of raising the mole ratio of DVB from 0.5% to 1.0% (reactions HB-BD-01 and HB-BD-02) is obviously due to the fact that more DVB has been incorporated into the polymer chains which has in turn increased the likelihood of chain coupling. Unfortunately, it could not be accurately determined whether all of the DVB was consumed into the polymer chains or only a part of it.

The next step in the investigation of copolymerisation was to keep the DVB ratio constant and to vary the reaction temperature. Reaction HB-BD-03 was identical to HB-BD-01 except that the temperature was raised to 60 °C which resulted in a dramatically increased extent of crosslinking. The SEC trace in figure 2.1.1 shows three peaks with peak 2 again being about double the molecular weight of peak 1 ($M_n = 16{,}200$ vs. $30{,}500\,g{\cdot}mol^{-1}$). However, in this case peak 3 has a relatively high molecular weight and a high polydispersity suggesting that HB-BD-03 was much more highly branched and represents an overlay of many different branched structures. To complete the picture, another reaction was carried out at the elevated temperature of 60 °C, and with a higher DVB composition than in HB-BD-03. Hence, the DVB content was increased from 0.5 to 1.0 % DVB at 60 °C (HB-BD-04) but gelation occurred before full conversion. Therefore any further increase in temperature or DVB content was deemed unnecessary, because based on the observations already made only faster gelation was to be expected.

It should be noted that a comparison of reaction HB-BD-01, HB-BD-02 and HB-BD-03 was possible due to the fact that all reactions had been carried out to high conversions ($> 85\,\%$). Therefore the linear analogues (i.e. chains yielded in absence of crosslinking agent, see figure 2.0.2 on page 19) had a very similar chain length, ensuring that the same extent of crosslinking would lead to the same molecular weight and, more importantly, a different extent of crosslinking would lead to a different molecular weight. The fact that the peaks which were very likely linear chains (peak 1 in each case in figure 2.1.1) did not align that well in the SEC trace as they were supposed to be might very well be due to variations in flow rate behaviour rather than variations in molecular weight.

As previously mentioned hexane had been chosen as the solvent for these reactions because it is non-polar, like toluene but with hexane as the solvent, chain transfer would not be possible. However it was thought logical to repeat at least one reaction in toluene, to see if the outcome would be similar. The most successful reaction in terms of branching, HB-BD-03, was chosen to be repeated in toluene. Unfortunately, the reaction in toluene (HB-BD-05) resulted in gelation instead. This would suggest that the degree of crosslinking was higher in toluene than it was in hexane, possibly due to a slightly difference in polarity. This means that the results in hexane are not directly transferable to reactions in toluene, although the influences of temperature and amount of DVB should be the same.

The microstructure of the resulting polymers was investigated by nuclear magnetic resonance spectroscopy (NMR) and in each case the vinyl content (1,2-enchainment) has been found to be eight to nine percent (see table 2.1.2), which would have been expected for the polymerisation of polybutadienes in the absence of any polar additives.[8]

**Table 2.1.2:** Preparation of branched polybutadiene by DVB addition without chain transfer additive. Molecular weight data correspond to figure 2.1.1.

| Code | yield/ % | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI | vinyl/ % |
|---|---|---|---|---|---|
| HB-BD-01 | 91 | 17,900 | 22,700 | 1.3 | 9 |
| HB-BD-02 | 88 | 19,600 | 29,500 | 1.5 | 8 |
| HB-BD-03 | 99 | 32,300 | 85,600 | 2.7 | 9 |
| HB-BD-04[a] | Gelation | | | | |
| HB-BD-05[b] | Gelation | | | | |

[a] Conditions: hexane, 60 °C, 1.0 mol-% DVB, 19 h, $M_{target} = 10{,}000$ g·mol$^{-1}$.

[b] Conditions: toluene, 60 °C, 0.5 mol-% DVB, 19 h, $M_{target} = 9{,}900$ g·mol$^{-1}$.

In summary it has been shown that not only an increase in the mole ratio of DVB but also an increase in temperature leads to more chain coupling. While a higher mole ratio of DVB is expected to affect exclusively the rate of incorporation of DVB into the polymer, and therefore the likelihood of chain coupling, the influence of temperature could not be determined precisely. Presumably both, the amount of DVB incorporated into the linear chains and the crosslinking efficiency (i.e. the reaction of the second vinyl group of the crosslinker) have been improved by an increase in temperature. Hence, all subsequent reactions have been carried out at 60 °C.

## 2.2 Anionic polymerisation of butadiene in toluene - the impact of chain transfer

In all controlled chain growth polymerisation mechanisms, chain transfer reactions result in a reduction in the molecular weight and an increase in the polydispersity compared to an analogous reaction in which chain transfer is absent. Sherrington exploited chain transfer to help prevent gelation in the synthesis of branched polymers *via* a free radical copolymerisation involving a difunctional monomer which serves as a crosslinking agent.[2] In the absence of chain transfer, gelation was unavoidable. In attempting to adapt the Strathclyde approach to use with living anionic polymerisation, we are faced with a further challenge - the absence of inherent chain termination reactions. It can be seen from the data in table 2.1.2 that with even very low levels of crosslinking agents, gelation is almost unavoidable at high conversions. Since the polymer chains remain living after complete consumption of all monomer, the living chains are capable of reacting with the second vinyl group on the DVB until gelation eventually occurs. The introduction of chain transfer to prevent gelation is therefore even more important when using a living polymerisation mechanism.

For this work potassium *tert*-butoxide (KOtBu) has been chosen as the Lewis base to promote chain transfer to toluene. Therefore two variables are to be considered in the investigation of chain transfer polymerisation: Firstly the ratio of KOtBu : BuLi (initiator) and secondly the target molecular weight ($M_{target}$). Here, $M_{target}$ describes the molecular weight which would be produced without chain transfer. It should be noted that $M_{target}$ is essentially a different expression for initiator concentration, but $M_{target}$ makes it more intuitive when the obtained molecular weights are compared to it.

All the reactions using KOtBu were carried out at a constant temperature of 60 °C which was adopted as a result of preliminary experiments described earlier, where this temperature had been found to be suitable for copolymerisation with the crosslinking agent. Each reaction was also carried out in a reaction flask of the same volume, using the same volume of solvent and mass of monomer. In each case 5 g of butadiene monomer have been used in 50 ml of toluene (with the exception of HB-BD-07 and HB-BD-08). Care was taken to have the correct KOtBu : BuLi ratio, as this is the most important variable in this series of reactions and directly affects the degree of chain transfer. Additionally, care was taken to recover the polymers as completely as possible, so the yield would accurately represent the conversion. Hence, the samples have not been recovered by precipitation (with the exception of HB-BD-09) but through solvent evaporation at room temperature, initially at atmospheric pressure but under reduced pressure in the later stages of the drying process. The polymers were dried to a constant mass.

The aim of this series of reactions was to find conditions where an appropriate degree of chain transfer occurs at 60 °C under the reaction conditions. Most importantly the obtained molecular weights can later be compared to reactions where a crosslinking agent is also present. This will give a good indication of how much crosslinking affects the molecular weight.

Chain transfer to toluene can also occur in the absence of any Lewis base, as has been shown for the anionic polymerisation of styrene[62] although the rate is very slow and only has a significant impact upon molecular weight and polydispersity in high molecular weight polymers. Therefore three initial polymerisation reactions were carried out without KOtBu which where conducted to produce polymers with a target molecular weight $M_{target}$ at approximately 10,000 g·mol$^{-1}$ to assess the impact of temperature upon chain transfer. These reactions - HB-BD-06, HB-BD-07 and HB-BD-08 (figure 2.2.1 and table 2.2.1) - were carried out at room temperature, 50 °C and 70 °C respectively and no detectable chain transfer was observed (see figure 2.2.1). The molecular weights were very close to the target molecular weight and the polydispersity was very narrow (see table 2.2.1). Hence no chain transfer was observed in the absence of KOtBu for a target molecular weight of about 10,000 g·mol$^{-1}$. Additionally, these results show that the vinyl groups of 1,2-units of polybutadiene are not capable to introduce branching.

**Table 2.2.1:** Investigation of the temperature dependence of butadiene polymerisation in toluene in the absence of both DVB and KOtBu. Molecular weight data for HB-BD-06, HB-BD-07 and HB-BD-08 correspond to the SEC traces in figure 2.2.1.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-06 | 14.6 | 10,200 | 10,600 | 1.04 |
| HB-BD-07 | 14.7 | 10,300 | 10,600 | 1.03 |
| HB-BD-08 | 14.6 | 11,600 | 12,000 | 1.03 |

HB-BD-06: toluene, RT, 24 h, $M_{target}$ = 9,700 g·mol$^{-1}$.

HB-BD-07: toluene, 50 °C, 20.5 h, $M_{target}$ = 9,600 g·mol$^{-1}$, 2 g scale.

HB-BD-08: toluene, 70 °C, 15 h, $M_{target}$ = 9,800 g·mol$^{-1}$, 1.5 g scale.

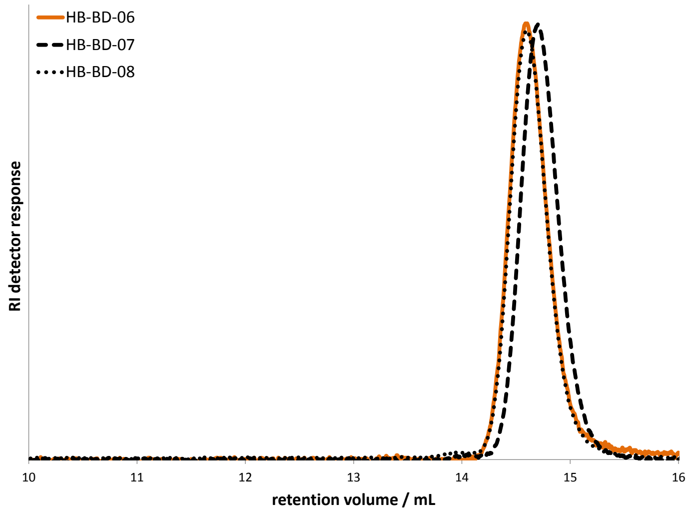

**Figure 2.2.1:** SEC analysis of HB-BD-06, HB-BD-07 and HB-BD-08. For molecular weight data see table 2.2.1.
HB-BD-06: toluene, RT, 24 h, $M_{target} = 9{,}700\,g{\cdot}mol^{-1}$.
HB-BD-07: toluene, 50 °C, 20.5 h, $M_{target} = 9{,}600\,g{\cdot}mol^{-1}$, 2 g scale.
HB-BD-08: toluene, 70 °C, 15 h, $M_{target} = 9{,}800\,g{\cdot}mol^{-1}$, 1.5 g scale.

All further reactions were carried out with KOtBu. A series of reactions were carried out in which the target molecular weight and ratio of potassium *tert*-butoxide : butyllithium was varied (table 2.2.2). In an initial reaction (HB-BD-09) a KOtBu : BuLi ratio of 1 : 1 was used at a target molecular weight of $9{,}600\,g{\cdot}mol^{-1}$. This resulted in a very high degree of chain transfer. The obtained molecular weight of $M_n = 250\,g{\cdot}mol^{-1}$ was significantly lower than the target molecular weight ($M_{target} = 9{,}600\,g{\cdot}mol^{-1}$), the polydispersity was very high (PDI = 16) and the majority of chains (>77 %) had a benzyl end group, indicating initiation *via* chain transfer. It would appear as if these reaction conditions would be ideal for subsequent reactions with a crosslinking agent present however this was not the case and an initial attempt to create branched polymers under these conditions (with 2 mol-% DVB) resulted in almost instantaneous gelation in a dangerously exothermic reaction. KOtBu not only promotes chain transfer but also substantially increases the rate of propagation in the polymerisation of butadiene[63] and consequently further chain transfer reactions were carried out with a lower ratio of KOtBu : BuLi. Additionally, subsequent reactions we carried out using less initiator (to give higher target molecular weights) since a lower concentration of propagating species also slows down the overall reaction, even if the rate of propagation per chain end remains the same. For details of subsequent reactions see table 2.2.2.

**Table 2.2.2:** Reaction conditions for the preparation of a series polybutadiene polymers to investigate the impact of chain transfer to solvent in the absence of a branching agent. Additionally, the vinyl content in the polybutadiene chains is presented as calculated from NMR. All reactions were carried out in toluene at 60 °C.

| Code | KOtBu : BuLi | $M_{target}$ / g·mol$^{-1}$ | time / min | vinyl / % |
|---|---|---|---|---|
| HB-BD-09 | 1.0 | 9,600 | 17 h | 36 |
| HB-BD-10 | 0.1 | 19,200 | 60 | 26 |
| HB-BD-11 | 0.2 | 41,800 | 60 | 30 |
| HB-BD-12 | 0.2 | 19,200 | 60 | 32 |
| HB-BD-13 | 0.2 | 10,300 | 10 | 25 |
| HB-BD-14 | 0.2 | 5,300 | 5 | 38 |

**Table 2.2.3:** Molecular weight data for HB-BD-09 to HB-BD-14 as calculated from the SEC traces in figure 2.2.2. Additionally, the percentage of benzyl-initiated chains is given as calculated from NMR. For experimental conditions see table 2.2.2.

| Code | Peak ret vol / ml | $M_n$ / g·mol$^{-1}$ | $M_w$ / g·mol$^{-1}$ | PDI | benzyl-initiated / % |
|---|---|---|---|---|---|
| HB-BD-09 | 14.8 | 250 | 4,000 | 16.1 | 77[a] |
| HB-BD-10 | 13.4 | 5,000 | 13,400 | 2.7 | 72 |
| HB-BD-11 | 13.3 | 8,400 | 17,500 | 2.1 | 90 |
| HB-BD-12 | 13.5 | 8,900 | 12,700 | 1.4 | 87 |
| HB-BD-13 | 14.0 | 5,200 | 8,700 | 1.7 | 51 |
| HB-BD-14 | 14.4 | 3,900 | 5,500 | 1.4 | 58 |

[a] Due to loss of low molecular weight polymer during precipitation, this value was supposedly much higher in the original polymer.

