The synthesis of fluorinated block copolymers via the living macroradical technique

Nadal, Francisco

THE SYNTHESIS OF FLUORINATED BLOCK COPOLYMERS VIA THE LIVING MACRORADICAL TECHNIQUE

By

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a Pere, Maria Gracia, Juan i Ruth

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Memorandum

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October, 1978 and July, 1980. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

ABSTRACT

The work reported in this thesis describes the preparation and characterization of homopolymers of vinyl acetate, trifluoroethyl acrylate, trifluoroethyl methacrylate, hexafluoroisopropyl acrylate and hexafluoroisopropyl methacrylate.

Block copolymers of vinyl acetate with the above monomers were prepared by the living macroradical technique. The products were characterized by a combination of analysis; infrared and nuclear magnetic resonance spectroscopy; gel permeation chromatography; solvent extraction; and observation of bulk physical properties.

C O N T E N T S

CHAPTER 1

General Introduction and Background

1.1. Introduction

The work to be reported in this thesis is concerned with the preparation of block copolymers. When block copolymers are formed from a pair of monomers whose individual homopolymers have very different properties the resulting copolymer often displays interesting properties. The main objective of the project, of which this thesis forms part, is the synthesis of block copolymers in which the largest blocks are derived from conventional monomers and these blocks are connected to relatively short segments of fluorocarbon materials. It is hoped that such materials may show specific surface segregation of the fluorocarbon block and that they may be capable of displaying the valuable surface properties of fluorinated materials without the usual associated penalty of high cost.

The thesis is divided into four chapters. In the remainder of this chapter the methods available for the synthesis and characterization of block copolymers are reviewed; and some of the uses of such materials are noted. The experimental work carried out is recorded in Chapter 2. In Chapter 3 the results obtained and their interpretation are discussed, while in Chapter 4 some conclusions from this work are drawn and suggestions for continuation of the project are made.

Many different methods of preparing block copolymers have been reported in the literature, and in the next few sections the main types are reviewed, the information being organized on a mechanistic basis.

1.2. The synthesis of block copolymers via radical mechanisms

1.2(i) Photochemical synthesis

Selective absorption of electromagnetic radiation in the visible and ultraviolet regions can result in the rupture of chemical bonds and the formation of free radicals. Photolysis of polymers containing bonds which can absorb electromagnetic radiation may lead to the formation of free

radical sites on the polymer backbone, and if the irradiation is carried out in the presence of another monomer block copolymerization may result. When none of the bonds within a system can be ruptured by radiation, photosensitizers may be used to promote copolymerization.

The first method of synthesizing block copolymers reported in the literature is that of Bolland and Melville.[1,2] In a study of the photo-initiation of the vapor-phase polymerization of monomers, a film of poly(methyl methacrylate) was deposited on the walls of an evacuated reaction vessel, chloropropene was then admitted and reacted with the unterminated radicals to give a block copolymer. Hicks and Melville[3,4] synthesized poly(styrene-b-butyl acrylate) using a "flow-method", polymerization of butyl acrylate was initiated by ultraviolet irradiation as the monomer was flowing through a capillary into a reservoir containing styrene; the macroradicals formed in the capillary reacted with the styrene to yield a block copolymer. Poly(styrene-b-acrylonitrile) and poly(n-butyl acrylate-b- 2-vinylpyridine) have also been prepared by this procedure.[5]

Irradiation of poly(vinyl methyl ketone) with ultraviolet light of wavelength 3130Å leads to decomposition of the polymer by photolytic degradation according to a scheme analogous to that for the decomposition of monomeric aliphatic ketones under identical conditions.[6]

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}R \xrightarrow{h\nu} R\cdot + \cdot CR \xrightarrow{\Delta} 2R\cdot + CO$$

Block copolymerization can be initiated by the resulting macroradicals, poly(vinyl methyl ketone-b-methyl methacrylate) has been synthesized using this technique.

Block copolymers are also obtained by photoinitiating the polymerization of a water-soluble monomer in which an oil-soluble monomer is suspended. When the polymer radicals generated in the aqueous phase diffuse across the

water-oil interface, the polymerization of the second monomer is initiated by the macroradical formed from the first monomer; block copolymers of methacrylic acid with styrene and vinyl acetate have been prepared in this way.[7-9]

Photopolymerization of a monomer in the presence of a precipitant for the polymer yields occluded radicals which may be used to initiate the block copolymerization of a second monomer. Bamford et al.[10] studied such occluded radicals of vinyl monomers, obtaining evidence for their existence via radical scavenger and electron paramagnetic resonance techniques.