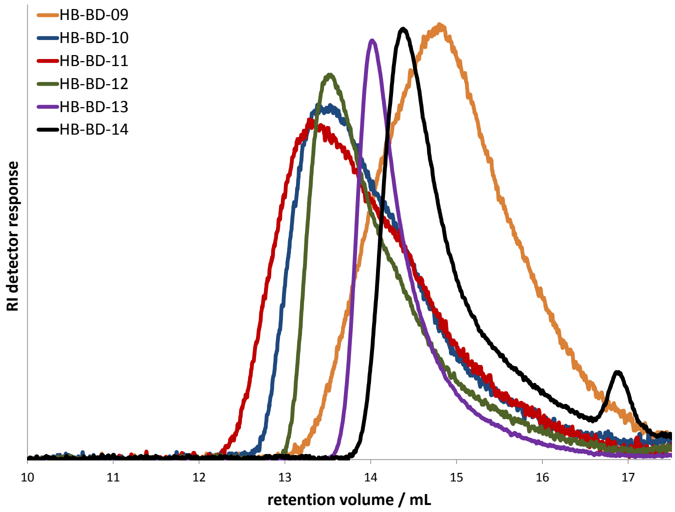

**Figure 2.2.2:** SEC analysis of HB-BD-09 to HB-BD-14. For the reaction conditions and molecular weight data see tables 2.2.2 and 2.2.3.

The determination of the reaction time is a difficult task for these polymerisations. For instance, no colour change is observable at the point where all the monomer has been consumed. Sampling would have been a possibility, but this always carries the risk of contamination of the reaction mixture. Additionally, it might not have been clearly evident from the SEC graph whether there had been a certain degree of contamination or not. Therefore it was decided to terminate the reactions deliberately before full conversion, but nonetheless at high conversion. Because care was taken to collect the polymer as completely as possible, the yield can be regarded as a reasonably accurate measure of conversion of monomer. If the yield is lower than 100 %, the rate of the reaction can be estimated. The reaction times (i.e. the time of deliberate termination) and the yields for reactions HB-BD-09 to HB-BD-14 are shown in table 2.2.4.

Reaction HB-BD-10 was carried out with the aim of utilising a much longer reaction time than with HB-BD-09. Therefore the KOtBu : BuLi ratio was lowered to 0.1 : 1 in the assumption that the polymerisation rate would decrease. At the same time the target molecular weight was increased to $M_{target} = 19{,}200\ g{\cdot}mol^{-1}$ (i.e. the number of propagating species was lower). The reaction was terminated after 60 min at a yield of 89 %. Hence the rate of reaction was successfully lowered. The obtained molecular weight ($M_n = 5{,}000\ g{\cdot}mol^{-1}$) was significantly lower than the target molecular weight, the polydispersity was high (2.7) and the majority of chains (72 %) had a benzyl end group, indicating a significant extent of re-initiation *via* chain transfer. Changing the ratio of KOtBu : BuLi to 0.2 : 1 in reaction HB-BD-12 dramatically increased the degree of chain transfer as is evident from the fact that now 87% of chains had a benzyl end group and it was decided to keep the KOtBu : BuLi ratio constant at 0.2 : 1 for subsequent reactions and alter the target molecular weight instead. An increase of the target molecular weight to $M_{target} = 41{,}800\,g{\cdot}mol^{-1}$ by reducing the amount of BuLi in reaction HB-BD-11 slightly increased the amount of benzyl-initiated chains to 90%.

It was of interest to prepare branched polymers with a variety of structures and molecular weights. Of particular interest was the synthesis of (hyper)branched polymers with low molecular weights ($<20{,}000\,g{\cdot}mol^{-1}$). Thus it was also of interest to investigate the chain transfer process in lower molecular weight polymers. Therefore the KOtBu : BuLi ratio was kept at 0.2 : 1 and the target molecular weight was reduced. The target molecular weight for HB-BD-13 was $M_{target} = 10{,}300\,g{\cdot}mol^{-1}$ and the degree of chain transfer dropped dramatically as only 51 % of the chains had a benzyl end group. A further decrease in the target molecular weight for HB-BD-14 with $M_{target} = 5{,}300\,g{\cdot}mol^{-1}$ resulted in 58 % of the chains having benzyl end groups. This was unexpected, because according to literature[62] the degree of chain transfer should decrease with decreasing target molecular weight. Likely the determination of the number of chains having a benzyl end group is prone to some experimental error.

Because a lower $M_{target}$ means that a higher concentration of initiator was used, the reactions were likely to exhibit an increased reaction rate. Therefore the reaction time before termination was reduced to 10 min and 5 min for HB-BD-13 and HB-BD-14, respectively. The yield of 84% and 95% for these reactions shows that this approximately equals the time to full conversion.

The ratio of KOtBu : BuLi has a noticeable impact upon the microstructure of the resulting polymers - generally speaking a higher ratio of KOtBu : BuLi resulted in an increase in the vinyl content (1,2-enchainment).[63] In this series of reactions the vinyl content was as high as 38 % (see table 2.2.2) compared to about 9 % (see table 2.1.2 on page 25) in the absence of KOtBu.

**Table 2.2.4:** Reaction times and yields of reactions HB-BD-09 to HB-BD-14.
The target molecular weight is inversely proportional to the amount of *sec*-BuLi used.
From the reaction time and yield, differing reaction rates can be estimated.

| Code | KOtBu : BuLi | $M_{target}$/g·mol$^{-1}$ | time/min | yield/% |
|---|---|---|---|---|
| HB-BD-09 | 1.0 | 9,600 | 17 h | >47[a] |
| HB-BD-10 | 0.1 | 19,200 | 60 | 89 |
| HB-BD-11 | 0.2 | 41,800 | 60 | 97 |
| HB-BD-12 | 0.2 | 19,200 | 60 | 99 |
| HB-BD-13 | 0.2 | 10,300 | 10 | 84 |
| HB-BD-14 | 0.2 | 5,300 | 5 | 95 |

[a] Due to loss of low molecular weight polymer during precipitation, the yield was supposedly lower than the actual conversion of monomer.

In summary it had been shown that for target molecular weights above 19,200 g·mol$^{-1}$ chain transfer is a useful tool to reduce the amount of initiator required to obtain a certain molecular weight. At lower target molecular weights the extent of chain transfer was significantly reduced, but the reaction time of 5 min for HB-BD-14 showed that it is still a viable and safe option to use these polymerisation conditions.

## 2.3 Anionic copolymerisation of butadiene and divinylbenzene with chain transfer

The previous sections we reported investigations into the copolymerisation of butadiene with DVB in the absence of chain transfer and the impact of various reaction parameters upon the chain transfer polymerisation of butadiene in the absence of DVB. Here the results of the preliminary studies were applied to conducting a series of reactions in which butadiene copolymerised with divinylbenzene by anionic chain transfer polymerisation. It has previously been shown that the presence of even small amounts of crosslinking agent DVB could lead to gelation and in the absence of termination reactions will eventually lead to gelation in most cases. The advantage of exploiting chain transfer during the copolymerisation with a crosslinking agent is that chain transfer should help to inhibit gelation by prematurely terminating chain growth and creating new chains. This has been shown to be the case previously in the case of an analogous free radical mechanism.[2] Incorporating chain transfer processes may also allow a larger ratio of DVB to used, resulting in a higher degree of crosslinking, whilst still producing a soluble polymer with high conversions of monomer.

However, it should be recognised that combining chain branching reactions and chain transfer process will require careful investigation and optimization. In particular it is well known that potassium *tert*-butoxide, the additive used to promote chain transfer, influences the reactivity ratios in a copolymerisation of butadiene with styrene and it is safe to assume the behaviour of styrene and DVB will be similar. Copolymerisation of styrene and butadiene carried out with varying KOtBu : BuLi ratios at an initial styrene concentration of 25 wt-% have been reported and the findings from literature should be disussed in more detail.[8] For an ideal random copolymerisation, the styrene content in the resulting copolymer would have also been 25 % at any conversion. However, in the absence of KOtBu the reactivity ratios are such that the result would be a tapered block copolymer, with butadiene polymerising first and almost no incorporated styrene during the early stages of the reaction. In contrast, it was found the presence of KOtBu dramatically altered the reactivity ratios such that a KOtBu : BuLi ratio of 0.067 resulted in a styrene content in the polymer of 32 % after 20 % monomer conversion and 30 % after 55 % monomer conversion. Hence, according to literature styrene and butadiene copolymerised almost randomly with a slight preference towards styrene .[8] Increasing the KOtBu : BuLi ratio further, caused further increases in the preference to incorporate styrene over butadiene - hence, the reactivity ratio of styrene was increased by an increase of the KOtBu : BuLi ratio and a similar effect was expected for the copolymerisation of divinylbenzene with butadiene. Furthermore potassium *tert*-butoxide is known to increase the rate of polymerisation significantly, as has been observed for the reactions described in section 2.2. The influence of divinylbenzene during chain transfer to toluene is unknown, but the relatively small amounts of divinylbenzene used (in the range of 0.1 mol-% relative to toluene) suggests that there should be no significant impact.

The overarching aim of this work is to produce highly (hyper)branched soluble polymers in a one-pot reaction using readily available starting materials. In all reactions, the aim was to avoid gelation and microgelation. The term microgelation is used in this work to describe the occurrence of insoluble particles in the reaction product. This is in contrast to the term gelation which generally describes the occurrence of a fully crosslinked network (gel) in which all chains are in some way interconnected with each other (i.e. a network). The reactions described below equate to an analogous reaction described in section 2.2 in terms of the reaction conditions, but with divinylbenzene added. Care was taken to make the divinylbenzene concentration and KOtBu : BuLi ratio as accurate as possible. As in section 2.2, great care was taken to recover the product as completely as possible so the yield would represent the conversion accurately. Therefore no precipitation was carried out, which could have resulted in loss of low molecular weight polymer fractions. Branched polybutadienes were synthesised in two different molecular weight ranges with an approximate target molecular weight (for the linear analogue) of i) 20,000 g·mol$^{-1}$ and ii) 5,000 g·mol$^{-1}$. These values were chosen with the aim of producing both high molecular weight, long-chain branched polymers and low molecular weight hyperbranched polymers and each constitutes slightly different synthetic challenges. In both cases, (micro)gelation must be avoided. In the lower molecular weight region, difficulties were expected to arise from a higher rate of propagation caused by the higher amount of initiator (i.e. a higher number of propagating species at the same time). Thus, issues with heat transfer during the reaction might occur. The reactions to produce higher molecular weight branched polymers will be discussed first and followed by the lower molecular weight reactions. In the initial reactions a larger mole faction of DVB was used than in the preliminary studies with the hope that chain transfer would inhibit gelation. HB-BD-15 was carried out using similar conditions to HB-BD-10 (KOtBu : BuLi = 0.1 : 1, $M_{target}$ = 20,300 g·mol$^{-1}$, 60 °C, 50 ml toluene, 5 g scale) with 5 mol-% DVB. Gelation occurred after 22 min suggesting that under these conditions, chain transfer was not able to prevent gelation occurring with the higher mole ratio of DVB. A second reaction, HB-BD-16, was conducted based on similar conditions to HB-BD-11 (table 2.2.4) with a higher target molecular weight ($M_{target}$ = 36,900 g·mol$^{-1}$,) and higher ratio of KOtBu : BuLi (0.2 : 1). All other parameters were kept constant (60 °C, 50 ml toluene, 5 g scale and 5 mol-% DVB). The rationale for these modifications was that the higher molecular weight and increased amount of KOtBu would result in enhanced chain transfer and less chance of gelation, however, gelation again occurred fairly rapidly, this time after 9 min. Useful analysis of gels is practically impossible so the reaction was repeated (HB-BD-17) and terminated earlier, after 7 min, prior to the gel point, resulting in a soluble product which could be analysed by SEC. The molecular weight of the resulting polymer was $M_n = 120{,}000\,g\cdot mol^{-1}$ with a polydispersity PDI = 2.9 (see table 2.3.1).

**Table 2.3.1:** Molecular weight data for HB-BD-17 determined from the SEC trace in figure 2.3.1.

| Code | Peak ret vol/ml | $M_n/g\cdot mol^{-1}$ | $M_w/g\cdot mol^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-17 | overall | 120,000 | 350,000 | 2.9 |
| HB-BD-17-1 | 12.5 | 74,000 | 85,000 | 1.15 |
| HB-BD-17-2 | 12.0 | 340,000 | 604,000 | 1.8 |

Conditions: toluene, 60 °C, 5.0 mol-% DVB, KOtBu : Li = 0.2 : 1, $M_{target} = 38{,}200\ g\cdot mol^{-1}$, 7 min.

The molecular weight distribution was bimodal (see figure 2.3.1) and the molecular weight of a broad peak in the retention volume range 10-12 ml was $M_n = 340{,}000\,g\cdot mol^{-1}$, PDI = 1.8 and a peak to higher retention volumes with a maximum at approximately 12.5 ml had a molecular weight (Mn of 74,000 $g\cdot mol^{-1}$. The high molecular weight and the bimodality of the distribution of the polymer would strongly suggest a high degree of branching had occurred. Moreover the tailing to low molecular weight (retention volume 13-15 ml) would also suggest significant amounts of chain transfer. However the recovered yield was only 25 % (due to premature termination) and accurately represents the conversion due to the careful recovery of the polymer. The fact that chain branching had occurred at relatively low conversions would imply that DVB had been incorporated into the polymer at this early stage in the reaction which is entirely consistent with the impact of potassium *tert*-butoxide on reactivity ratios of butadiene and DVB.

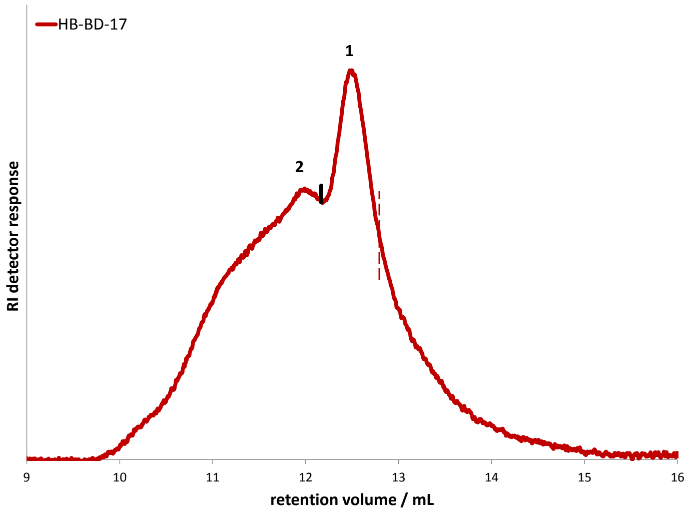

**Figure 2.3.1:** SEC analysis of HB-BD-17. Dashed line indicates retention volume of target molecular weight. For molecular weight data see table 2.3.1.
Conditions: toluene, 60 °C, 5.0 mol-% DVB, KOtBu : Li = 0.2 : 1,
$M_{target}$ = 38,200 g·mol$^{-1}$, 7 min.

Although these results were encouraging, one of our primary aims was to produce soluble polymers at high monomer conversion, so it was necessary to modify reaction conditions to delay the onset of gelation. The two obvious ways to achieve this aim are to increase the extent of chain transfer by increase the ratio of KOtBu : BuLi or reducing the mole fraction of DVB. Since previous reactions with higher ratios of KOtBu : BuLi had been dangerously exothermic it was decided to reduce the mole fraction of DVB from 5 mol % in HB-BD-17 to 1 mol % in the next reaction, HB-BD-18. Microgelation occurred after approximately 43 % monomer conversion, a significant improvement upon the value of 25 % achieved in HB-BD-17 but still some way short of high conversion. Experiment HB-BD-19 was carried out in identical fashion with the exception of a lower target molecular weight to $M_{target}$ = 18,700 g·mol$^{-1}$ although this resulted in only a slight improvement and gelation occurred at about 49 % conversion. This was a slight improvement compared to 43 % in HB-BD-18. Further improvements would require either a further reduction of the amount of DVB or an increase in the extent of chain transfer. At this point it was considered whether the appropriate ratio of DVB could be theoretically predicted to avoid gelation. In the introduction (chapter 1.2.2), equation 19 was derived based on theoretical models from literature.

$$x = \frac{M_{monomer}}{M_{w,linear} \times [DVB]} \tag{19}$$

The variable x is the conversion at the point of gelation, $M_{monomer}$ denotes the molecular mass of the monomer, [DVB] is the amount of DVB (value in mol × 10$^{-2}$) and $M_{w,\,linear}$

is the weight-averaged molecular weight of the linear analogue. Despite the theoretical assumptions made in this equation as discussed in the introduction, the results of the reactions HB-BD-17, HB-BD-18 and HB-BD-19 were used to verify the predictions. Thereby it was possible to see whether the equation could be used to predict the outcome of future reactions. For $M_{monomer}$ the molar mass of butadiene (54.1 g·mol$^{-1}$) was used for simplification, despite the fact that a second monomer is present. This is reasonable as the amount of DVB was 5 mol % or less. For $M_{w,\ linear}$, $M_{target}$ could have been used. However, the influence of chain transfer would not have been captured by using this value and therefore, the $M_w$ determined in the corresponding reactions where chain transfer occurred (without DVB) in section 2.2 was used as $M_{w,\ linear}$ (i.e. the $M_w$ from HB-BD-11 was used in predicting the outcome of reactions HB-BD-17 and HB-BD-18 and $M_w$ from HB-BD-12 was used for HB-BD-19). This is a legitimate approach, as the reactions are identical to each other apart from the presence of DVB. For the comparison of the predictions with the experiments, the yields were used as the variable x (conversion at the point of gelation). This is slightly inaccurate as HB-BD-17 was terminated just before gelation, HB-BD-18 showed some microgelation and HB-BD-19 showed extensive gelation. Nonetheless, using the yields as the variable x should at least give an appropriate estimate and the results are shown in table 2.3.2.

**Table 2.3.2:** Comparison of the theoretical prediction of the point of gelation calculated from equation 19 with the yields ( = $x_{exp.}$) of reactions HB-BD-17, HB-BD-18 and HB-BD-19.

| Code | $M_{w,\ linear}$/g·mol$^{-1}$ | [DVB]/10$^{-2}$ | $x_{exp.}$$^{b}$/ % | $x_{theor.}$$^{c}$/ % |
|---|---|---|---|---|
| HB-BD-17 | 17,500 ( = HB-BD-11[a]) | 5 | 25 | 6 |
| HB-BD-18 | 17,500 ( = HB-BD-11[a]) | 1 | 43 | 31 |
| HB-BD-19 | 12,700 ( = HB-BD-12[a]) | 1 | 49 | 43 |

$M_{monomer}$ = 54.1 g·mol$^{-1}$ was used in the calculation.

[a] See table 2.2.3 in section 2.2 on page 29.

[b] Denotes the yield. reactions were terminated at the point of gelation.

[c] Theoretical prediction of the point of gelation.

The theoretical prediction underestimates the conversion at the point of gelation, as can be seen from table 2.3.2. For HB-BD-17 the deviation of the theoretical from the experimental value was significant (76 %). However, for HB-BD-18 and HB-BD-19 the deviation of the theoretical value from the experimental yield was much smaller (relative deviation of 28 % and 12 %). Numerous reasons could have been responsible for the better agreement of the values for HB-BD-18 and HB-BD-19, for instance the higher yield and the lower amount of DVB. Moreover absolute point of gelation is not easy to define accurately because anything between some microgelation and complete gelation could be described by this term. In light of the assumptions made the predictions for HB-BD-18 and 19 acceptable for practical use. To further test this theoretical prediction the next reaction was carried out under the same conditions as HB-BD-19 but the amount of amount of DVB was reduced from 1 % to 0.31 mol-%. Under these conditions equation 19 predicts the theoretical conversion at the point of gelation to be 137 % ($M_{monomer} = 54{,}1\,g{\cdot}mol^{-1}$, $M_{w,\,linear} = 12{,}700\,g{\cdot}mol^{-1}$, $[DVB] = 0.31 \times 10^{-2}$). Because an actual polymerisation obviously can only have a maximum conversion of 100 % of monomers, no gelation is to be expected if the calculated value is higher than 100 %. Accordingly, HB-BD-20 was terminated after 20 minutes with a yield of 97 % (effectively equating to 100 % conversion) - no gelation had occurred. Hence, the optimum amount of DVB for the current set of conditions (KOtBu : BuLi = 0.2 : 1, $M_{target} \approx 20{,}000\,g{\cdot}mol^{-1}$) has to be between 0.31 mol-% (HB-BD-20) and 1.0 mol-% (HB-BD-19, gelation at 49 % conversion). The molecular weight was $M_n = 19{,}100\,g{\cdot}mol^{-1}$, $M_w = 61{,}000\,g{\cdot}mol^{-1}$ and the polydispersity PDI = 3.2 (see table 2.3.3). The molecular weight and shape of the SEC chromatogram (figure 2.3.2), suggests a considerable fraction of HB-BD-20 was branched.

**Table 2.3.3:** Molecular weight data for HB-BD-20 and HB-BD-21 as determined from the SEC traces in figure 2.3.2. The reactions were carried out in order to fine tune the DVB concentration for maximised branching without gelation.

| Code | Peak ret vol/ml | $M_n/g{\cdot}mol^{-1}$ | $M_w/g{\cdot}mol^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-20 | 13.1 | 19,100 | 61,000 | 3.2 |
| HB-BD-21 | 12.8 | 23,000 | 195,000 | 8.5 |

HB-BD-20: 0.31 mol-% DVB, $M_{target} = 20{,}700\ g{\cdot}mol^{-1}$.
HB-BD-21: 0.4 mol-% DVB, $M_{target} = 20{,}300\ g{\cdot}mol^{-1}$.
Further conditions: toluene, 60 °C, KOtBu : BuLi = 0.2 : 1, 20 min.

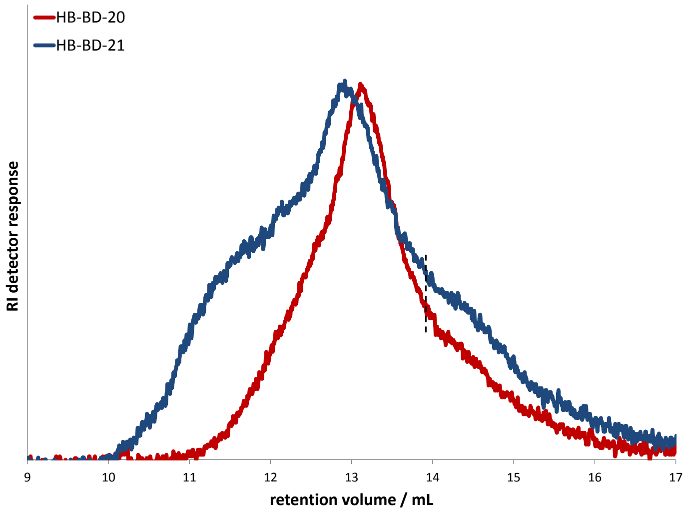

**Figure 2.3.2:** SEC analysis of HB-BD-20 and HB-BD-21. Dashed line indicates target molecular weight. Molecular weights are presented in table 2.3.3.
HB-BD-20: 0.31 mol-% DVB, $M_{target}$ = 20,700 g·mol$^{-1}$.
HB-BD-21: 0.4 mol-% DVB, $M_{target}$ = 20,300 g·mol$^{-1}$.
Further conditions: toluene, 60 °C, KOtBu : BuLi = 0.2 : 1, 20 min.

In an attempt to find the optimal mole fraction of DVB to maximise chain branching the amount of DVB was increased to 0.4 mol-% based on the theoretical predication that onset of gelation would occur at 106 % conversion ($M_{monomer} = 54{,}1$ g·mol$^{-1}$, $M_{w,\ linear} = 12{,}700$ g·mol$^{-1}$, $[DVB] = 0.4 \times 10^{-2}$). This means that the actual polymerisation, which can never exceed 100 % conversion of monomers, should not show gelation.

**Table 2.3.4:** Preparation of branched polybutadiene at low molecular weight.

| Code | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI | yield % | vinyl/ % |
|---|---|---|---|---|---|
| HB-BD-22 | 5,800 | 11,300 | 1.9 | 80 | 35 |
| HB-BD-23 | 9,500 | 20,300 | 2.1 | 60[a] | 30 |
| HB-BD-24 | 8,500 | 14,700 | 1.7 | 82 | 32 |
| HB-BD-25 | 12,600 | 27,100 | 2.2 | 96 | 37 |
| HB-BD-26[b] | 14,900 | 27,600 | 1.6 | 97 | 27 |

[a] Some microgelation occurred.
[b] Reaction carried out in benzene.

HB-BD-21 was terminated after 20 minutes and again showed no evidence of gelation at a yield/conversion of 92 %. The molecular weight of the resulting polymer was determined as $M_n = 23{,}000$ g·mol$^{-1}$, $M_w = 195{,}000$ g·mol$^{-1}$ and the polydispersity was PDI = 8.5 (see table 2.3.3). As expected the higher fraction of DVB has resulted in more chain coupling (a greater extent of crosslinking) as suggested by the molecular weight of HB-BD-20 compared to HB-

BD-20. The SEC traces of both reactions are superimposed in figure 2.3.2 and the additional shoulder at low retention volumes in HB-BD-21 is consistent with greater chain coupling.

Different challenges were faced in the synthesis of lower molecular weight hyperbranched polymer. The presence of potassium *tert*-butoxide and a higher concentration of initiator will both serve to increase the rate of polymerisation and a dangerous overheating of the reaction could occur. Based on preliminary experiments the conditions used in reaction HB-BD-14 (table 5) were chosen for the preparation of lower molecular weight polymers. The KOtBu : BuLi ratio was 0.2 : 1 as in the reactions described above, hence the same effect of early DVB incorporation should occur and the molecular weight and PDI of HB-BD-14 would suggest that chain transfer was observed. The reaction time of HB-BD-14 was only 5 min and yielded a conversion of 95 % (see table 2.2.4 on page 32) and was this time considered to be long enough to prevent overheating. The target molecular weight was $M_{target} = 5{,}300\,g{\cdot}mol^{-1}$. Hence, all attempts to produce low molecular weight branched butadiene were based on this set of conditions. Again theoretical predictions were made concerning the amount of DVB to be added to the reaction. For a mole fraction of 0.5 % DVB the theoretical conversion at the point of gelation was calculated to be 204 % ($M_{monomer} = 54{,}1\,g{\cdot}mol^{-1}$, $M_{w,\,linear} = 5{,}300\,g{\cdot}mol^{-1}$, $[DVB] = 0.5 \times 10^{-2}$). This means that no gelation should occur during a reaction with 0.5 mol-% DVB. However this first attempt was deliberately terminated slightly earlier after 4 min and 30 sec to ensure no gelation but still a high yield/conversion. Accordingly, HB-BD-22 showed no microgelation and some chain coupling/branching was evident from the overall molecular weight and PDI (see table 2.3.4), which was above the target molecular weight of $M_{target} = 4{,}950\,g{\cdot}mol^{-1}$. The SEC trace in figure 2.3.3 shows a main peak with a distinct shoulder in the higher molecular weight region (lower retention volume). Separate integration of the peak and the shoulder was carried out. For the peak itself, a molecular weight of $M_n = 5{,}700\,g{\cdot}mol^{-1}$ and a polydispersity of $PDI = 1.2$ was determined (see table 2.3.5). The similarity of this molecular weight to the target molecular weight of $M_{target} = 4{,}950\,g{\cdot}mol^{-1}$ strongly suggests the polymer chains represented in this peak are not branched. Arguably, the small difference in molecular weights is caused simply by the inaccuracy of the SEC measurement. In contrast to that, the molecular weight of the shoulder was significantly higher than the target molecular weight, with a molecular weight of the polymer of $M_n = 21{,}000\,g{\cdot}mol^{-1}$ and a polydispersity of $PDI = 1.2$. Therefore, the polymer chains in this molecular weight region have to be branched.

**Table 2.3.5:** Molecular weight data for HB-BD-22 and HB-BD-23 as derived from the SEC traces in figure 2.3.3.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-22-1 | 14.5 | 5,700 | 6,700 | 1.2 |
| HB-BD-22-1 | shoulder | 21,000 | 25,000 | 1.2 |
| | | | | |
| HB-BD-23-1 | 14.6 | 7,500 | 7,900 | 1.05 |
| HB-BD-23-2 | 13.6 | 28,000 | 40,000 | 1.4 |

HB-BD-22: 0.5 mol-% DVB, $M_{target}$ = 4,950 g·mol$^{-1}$.
HB-BD-23: 1.0 mol-% DVB, $M_{target}$ = 5,150 g·mol$^{-1}$.
Further conditions: toluene, 60 °C, KOtBu : BuLi = 0.2 : 1, 4 min 30 s.

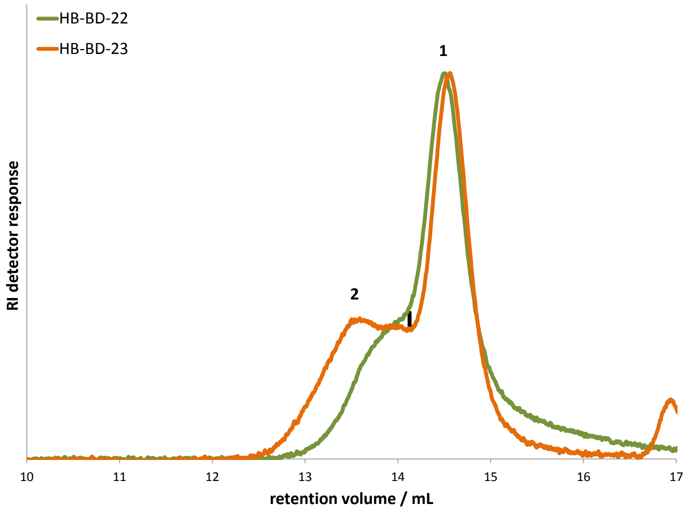

**Figure 2.3.3:** SEC analysis of HB-BD-22 and HB-BD-23. Vertical line indicates integration limit between peaks. For molecular weight data see table 2.3.5.
HB-BD-22: 0.5 mol-% DVB, $M_{target}$ = 4,950 g·mol$^{-1}$.
HB-BD-23: 1.0 mol-% DVB, $M_{target}$ = 5,150 g·mol$^{-1}$.
Further conditions: toluene, 60 °C, KOtBu : BuLi = 0.2 : 1, 4 min 30 s.

In an attempt to increase the extent of crosslinking, the amount of DVB was increased from 0.5 mol-% to 1.0 mol-% in HB-BD-23 and the theoretical conversion at the point of gelation was calculated to be 102 % ($M_{monomer} = 54{,}1$ g·mol$^{-1}$, $M_{w,\,linear}$ = 5,300 g·mol$^{-1}$, [DVB] = $1.0 \times 10^{-2}$). SEC analysis of the resulting polybutadiene showed that it was branched, but some microgelation occurred. The SEC trace of HB-BD-23 is superimposed with HB-BD-22 in figure 2.3.3. HB-BD-23 has a low molecular weight peak 1 (higher retention volume - 14.6 ml) which is very similar to HB-BD-22, but in the higher molecular weight region HB-BD-23 shows an apparently multimodal peak 2. In line with the arguments made above, peak 1 was essentially linear (not branched) as the molecular weight was $M_n = 7{,}500\,g{\cdot}mol^{-1}$ and the polydispersity was PDI = 1.05 (see table 2.3.5). In contrast, peak 2 was definitely branched arising as a result of chain coupling and has the molecular weight of $M_n = 28{,}000\,g{\cdot}mol^{-1}$ (PDI = 1.4). The presence of microgelation would suggest that the ideal amount of DVB under these conditions is between 0.5 mol-% (HB-BD-22) and 1.0 mol-% (HB-BD-23). Additionally, the reaction time for both reactions was 4 min 30 sec, but the yield was 80 % for HB-BD-22 and 60 % for HB-BD-23. While the significant difference might be attributed to the microgelation in HB-BD-23 (which made the complete recovery of the product more difficult), the reason might very well be the different amount of DVB. Divinylbenzene can stabilise an anion better than butadiene and a DVB monomer unit at the chain-end will stabilise the propagating anion more than butadiene, which causes in a higher activation energy to add the next monomer. Therefore the addition of the next monomer is slower than it would be for butadiene on the chain-end. For the reaction as a whole, this means an overall lower rate of propagation the more DVB is involved, which causes a lower yield in the same reaction time. The influence of DVB upon the rate of the reaction was not further investigated. Despite the fact that the reaction time of both HB-BD-22 and HB-BD-23 was only 30 sec shorter than that of HB-BD-14 (95 % yield), we consider deviation from full conversions to be real if a little surprising. Thus in a subsequent reaction, HB-BD-24, the reaction time was extended from 4 min 30 sec to 5 min 30 sec to ensure full conversion and the DVB mole fraction was 0.7 % DVB. The theoretical conversion at the point of gelation was calculated to be 146 % ($M_{monomer} = 54{,}1\,g{\cdot}mol^{-1}$, $M_{w,\,linear} = 5{,}300\,g{\cdot}mol^{-1}$, $[DVB] = 0.7 \times 10^{-2}$). HB-BD-24 was also scaled up to 10 g and was carried out in a reaction flask twice the size of the previous reactions resulting in similar BD pressure therefore ensuring that the scale up had no impact upon the reaction. In this reaction no microgelation was observed and the yield was reasonably high (82 %). Because no microgelation occurred and the conversion of the monomer was apparently not complete, the reaction was repeated (HB-BD-25) and the reaction time increased significantly to 9 min. For better comparability to the previous reactions, the reaction was repeated on the usual 5 g scale.

**Table 2.3.6:** Molecular weight data for HB-BD-24 and HB-BD-25 determined from SEC traces in figure 2.3.4. The influence of reaction time before deliberate termination was investigated.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-24-1 | 14.4 | 6,700 | 7,300 | 1.09 |
| HB-BD-24-2 | shoulder | 22,400 | 28,400 | 1.3 |
| | | | | |
| HB-BD-25-1 | 14.2 | 10,900 | 11,600 | 1.06 |
| HB-BD-25-2 | 13.6 | 44,000 | 64,000 | 1.5 |

HB-BD-24: 5 min 30 s, 10 g scale.

HB-BD-25: 9 min.

Further conditions: toluene, 60 °C, 0.7 mol-% DVB, KOtBu : BuLi = 0.2 : 1, $M_{target}$ = 5,250 g·mol$^{-1}$.

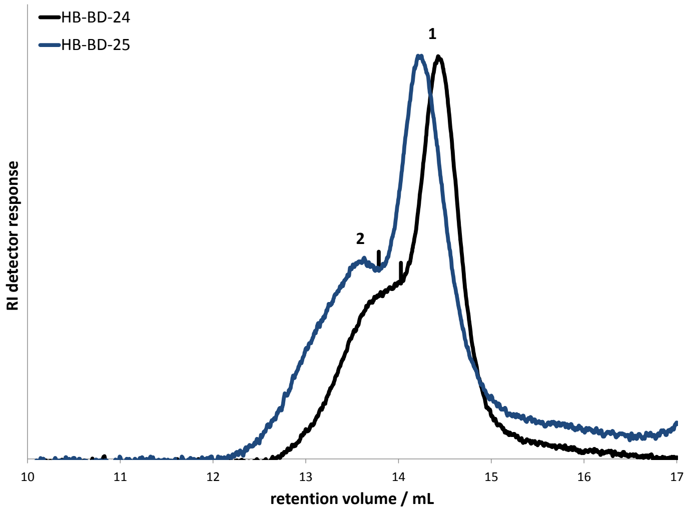

**Figure 2.3.4:** SEC analysis of HB-BD-24 and HB-BD-25. Vertical line indicates integration limit between peaks. For molecular weight data see table 2.3.6.
HB-BD-24: 5 min 30 s, 10 g scale.
HB-BD-25: 9 min.
Further conditions: toluene, 60 °C, 0.7 mol-% DVB, KOtBu : BuLi = 0.2 : 1, $M_{target}$ = 5,250 g·mol$^{-1}$.

HB-BD-25 showed no microgelation at a yield of 96 %. The RI trace of the SEC analysis is superimposed with that of HB-BD-24 in figure 2.3.4. Both reactions show a similar shape, but HB-BD-25 is shifted towards higher molecular weights (lower retention volume). This is consistent, as the higher conversion of HB-BD-25 should give a higher molecular weight. Furthermore, HB-BD-25 shows two distinctive peaks. Peak 1 has a molecular weight of $M_n$ = 10,900 g·mol$^{-1}$ and a polydispersity of PDI = 1.06 (see table 2.3.4). This is above the target molecular weight of $M_{target} = 5{,}250\,g{\cdot}mol^{-1}$, which suggests traces of impurities deactivating some of the initiator. In contrast to that, peak 2 which is broad and has a substantially higher molecular weight, definitely represents branched polybutadiene, as the molecular weight was $M_n = 44{,}000\,g{\cdot}mol^{-1}$ and the polydispersity was PDI = 1.5. Integration of the SEC trace of HB-BD-25 was done for both peaks. The percentage of the total area belonging to peak 2 was 33 % suggesting that at least 33 wt-% of HB-BD-25 comprises branched polymer chains.

It should also be noted that the shape of the chromatograms of polymers HB-BD-22 to 25 are rather similar to those of HB-BD-01 to 03 in which chain transfer was not possible. The shape of the chromatogram would suggest that when the target molecular weight is low the impact of chain transfer is limited. In order to test this hypothesis and establish the extent of chain transfer in these latter reactions HB-BD-25 was repeated in identical fashion except the reaction was carried out in benzene. Benzene was chosen as a solvent almost identical in nature to toluene with only a slightly different polarity but importantly chain transfer to solvent cannot take place as the aromatic protons of benzene are not acidic enough. The slight difference in polarity has some impact on the rate of polymerisation - the polymerisation of butadiene in benzene is slower than it is in toluene[8] - and the reaction time was increased from 9 min to 15 min in order to achieve full conversion as in HB-BD-25 for good comparability. Chain transfer (if it occurs) would be expected to reduce the molecular weight of the linear analogue.

**Table 2.3.7:** Molecular weight data for HB-BD-25 and HB-BD-26 as determined from SEC traces in figure 2.3.5.

| Code | Peak ret vol/ml | $M_n/g{\cdot}mol^{-1}$ | $M_w/g{\cdot}mol^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-25-1 | 14.2 | 10,900 | 11,600 | 1.06 |
| HB-BD-25-2 | 13.6 | 44,000 | 64,000 | 1.5 |
| | | | | |
| HB-BD-26-1 | 14.1 | 11,600 | 12,400 | 1.07 |
| HB-BD-26-2 | 13.5 | 38,400 | 50,700 | 1.3 |

HB-BD-25: toluene, 9 min, $M_{target} = 5{,}250\ g{\cdot}mol^{-1}$.
HB-BD-26: benzene, 15 min, $M_{target} = 5{,}500\ g{\cdot}mol^{-1}$.
Further conditions: 60 °C, 0.7 mol-% DVB, KOtBu : BuLi = 0.2 : 1.

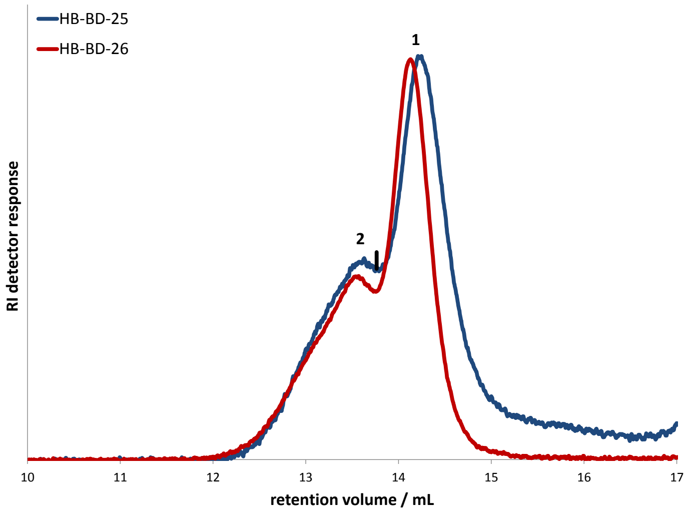

**Figure 2.3.5:** SEC analysis of HB-BD-25 and HB-BD-26. Vertical line indicates integration limit between peaks. For molecular weight data see table 2.3.7.
HB-BD-25: toluene, 9 min, $M_{target}$ = 5,250 g·mol$^{-1}$.
HB-BD-26: benzene, 15 min, $M_{target}$ = 5,500 g·mol$^{-1}$.
Further conditions: 60 °C, 0.7 mol-% DVB, KOtBu : BuLi = 0.2 : 1.

A comparison of the results of HB-BD-25 and 26 can be found in table 2.3.7 and figure 2.3.5. The yield of HB-BD-26 was 97 % and therefore a valid comparison with reaction HB-BD-25 was possible. The SEC trace of HB-BD-26 is superimposed with that of HB-BD-25 in figure 2.3.5 - the two traces are very similar. The only noticeable difference is the slightly more pronounced tailing at higher retention volumes in the main peak of HB-BD-25 and what looks like a slight broadening in this peak but even this is rather minor and is not borne out by the analysis. The molecular weight and PDI of the two main peaks are very similar and are in stark contrast to the preliminary experiments into the impact of chain transfer - see HB-BD-14 (tables 2.2.2 and 2.3.4 as well as figure 2.2.2). It would appear that the level of chain transfer is almost negligible in HB-BD-25 and this may go some way towards explaining the formation of microgelation in HB-BD-23 i.e. chain transfer is a vital factor in inhibiting gelation and the absence of significant levels chain transfer may explain the onset of gelation.

In summary, soluble branched polybutadienes were successfully prepared in high yields. The described strategy proved more successful when making high molecular weight branched polymers with high target molecular weights. HB-BD-20 and HB-BD-21 were probably the most successful with reaction HB-BD-21 having a molecular weight of $M_n = 23{,}000$ g·mol$^{-1}$, $M_w = 195{,}000$ g·mol$^{-1}$ and a polydispersity of PDI = 8.5. The reaction was reasonably fast and an almost quantitative yield of 92 % was achieved after 20 min.
Attempts to prepare branched polymers with lower molecular weights were less successful

resulting a mixture of mainly primary linear chains and some chain branching - approximately 33 % branched polymer was attained in reaction HB-BD-25. The resulting polymer had a molecular weight of $M_n = 12{,}600\ g{\cdot}mol^{-1}$, $M_w = 27{,}100\ g{\cdot}mol^{-1}$ and a polydispersity of PDI = 2.2. The yield was 96 % after 9 min. It is likely that the lower level of branching in the lower molecular weight polymers is due to the shorter chain lengths and shorter reaction times.

The use of potassium *tert*-butoxide as an additive for these reactions was found to be very useful for two reasons. Potassium *tert*-butoxide changes the reactivity ratios to promote the incorporation of the crosslinking agent (divinylbenzene) even at low conversions. As a result, branching can take place continuously during the reaction and not just at the very end, as occurs in the absence of potassium *tert*-butoxide. This makes the branching much more uniform, potentially leading to interesting mechanical properties. Potassium *tert*-butoxide also promotes chain transfer to solvent which is crucial in helping to inhibit crosslinking, and produce soluble products at high conversions. Chain transfer proved to be less effective in the synthesis of low molecular weight branched polymers.

It would be wrong to suggest that all avenues have been explored. It would be possible to further vary the key parameters (namely the relative amounts of initiator, butadiene, potassium *tert*-butoxide and DVB) to try and enhance the degree of crosslinking but time did not permit.

All of the above reactions were carried out in batch reactor in which all of the reaction ingredients were added at the start of the reaction. The use of a batch reactor has some limitations. In a batch reactor, all butadiene is present at the start of the reaction and the ability to tailor the relative rate of propagation, branching and chain transfer is limited. It would be desirable to increase the amount of DVB by an order of magnitude (to increase the extent of crosslinking) and yet still produce a soluble product. This would require dramatic changes to the rates of chain transfer and propagation and such dramatic changes are not possible in a simple batch reaction.

In the next chapter we will describe a series of reactions carried out in a constant feed reactor. In this case the main monomer (butadiene) is added into the reactor at a constant rate during the polymerisation. At any given time the polymerisation may be proceeding under starved monomer conditions and under these conditions the relative rates of propagation and chain transfer (the transfer constant) will be vastly different. The different experimental setup makes it impossible to directly reproduce the reactions above, but also opens the possibilities to further improve the synthesis.

## 2.4 Synthesis of branched polybutadiene in a controlled monomer feedrate reactor

This study has demonstrated it is possible to prepare branched polymers by the anionic copolymerisation of butadiene and DVB in batch reactions. However in these reactions the impact of chain transfer was limited. In these previously described reactions, the experimental set up dictated that all the butadiene (and DVB) monomer was added at the start of the reaction. This section describes a series of relatively large-scale reactions carried out in a reactor in which butadiene monomer could be fed into the reaction at a predetermined metered rate. Hence, the reactions have been carried out under conditions in which the concentration of butadiene monomer is low at any given point in the reaction rather than the batch conditions in the previous parts of this work. This change has implications for the rate of propagation and the extent of chain transfer - the former will be suppressed and the latter enhanced. Under continuous feed it would be expected that for the propagation to be suppressed since the polymerisation will be under almost starved monomer conditions. The reduced rate of propagation will result in an increase in the transfer constant ($k_{trans}/k_{prop}$). It was anticipated that under these conditions the enhanced contribution of chain transfer would serve to inhibit crosslinking and in turn may allow the addition of higher levels of DVB to the copolymerisation. The ultimate aim of these experiments was to increase both the degree crosslinking and the ultimate yield of polymer.

Additional variables arise from the configuration of a constant monomer feed reactor compared to batch reactions. The butadiene (BD) addition into the reactor is characterised by the BD feed rate. The reaction time characterises the period of time over which BD is added into the reactor. Additionally, post reaction heating was carried out, whereby the reaction is not terminated, but the BD feed is switched off. Hereby it is ensured that all the BD has reacted for safety purposes. Due to the reactor size, the temperature was controlled by a cooling/heating jacket rather than an oil bath as in the batch reactions. The temperature of the reactor was measured internally and was 60 °C in all cases in common with the batch reactions previously described. The stirrer speed was kept constant at 300 rpm, except when the heat transfer was not sufficient in which case stirring rate was increased for safety reasons. In a batch reaction, the amount of butadiene was limited due to concerns about pressure whereas in the controlled feed reactor the final polymer concentration (i.e. the amount of polymer in the same volume of solvent) could be much higher since the amount of monomer is low at any given time. The influence of the BD feed rate, of the final polymer concentration and the amount of DVB was investigated in these reactions.

The nomenclature for the reactions described below was thus; reactions were given the code

HB-BD-CF01 where HB-BD refers to hyperbranched butadiene and CF denotes ”continuous feed” in contrast to the experiments described above which were given the code HB-BD-01 etc.

In the previous ”batch” reactions, attempts to prepare low molecular weight, highly (hyper)branched polymers had limited success. It was possible to produce polymers with a high yield and chain branching (for example HB-BD-25 and 26) but the extent of crosslinking was modest. The amount of branching agent (DVB) was kept necessarily low to prevent crosslinking because the impact of chain transfer was negligible.

**Table 2.4.1:** Preparation of branched polybutadiene in a controlled feed reactor. Target molecular weight for all reactions was $M_{target} = 5{,}000\,g{\cdot}mol^{-1}$.

| Code | $M_n$ / g·mol$^{-1}$ | $M_w$ / g·mol$^{-1}$ | PDI | vinyl / % |
|---|---|---|---|---|
| HB-BD-CF01 | 1,900 | 3,000 | 1.6 | 35 |
| HB-BD-CF02 | 4,500 | 14,700 | 3.3 | 25 |
| HB-BD-CF03 | 5,000 | 17,800 | 3.1 | 34 |
| HB-BD-CF04 | 5,300 | 33,200 | 6.3 | 35 |

The initial experiments using the controlled feed reactor were aimed at establishing the impact of a continuous feed of monomer to the reaction upon chain transfer. With this in mind we repeated experiment HB-BD-14 (in which no DVB was added) under continuous monomer feed. However, some modifications to HB-BD-14 were required to account for the continuous monomer feed. Thus the BD feed rate was set to 1.35 L/min in order to produce a total of 200 g of polymer within 60 min plus 30 min post-reaction heating. The final polymer concentration of 11.8 wt-% (correlating to 1,500 g of toluene) was in the range of the polymer concentrations of the batch reactions above, ensuring some comparability.
Due to the absence of a crosslinking agent, the resulting polymer HB-BD-CF01 was linear as is evident from the log(intrinsic viscosity) vs. log(molecular weight) plot in figure 2.4.1.

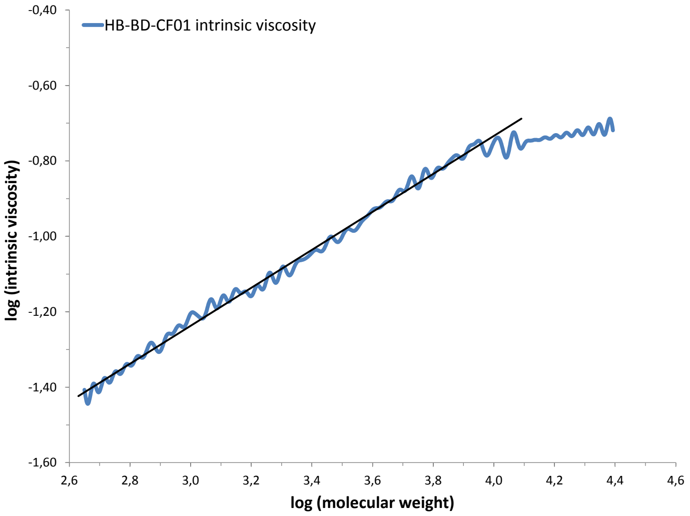

**Figure 2.4.1:** Plot of log(intrinsic viscosity) vs. log(molecular weight) of HB-BD-CF01. The linear correlation over a wide range of molecular weights is an indication for the non-branched nature of the polymer.

In general, a plot of log(intrinsic viscosity) vs. log(molecular weight) gives qualitative information about long chain branching. Branched polymers show a contracted molecular size compared to a linear polymer of the same molecular weight. Therefore their intrinsic viscosity is smaller than for a linear polymer. The triple detection SEC also analyses the samples by right-angle light scattering, determining the molecular size accurately in absolute terms. Hence, long-chain branched polymers can be identified by the log(intrinsic viscosity) vs. log(molecular weight) plot. If there is a mixture of linear and branched polymers present, as is the case for most of the polymers synthesised in this work, the slope of the plot should change after a linear part. The deviation from the linear dependency would indicate long-chain branching. However, for HB-BD-CF01 (figure 2.4.1) the correlation is linear over a wide range of molecular weights indicating an all linear polymer, consistent with the absence of DVB.

As expected, the degree of chain transfer in HB-BD-CF01 was far greater than in the batch reactor, as evidenced by the significant reduction in the molecular weight and an increase in the molecular weight distribution. HB-BD-CF01 had a molecular weight of $M_n = 1{,}900\,g{\cdot}mol^{-1}$ ($M_{target} = 5{,}000\,g{\cdot}mol^{-1}$, see table 2.4.1) compared to $M_n = 3{,}900\,g{\cdot}mol^{-1}$ obtained in HB-BD-14 ($M_{target} = 5{,}300\,g{\cdot}mol^{-1}$, see table 2.2.3 in chapter 2.2). The increased degree of chain transfer was undoubtedly caused by a reduced rate of propagation, thereby favouring the chain transfer reaction over the propagation reaction. The higher degree of chain transfer was also evident from the higher polydispersity of PDI = 1.6 (HB-BD-CF01) compared to PDI = 1.4 (HB-BD-14). The more important factor when it comes to branching reactions though is $M_w$, because longer chains are more likely to incorporate DVB and cause branching. The impact of $M_w$ of the linear chains upon branching was already discussed in the introduction (chapter 1.2.2). The weight-average molecular weight for HB-BD-CF01 was $M_w = 3{,}000\,g{\cdot}mol^{-1}$ as opposed to $M_w = 5{,}500\,g{\cdot}mol^{-1}$ (HB-BD-14). Therefore branching reactions based on HB-BD-CF01 were less likely to cause microgelation than branching reactions based on HB-BD-14 at the same amount of DVB . Thus a subsequent reaction (HB-BD-CF02) was carried out under otherwise identical conditions to HB-BD-CF01 but with the addition with 0.7 mol-% DVB.

At this point it should be noted that it was decided not to add the DVB at the start of the reaction, as was the case in the ”batch” reactions as this would result in DVB being the only monomer present at the initiation of the reaction and would inevitably lead to the formation of insoluble crosslinked particles. Therefore in order to avoid this problem in the controlled feed reactor, DVB was injected after the BD feed had commenced which in turn occurred shortly after the addition of initiator. Generally the BD feed rate is increased steadily over the first 5 minutes (induction period) towards the set feed rate value in order to improve the response of the cooling jacket. This causes some unsteady values for the BD feed rate if the reaction time is adjusted because the ”induction period” is always 5 minutes, which changes the slope of the BD feed rate. Nevertheless the reported values for the BD feed rate are precise. The earliest point at which DVB is added was 6 minutes after the start of the BD feed, i.e. 1 minute after the ”induction period”. The point in time at which injections were made (and samples taken) is reported in terms of the percentage of the total amount of monomer which had been added at this point (% BD feed). The percentage of BD feed quite accurately translates into conversion of monomer at this point as the reaction set-up is inherently designed for polymerisation under starved conditions as mentioned above.

Thus the addition of 0.7 mol-% DVB to reaction HB-BD-CF02 resulted in chain branching of the polybutadiene. The SEC trace of HB-BD-CF02 is pictured in figure 2.4.3, superimposed with that of HB-BD-CF01. The molecular weight for HB-BD-CF02 was $M_n = 4{,}500\,g{\cdot}mol^{-1}$, $M_w = 14{,}700\,g{\cdot}mol^{-1}$ with a PDI = 3.3 (see table 2.4.1). The increase of the molecular weight even beyond the target molecular weight of $M_{target} = 5{,}000\,g{\cdot}mol^{-1}$ proves that HB-BD-CF02 is branched as anionic polymerisation does not allow for an increase of molecular weight beyond the target molecular weight without branching (assuming the absence of impurities). More importantly, the non-linearity of the log(intrinsic viscosity) vs. log(molecular weight) plot in figure 2.4.2 directly proves that long-chain branched polymers were present in HB-BD-CF02 as can be seen from the significant deviation from linearity at log 4.0 (i.e. $10^4\,g{\cdot}mol^{-1}$).

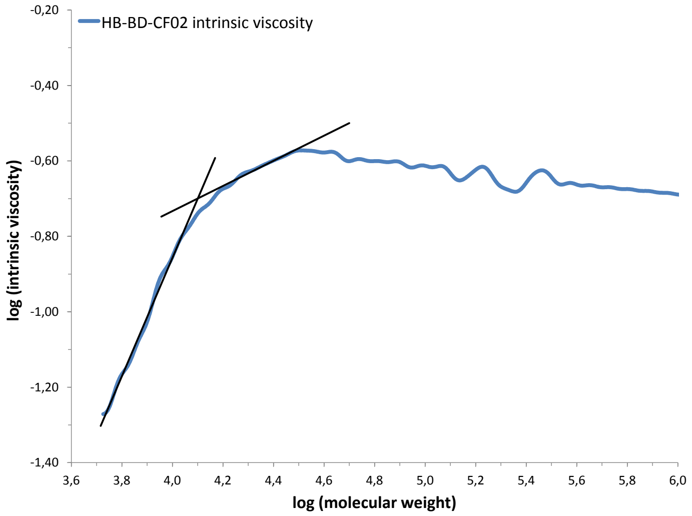

**Figure 2.4.2:** Plot of log(intrinsic viscosity) vs. log(molecular weight) of HB-BD-CF02. The non-linearity of the graph indicates long-chain branching in the polymer.

Reaction HB-BD-CF02 can be considered a success since it produced a branched polymer, in quantitative yield in the absence of any gelation. The objective in subsequent reactions was to explore the various variables associated with the controlled feed reactor set-up in order to increase the degree crosslinking whilst preventing the onset of gelation for the same target molecular weight of $M_{target} = 5{,}000\ g{\cdot}mol^{-1}$.

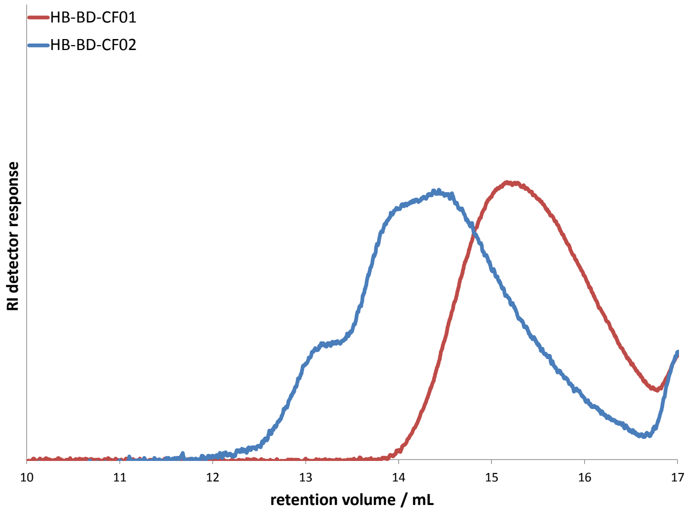

**Figure 2.4.3:** SEC analysis of HB-BD-CF01 and HB-BD-CF02.
HB-BD-CF01: No injection of DVB.
HB-BD-CF02: 0.7 mol-% DVB injected at 6 % BD feed.
Further conditions: toluene, 60 °C, BD feed = 1.35 L/min, 60 min, $M_{target} = 5{,}000\,g{\cdot}mol^{-1}$, 11.8 wt-% polymer, KOtBu : Li = 0.2 : 1, 30 min post-reaction heating.

In the next reaction (HB-BD-CF03) the influence of the BD feed rate was explored. The reaction time was halved from 60 minutes to 30 minutes, which approximately doubles the BD feed rate to 2.83 L/min as the final polymer concentration was kept constant at 11.8 wt-%. The BD feed rate is slightly higher than 2 x 1.35 L/min as a result of the constant induction period of 5 min. The addition of DVB was again carried out after 6 minutes as above, which equates to a BD feed of 13 %. There is therefore a slight inconsistency in that in the previous reaction the DVB was added after approximately 6 % BD feed, but since the DVB was added early in the reaction in both cases, a comparison of this and the previous reaction should still give good evidence of the influence of the BD feed rate.

The SEC trace of HB-BD-CF03 is shown in figure 2.4.4 superimposed with HB-BD-CF02. Overall the degree crosslinking and therefore molecular weight had increased. The molecular weight in HB-BD-CF03 was $M_n = 5{,}000\,g{\cdot}mol^{-1}$, $M_w = 17{,}800\,g{\cdot}mol^{-1}$ and the polydispersity was PDI = 3.1 (see table 2.4.1). The SEC trace of HB-BD-CF03 shows a very pronounced high molecular weight peak at 13 mL (retention volume). In literature a distinct peak at the high molecular weight end of a branched polymer distribution was explained as the coupling of previously branched molecules.[64]

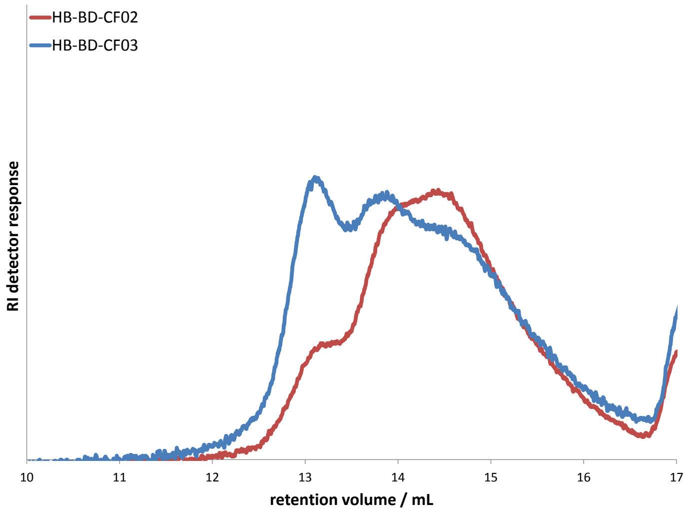

**Figure 2.4.4:** SEC analysis of HB-BD-CF02 and HB-BD-CF03.
HB-BD-CF02: BD feed = 1.35 L/min, 60 min, 0.7 mol-% DVB at 6 % BD feed.
HB-BD-CF03: BD feed = 2.83 L/min, 30 min, 0.7 mol-% DVB at 13 % BD feed.
Further conditions: toluene, 60 °C, $M_{target} = 5{,}000\,g{\cdot}mol^{-1}$, 11.8 wt-% polymer, KOtBu : Li = 0.2 : 1, 30 min post-reaction heating.

A sample was withdrawn from reaction HB-BD-CF03 for SEC analysis after half of the reaction time (at 45 % BD feed) and the SEC trace is shown in figure 2.4.5.

**Table 2.4.2:** Molecular weight data for HB-BD-CF03. The comparison of the molecular weight of the sample during reaction with the final product allows to draw conclusions about the development of branching.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-CF03 after 45% feed | 15.0 | 4,100 | 13,600 | 3.3 |
| HB-BD-CF03 product | 13.1 | 5,000 | 17,800 | 3.6 |

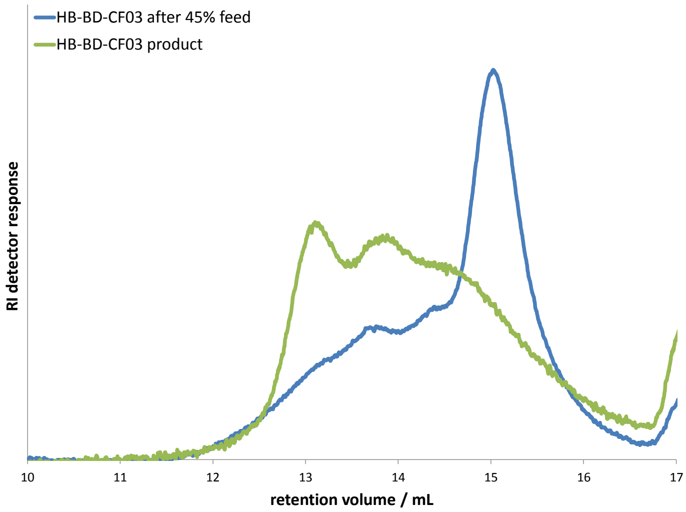

**Figure 2.4.5:** SEC analysis of HB-BD-CF03.
For molecular weight data see table 2.4.2
Conditions: toluene, 60 °C, BD feed = 2.83 L/min, 30 min, $M_{target} = 5{,}000\ g\cdot mol^{-1}$, 11.8 wt-% polymer, 0.7 mol-% DVB at 13 % BD feed, KOtBu : Li = 0.2 : 1, 30 min post-reaction heating.

It is clear that polymerisation HB-BD-CF03 was proceeding and the shape of the chromatogram is interesting and in some way similar to the chromatogram of HB-BD-25 in so much as there is a well-defined and rather narrow peak at approximately 15 ml and then a broader less well-defined, multimodal shoulder to lower retention volumes (higher molecular weight). We might speculate that the narrow peak at 15 ml corresponds to primary, linear chains which have not yet undergone chain coupling, even though these primary chains may contain DVB repeat units, and the broader shoulder at lower retention volumes corresponds to branched polymers arising from chain coupling. Moreover it is almost certain that the higher molecular weight "branched" polymers have formed by coupling of the lower molecular weight primary chains which is consistent with the observation that the peak at 15 ml retention volume is much diminished in intensity in the final product.

It is likely that the increase in the BD feed rate will result in a change in the distribution of the DVB molecules inside the polybutadiene backbone. A higher BD feed rate will increase the concentration of BD monomer inside the reactor and in the competitive copolymerisation of the two monomers a higher BD concentration implies a preferable addition of BD onto the living chain end and a decrease in the rate of incorporation of DVB. Hence DVB might be more evenly distributed throughout the polybutadiene chains, both within any given chain and between chains. It is also certain that the higher BD feed rate will have caused a increase in the rate of propagation and a consequent decrease in chain transfer will have resulted in an increase in the molecular weight of the resultant chains The final molecular weight distribution of HB-BD-CF03 was multimodal, with distinct peaks (13.2 mL and 13.8 mL retention volume) and a shoulder (14.5 mL retention volume) suggest that the branching is not entirely random. It would have been desirable to explore the possibility of continuously feeding the DVB into the reaction as well as the BD monomer but this was not possible using the current experimental set up, which certainly would have made the DVB incorporation much more uniform. However, to explore the impact of the delivery of DVB into the polymerisation, in subsequent reactions the DVB was added in two aliquots with all other experimental conditions remaining unchanged. DVB was injected in two equal aliquots of 0.35 mol-% at 13 % BD feed and 0.35 mol-% at 49 % BD feed, keeping the total amount of DVB constant at 0.7 mol-%. It is clear that adding the DVB in two separate injections has a significant impact upon the molecular weight distribution of the resulting polymer compared to HB-BD-CF03. The SEC trace of HB-BD-CF04 is superimposed with that of HB-BD-CF03 in figure 2.4.6.

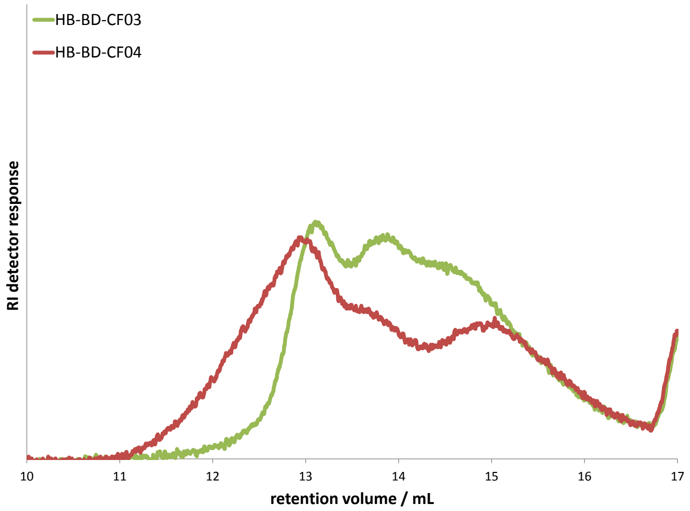

**Figure 2.4.6:** SEC analysis of HB-BD-CF03 and HB-BD-CF04.
For molecular weight data see table 2.4.1.
HB-BD-CF03: DVB injection at 13 % BD feed.
HB-BD-CF04: DVB injection at 13 % and 49 % BD feed.
Further conditions: toluene, 60 °C, BD feed = 2.83 L/min, 30 min,
$M_{target} = 5{,}000\ g{\cdot}mol^{-1}$, 11.8 wt-% polymer, total of 0.7 mol-% DVB,
KOtBu : Li = 0.2 : 1, 30 min post-reaction heating.

The molecular weight for HB-BD-CF04 was $M_n = 5{,}300\ g{\cdot}mol^{-1}$, $M_w = 33{,}000\ g{\cdot}mol^{-1}$ and the polydispersity was PDI = 6.2. Although the SEC trace does not give any direct evidence of the molecular architecture of the resulting polymers it is possible to draw some conclusions from these data and our understanding of the polymerisation reactions. It is known that under the current reaction conditions i.e. continuous butadiene monomer feed and the presence of potassium butoxide, the rate of incorporation of DVB and the rate of chain transfer is enhanced. When all of the DVB is added in a single shot immediately after the induction period (low BD conversion) it is likely that all of the DVB is consumed relatively quickly and will be incorporated into the primary linear chains. Chain transfer is efficient and it is also likely that polymer chains created in the latter stages of the polymerisation as a result of chain transfer and re-initiation will not contain DVB. Of course these chains could help to form branched polymers by coupling to other chains containing DVB.

**Table 2.4.3:** Molecular weight data for HB-BD-CF04. The comparison of the molecular weight of the sample (after 45 % feed) taken during the reaction with the final product allows to draw conclusions about the development of branching.

| Code | Peak ret vol/ml | $M_n$/g·mol$^{-1}$ | $M_w$/g·mol$^{-1}$ | PDI |
|---|---|---|---|---|
| HB-BD-CF04 after 45% feed | 15.1 | 2,900 | 6,400 | 2.2 |
| HB-BD-CF04 product | 13.0 | 5,300 | 33,000 | 6.2 |

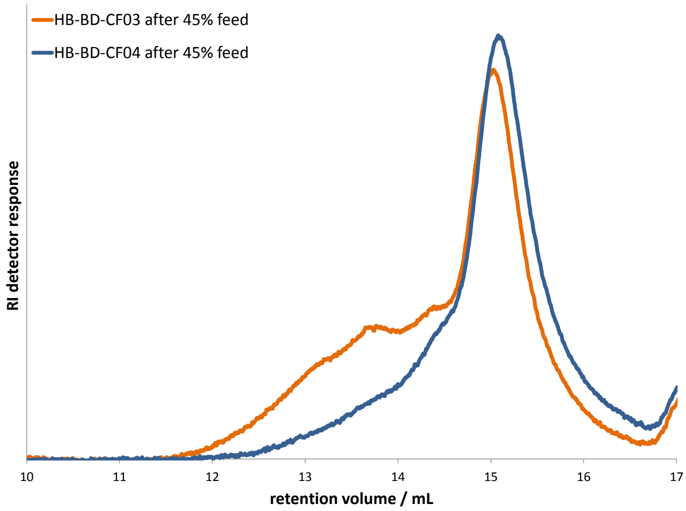

**Figure 2.4.7:** SEC analysis of HB-BD-CF03 and HB-BD-CF04, both after 45 % BD feed.
HB-BD-CF03: DVB injection at 13 % BD feed.
HB-BD-CF04: DVB injection at 13 % and 49 % BD feed.
Further conditions: toluene, 60 °C, BD feed = 2.83 L/min, 30 min, $M_{target}$ = 5,000 g·mol$^{-1}$, 11.8 wt-% polymer, total of 0.7 mol-% DVB, KOtBu : Li = 0.2 : 1, 30 min post-reaction heating.

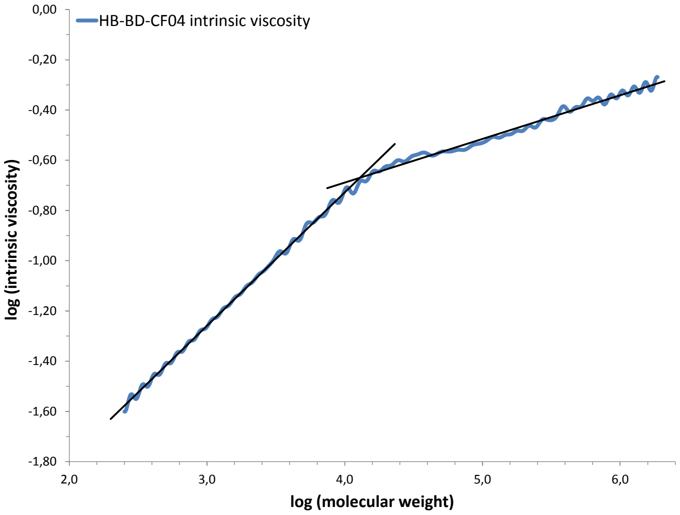

**Figure 2.4.8:** Plot of log(intrinsic viscosity) vs. log(molecular weight) of HB-BD-CF04. The deviation from linearity is an indication of long-chain branching.

The SEC chromatograms in figure 2.4.7 relate to samples withdrawn from HB-BD-CF03 and 04 after 45 % BD feed - so in the case of HB-BD-CF04 that is before the addition of the second aliquot of DVB. In both cases we can see a main peak at about 15 ml retention volume. This peak almost certainly represents linear polymer chains. In the case of HB-BD-CF03 these chains will contain a greater fraction of DVB repeat units than in HB-BD-CF04 since in the latter case only half of the DVB has been added. This has resulted in a greater extent of crosslinking as suggested by the more significant shoulder to higher molecular at lower retention volumes (12.0 - 14.5 ml). So unsurprisingly, a higher concentration of DVB added in the early stages of the polymerisation results in a greater degree crosslinking in the early stages. However, a comparison of the final products of HB-BD-CF03 and 04 (figure 2.4.6), shows that the final molecular weight of HB-BD-CF04 is higher ($M_w = 33{,}000\,g{\cdot}mol^{-1}$ compared to $17{,}800\,g{\cdot}mol^{-1}$ for HB-BD-CF03) and the distribution broader. It seems reasonable to suggest that the increase in molecular weight is due to increased chain branching. This is strongly supported by the non-linearity of the log(intrinsic viscosity) vs. log(molecular weight) plot in figure 2.4.8. The deviation from linearity is an indication of long-chain branching, as was discussed earlier. Therefore the addition of the DVB in two aliquots with the second addition made after about half the butadiene monomer had been added results in a delayed onset to the formation of significant degrees of branching but ultimately leads to a higher degree crosslinking. One final conclusion can be drawn from the data in figures 2.4.6 and 2.4.7. The peak at 15 ml (figure 2.4.7) that we suppose arises from the presence of linear polymer chains, can still be seen in the final product (figure 2.4.6) - albeit at much lower intensity. This would suggest that there is still a proportion of linear polymer chains in the

final product and there may be some room to improve the degree crosslinking. Longer reaction times are not an option. Under these reaction conditions all the chains will be rapidly terminated at the end of the reaction *via* chain transfer to solvent. Continuously feeding the DVB into the reactor may result in some improvement but alas this was also not possible.
The vinyl content for all reactions in the continuous butadiene feed reactor was in the range of the vinyl content of the polybutadienes produced in batch reaction in chapter 2.3 (see table 2.3.4 on page 39 and table 2.4.1 above). As all these reactions were carried out at 60 °C and a potassium *tert*-butoxide amount of $\mathrm{KOtBu} : \mathrm{Li} = 0.2 : 1$ this was to be expected according to literature.[8]

In conclusion, the use of a continuous butadiene feed reactor led to some significant advances in this work. We found that it was possible to prepare polymers with similar molecular weight distributions in the continuous butadiene feed reactor to those obtained in the batch reactions described earlier. However the use of a continuous butadiene feed reactor offered a number of advantages. Firstly, it is possible to carry out the reactions on a much larger scale due to the considerably lower instantaneous concentration of (gaseous) monomer. This is an important step towards the commercialisation of any product. Secondly, the lower concentration of monomer significantly reduces the rate of propagation relative to the rate of chain transfer leading to increases in the transfer constant. Under the right conditions (HB-BD-CF02 to 04) this allowed the synthesis of polymers which were more highly branched, in quantitative yields with no evidence of microgelation. It is possible that the degree crosslinking could be further enhanced by increasing the mole fraction of DVB.

# 3 Experimental

## 3.1 One-pot batch reactions

### 3.1.1 Materials

Benzene (HPLC grade, Aldrich) and toluene (HPLC grade, Fisher Scientific) were dried and degassed by stirring over $CaH_2$ (93%, Aldrich) and by performing a series of freeze-pump-thaw cycles. THF (HPLC grade, Fisher Scientific) was dried and degassed over sodium wire (Aldrich) and benzophenone (Aldrich) by freeze-pump-thaw cycles until the solution turned purple. All solvents were freshly distilled prior to use. KOtBu (sublimed grade, 99.99% trace metal basis, Aldrich) and *sec*-butyllithium (1.3 M in cyclohexane/hexane) has been used as received. Butadiene (>99%, Aldrich) was purified by passing monomer successively through columns of Carbosorb (Aldrich) and molecular sieve to remove any inhibitor and moisture, respectively. Divinylbenzene (technical grade, 80%, mixture of isomers, Aldrich) was prepared by the method detailed in 3.1.2.

### 3.1.2 Purification of divinylbenzene

Divinylbenzene (technical grade, 80%, mixture of isomers, Aldrich) was dried by stirring over $CaH_2$ and degassed by several freeze-pump-thaw cycles. The composition of the crude material was determined by NMR (see below, section 3.1.6) as 55.18 % meta-DVB, 25.40 % para-DVB, 19.27 % ethylvinylbenzene (para- and meta-isomers) and 0.15 % diethylbenzene (para- and meta-isomers). The dried and degassed mixture was distilled under high vacuum into a Young's ampule prior to use for every single reaction in order to remove the inhibitor. Furthermore, the ampule was filled with nitrogen and the composition of the distillate was checked by NMR. Because ethylvinylbenzene and diethylbenzene seem to have lower boiling points compared to DVB, the DVB content in the distillate was always lower than 80 %. The distillate was injected into the reaction vessel with a gas-tight glass syringe. The required volume was calculated under the assumption that the density of the distillate is the same as the crude material (0.914 g/cm$^3$ according to Aldrich), regardless of the composition. The molecular weight of the distillate has been approximated as

$$M_{distillate} = \sum_i M_i \times x_i \tag{20}$$

with $M_i$ being the molecular weight and $x_i$ the molar fraction of component $i$.

### 3.1.3 Reaction vessel and preparation procedure

A specific amount of KOtBu was placed in a sidearm of the reaction vessel by differential weighing. The whole reaction vessel (including the side arms) was evacuated under high vacuum for 1 h and subsequently cleaned with a living solution of oligomeric styrenyl anions in benzene (except the sidearm with KOtBu). After 1 hour under high vacuum, THF (approx. 10 ml) was distilled into the reaction vessel. The THF was used to decant KOtBu from the sidearm into the main reaction vessel and subsequently distilled off. Hereby residual water or *tert*-butanol (originated from the reaction of KOtBu with water) was removed.[65] Furthermore, THF (approx. 10 ml) was distilled into the reaction vessel and subsequently distilled off. The last step was repeated once more with the intended reaction solvent (approx. 10 ml). Thus, it was ensured that THF was completely removed from the KOtBu. The reaction vessel was now completely dried and the specific amount KOtBu placed within it. The intended reaction solvent (50 ml) was distilled into the reaction vessel. Additionally DVB and BD were distilled into separate Young's ampules (for DVB see section 3.1.2). Once the exact amount of BD was known, the required amount of DVB was calculated (taking into account the impurities EVB and DEB) and injected into the reaction vessel using a gas-tight glass syringe. The mixture of toluene, DVB and KOtBu inside the reaction vessel was frozen with liquid nitrogen and evacuated under high vacuum for 1 h. Directly after that BD was distilled into the reaction vessel, which was then cautiously heated to room temperature. Afterwards the reaction vessel was placed in a pre-heated oil bath (temperature probe inside oil bath) for a maximum of 5 min and the reaction started by the injection of *sec*-BuLi using a gas-tight glass syringe. After the desired polymerisation time the reaction was terminated with 500 µl nitrogen-purged methanol. The product solution was stabilised with BHT and the solvent was removed under reduced pressure at room temperature to constant mass.

### 3.1.4 Analysis

### 3.1.5 Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) was used to determine the molecular weight. The measurements were carried out on a Viscotek TDA 302 with a triple detection system (refractive index, viscosity, right angle light scattering). A constant value of 0.124 $\mathrm{mlg^{-1}}$ for d*n*/d*c* was used for both linear and branched polybutadienes. THF was used as eluent at 30 °C with a flow rate of 1.0 $\mathrm{mlmin^{-1}}$. Separation was achieved by 2 x 300 mm PLgel 5 µm mixed C-columns (linear range of molecular weight from 200 - 2,000,000 $\mathrm{g{\cdot}mol^{-1}}$ for polystyrene).

### 3.1.6 Nuclear Magnetic Resonance Spectroscopy

$^1$H-NMR analysis was carried out on either a Bruker-400 MHz or a Varian VNMRS-700 MHz spectrometer using $CDCl_3$ as a solvent. The residual solvent peak ($CHCl_3$, 7.26 ppm)[66] was used as internal standard.

For the purification of divinylbenzene (see above, section 3.1.2) it was necessary to assign the peaks for a mixture of DVB, ethylvinylbenzene (EVB) and diethylbenzene (DEB) (meta and para isomers of each compound present). The peaks for the vinyl-protons have been assigned according to the coupling constants. Therefore, two peak data sets of DVB (one of each isomer) could be derived. The distinction between the two data sets has been achieved by comparison of the respective areas to the area of the singlet peak at 7.26 ppm. This peak has to be the singlet of the aromatic protons of the para-isomer overlapped by the residual solvent peak ($CHCl_3$), because this was the only singlet with a sufficiently large area. The area of the singlet at 7.26 ppm was too large for one dataset and too small for the other data set, respectively. Hence, the data set providing an area too small for the 7.26 ppm peak has to be the para-isomer, because the area of the 7.26 ppm peak is already increased by the overlap with the solvent peak of $CHCl_3$.
Because the aromatic protons of para-EVB are not magnetically equivalent, both isomers of EVB show multiplets in the aromatic region. Hence, the above distinction between the two data sets could not be realised. Because the determination of the EVB content was only important for the calculation of the injection volume of DVB, a distinction of isomers was not necessary for this work.
The assignment for the DEB isomers has been done by general experience, because the DEB content was too small (usually below 1 %) to be analysed directly. Additionally, the chemical shifts seem to be very similar to the ones of EVB. Therefore, no coupling constants are given. Also, the chemical shift of the singlet of para-DEB could not be determined. The determination of the DEB content was carried out by the calculation of the theoretical area of the EVB peaks at 1.14 ppm. It has been assumed that the excess area at this chemical shift belongs entirely to DEB. Below, the peak assignment for the crude divinylbenzene with its main impurities are given.

**meta-DVB**: $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 5.15$ (dd, $J = 10.9$, 1 Hz, 2H, -CH=C(H)$\mathbf{H_{cis}}$), 5.66 (dd, $J =$ 17.6 Hz, 1 Hz, 2H, -CH=C(H)$\mathbf{H_{trans}}$), 6.61 (dd, $J = 17.6$ Hz, 10.9 Hz, 2H, -**CH**=CH$_2$), 6.96-7.34 (m, 4H, H$_{ar}$) ppm.

**para-DVB**: $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 5.14$ (dd, $J = 10.9$, 1 Hz, 2H, -CH=C(H)$\mathbf{H_{cis}}$), 5.64 (dd, $J = 17.6$ Hz, 1 Hz, 2H, -CH=C(H)$\mathbf{H_{trans}}$), 6.59 (dd, $J = 17.6$ Hz, 10.9 Hz, 2H, -**CH**=CH$_2$), 7.26 (s, 4H, H$_{ar}$) ppm.

**meta-EVB** and **p-EVB**: $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.14$ (t, $J = 7.6$ Hz, 3H), 2.54 (q, $J = 7.6$ Hz, 2H), 5.15 (dd, $J = 10.9$ Hz, 1 Hz, 1H, -CH=C(H)$\mathbf{H_{cis}}$), 5.66 (dd, $J = 17.6$ Hz, 1 Hz, 1H, -CH=C(H)$\mathbf{H_{trans}}$), 6.61 (dd, $J = 17.6$ Hz, 10.9 Hz, 1H, -C**H**=CH$_2$), 6.96-7.34 (m, 4H, H$_{ar}$) ppm.

**meta-DEB**: $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.14$ (t, 6H, -CH$_2$-C**H**$_3$), 2.54 (q, 4H, -C**H**$_2$-CH$_3$), 6.96-7.34 (m, 4H, H$_{ar}$) ppm.

**para-DEB**: $^1$H-NMR (400 MHz, CDCl$_3$, 25,°C): $\delta = 1.14$ (t, 6H, -CH$_2$-C**H**$_3$), 2.54 (q, 4H, -C**H**$_2$-CH$_3$), 6.96-7.34 (s, 4H, H$_{ar}$) ppm.

The vinyl content (1,2-enchainment) of the samples, $v$, was calculated according to equation 21 (analogous to Yang et al.[67]). The calculation was based on peak assignments as stated below.[8,68]

$$v = \frac{2 \times Area_{4.70-5.10\,ppm}}{Area_{4.70-5.10\,ppm} + 2 \times Area_{5.10-5.90\,ppm}} \tag{21}$$

**PBD**: $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.10$-1.50 (m, 2H, vinyl-secondary aliphatic), 1.70-2.40 (m, 4H, 1,4-aliphatic), 1.70-2.40 (m, 1H, vinyl-tertiary aliphatic), 4.70-5.10 (m, 2H, vinyl-terminal), 5.10-5.50 (m, 2H, 1,4-olefinic), 5.50-5.90 (m, 1H, vinyl-internal) ppm.

## 3.2 Controlled feedrate reactor

### 3.2.1 Materials

Divinylbenzene (technical grade, 80 %, mixture of isomers, Aldrich) was dried overnight over NaOH without any further preparation prior to the reaction. Potassium *tert*-butoxide (>99 %) was weighed into a dry glass jar under nitrogen atmosphere. n-Butyllithium (3.24 M, Chemetall) was stored in a fridge prior to use. Toluene was dried over a 4 Å-molecular sieve overnight.

### 3.2.2 Reaction vessel and preparation procedure for continuous feed reactions

The polymerisations were carried out in a reaction vessel under a nitrogen atmosphere. The vessel was connected to the nitrogen atmosphere *via* a condenser (dry ice in acetone), allowing us to keep the nitrogen constant at atmospheric pressure inside the vessel and to condense back any monomer that diffuses out of the reaction solution. The temperature was controlled by a cooling/heating jacket and the temperature probe was positioned inside the vessel. The reaction vessel (6 litres internal volume) was kept under living conditions between reactions. The vessel was charged with 1500 g of toluene and the required amount of potassium *tert*-butoxide and purged with nitrogen. The stirrer speed was set to 300 revolutions per minute and the vessel was pre-heated to 60 °C and the required amount of n-butyllithium solution was injected. The reaction was started by the addition of butadiene monomer, feeding at a continuous rate after an induction period of 5 min in which the butadiene feed rate was steadily raised towards the intended level. Injections of divinylbenzene were carried out through an injection valve covered by a rubber septum. Post-reaction heating was carried out for 30 min. Afterwards the reaction was cooled down quickly and terminated with a proton-donor terminating reagent. The samples were stabilised with BHT, purged with nitrogen and the solvent was removed by distillation under reduced pressure and heating to up to 200 °C.

### 3.2.3 Analysis

The vinyl content (1,2-enchainment) was analysed by infrared spectroscopy. Size exclusion chromatography was carried out with polybutadiene standards, which were analysed by triple detection SEC beforehand. By using polybutadiene standards accuracy was increased in the very low molecular weight regions in which the light scattering signal in the triple detection mode is relatively unreliable, ensuring consistent molecular weight calculations.

# 4 Conclusions

Soluble branched polybutadiene polymers were successfully obtained in a one-pot anionic copolymerisation with a divinyl crosslinker, divinylbenzene. Reactions were typically carried out at 60 °C in toluene with potassium *tert*-butoxide as an additive. In all cases there were strong indications that linear chains were present in the products of the polymerisation. The highest percentage of branched polymer was estimated to be 77 % in a sample of a molecular weight of $M_n = 23{,}000\,g{\cdot}mol^{-1}$ and a polydispersity of PDI = 8.5, with the remainder being linear (not crosslinked) chains. Chain transfer to toluene helped to prevent gelation, although its influence was shown to be minimal in two nearly identical reactions; one in toluene (chain transfer to solvent occurs) and the other using benzene (chain transfer to solvent cannot take place). Generally the degree of branching seemed to be higher in high molecular weight samples ($M_n \approx 20{,}000\,g{\cdot}mol^{-1}$) than in low molecular weight samples ($M_n \approx 10{,}000\,g{\cdot}mol^{-1}$).

In addition to the one pot reactions, experiments were carried out on a larger scale (200 g monomer) in a continuous butadiene feed reactor under nitrogen at atmospheric pressure. The samples prepared were in the low molecular weight region ($M_n \approx 10{,}000\,g{\cdot}mol^{-1}$ with a polydispersity of PDI ≈ 3 - 6). The different reaction set-up caused a higher degree of chain transfer to toluene. Analysis with triple detection size exclusion chromatography strongly indicated the branched nature of the polybutadiene samples by a double-logarithmic plot of intrinsic viscosity vs. molecular weight.

Vinyl contents (1,2- enchainment) for the most promising reactions were up to 37 %, which is consistent with literature on butadiene polymerisation in non-polar solvents in presence of polar additives (potassium *tert*-butoxide in this work).

# 5 Future work

Further investigation of butadiene copolymerisations with a divinyl crosslinker may be carried out to explore the influence of variables which were not directly covered by this work. Mechanical properties of polybutadienes are strongly influenced by their vinyl content (1,2-enchainment). Some variation of the vinyl content may be achieved by higher reaction temperatures, which additionally would cause more chain transfer to solvent. Lower reaction temperatures may also be investigated in order to change the vinyl content, although the solubility of additives might cause challenges.

One-pot reactions have been shown to always obtain some linear (not crosslinked) chains along the branched structured (crosslinked) species. A continuous feed of the divinyl crosslinker (divinylbenzene) might avoid the issue of un-crosslinked chains, whereby the knowledge of the influence of additives on commoner incorporation obtained in this work can be used for optimising the amount of divinyl crosslinker needed. Furthermore, incorporation levels for the divinyl comonomer were optimised in this work by the addition of varying levels of a polar additive (potassium *tert*-butoxide). In a different approach, incorporation levels might be varied by using different solvents than toluene or even solvent mixtures. More generally, a different divinyl crosslinker might be used, but the wide availability of divinylbenzene and the results obtained in this work do not suggest a necessity for that.

Samples of branched polybutadienes might be analysed more critically with liquid chromatography under critical conditions, which can be used to separate linear (not crosslinked) from branched (crosslinked) species, presumably giving an accurate degree of branching (i.e. ratio of branched chains to the whole sample). More detailed information might be obtained by temperature gradient interaction chromatography, which is capable of separating branched species not only by molecular weight but also by their degree of branching. Therefore temperature gradient interaction chromatography can identify whether a small number of very specific branched species or a broad random spectrum of branched structures was obtained. Rheology might be used for characterisation for samples with very low levels of linear (not crosslinked) chains, possibly revealing mechanical properties differing from linear polybutadienes.

The use of a continuous monomer feed reactor is favourable compared to one pot batch reactors, as the reaction can be easier manipulated and the monomer pressure is constant over the course of the whole reaction, which makes it easier to regulate the vinyl content (1,2-enchainment) of the samples in cases where this is wished. Higher final polymer concentrations (i.e. higher mass of monomer per mass of solvent) might improve the branching efficiency of the crosslinker due to the higher proximity of living chain ends to each other, although crosslinker amounts might have to be adjusted in order to prevent gelation.

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