1.2.(ii) Synthesis using higher energy irradiation

The types of high energy radiation which have been used to initiate free radical chain reactions include α-particles, β-, γ-, and X-rays. When organic polymers are irradiated, simultaneous cross-linking and degradation of the chains occurs. The overall result is dependant upon the type of radiation, the total energy absorbed, the rate at which energy is absorbed, and the radiation sensitivity of the materials. Subsequent reactions of the initially generated active species are chemical phenomena dependant upon variables such as temperature, concentration, etc.[11] If the polymer is irradiated in the solid state, the radical formed can be trapped, a second monomer can be added which can diffuse to the reactive sites resulting in the preparation of block copolymers. Poly(vinyl acetate-b-methyl methacrylate)[12] has been prepared by emulsion polymerizing vinyl acetate under the influence of γ-radiation; the macroradicals thus formed can initiate the polymerization of the second monomer. Other block copolymers have also been synthesized using this technique.[13]

1.2.(iii) Synthesis via mechanical degradation of homopolymers

Mechanochemical degradation of polymers is the rupture of carbon-carbon bonds (or, less frequently, of other bonds) by the application of mechanical

forces. This results in the formation of polymeric free radicals or polymeric ions by homolytic or heterolytic scission, respectively. Mechanochemical degradation is the primary degradative process that occurs during comastication of two polymers;[14] mastication of a polymer in the presence of a monomer;[15] ultrasonic degradation of two polymers in solution;[16] alternating freezing and thawing of polymer-monomer mixtures;[17] shaking and stirring of polymer-monomer systems;[18] swelling of polymers with monomers;[19] mechanochemical peroxidation;[20] high voltage discharge;[21] heating and rolling;[22] vibration milling;[23] ballmilling;[24] and microgrinding[25] of polymers have all been used to synthesize block copolymers. For example, block copolymers of styrene and methyl methacrylate[26] have been produced by the ultrasonic degradation of polystyrene in the presence of methyl methacrylate. Polyethylene oxide solutions in methyl methacrylate have been stirred at high speed causing scission of the polyethylene oxide molecules with the resultant formation of poly(ethylene oxide-b-methyl methacrylate).[27] Likewise, poly(vinyl chloride-b-methyl methacrylate) has been synthesized by shearing polyvinyl chloride in the presence of methyl methacrylate monomer.[28] A block copolymer is one of the products obtained when natural rubber is milled with methyl methacrylate.[29]

Natural rubber and other polyisoprenes degrade during mastication in air with the formation of peroxidic and hydroperoxidic groupings which can be used in the synthesis of block copolymers.[22,23]

Much work in the mechanochemical degradation of polymers has been done by Ceresa whose review[21] should be consulted for further details.

1.2.(iv) Synthesis via radical attack on macromolecules

a) Chain transfer reaction on polymer backbones

One of the common reactions of macroradicals in an oxygen free atmosphere is chain transfer. Flory[30] defined chain transfer as a process in which growth of individual polymer molecules is limited but the number of active

centres remains unchanged. A macroradical abstracts a hydrogen atom or a radical from some other substance to yield a terminated polymer and a new radical. Transfer constants for polymers can be obtained from data on low molecular weight compounds of similar structure,[31] assuming identical reactivity towards the attacking radical. The validity of this assumption has been confirmed by transfer constant determinations in the presence of oligomers.[32,33] Chain transfer is a function of environment; thus chain transfer constants for water-insoluble agents are similar for bulk and emulsion polymerization. However, since chain transfer in emulsion polymerization occurs primarily in the miscelles or monomer swollen polymer particles, chain transfer by water soluble agents is less efficient in emulsion than in bulk polymerization systems because the transfer agents reside largely in the aqueous phase. The mechanism of the formation of macroinitiators and the direct formation of block copolymers depends on the chemical character of the active terminal group introduced into the homopolymer block. Thus, block copolymerization may be initiated by:

1) Terminal hydroperoxide groups

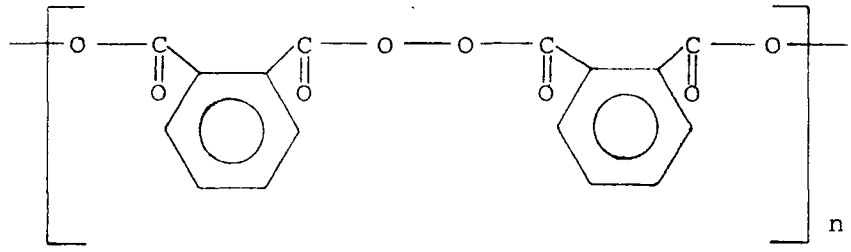
Homopolymer fragments containing terminal hydroperoxide groups are obtained by polymerizing monomers in the presence of dihydroperoxides under conditions ensuring the homolytic decomposition of only one hydroperoxide group, to avoid the formation of an inactive homopolymer.[34] Molyneux[35] studied the formation of block copolymers of styrene and methyl methacrylate by thermally polymerizing styrene at 70°C in the presence of m-diisopropyl benzene dihydroperoxide to give polystyrene with terminal hydroperoxide groups. The block copolymer was prepared by suspension polymerization at 0-25°C in the presence of Fe^{2+} ions and sodium pyrophosphate.

Polyvinyl chloride terminated with aldehyde groups has been converted to a hydroperoxide terminated polymer by reaction with hydrogen peroxide, block copolymers were produced by the addition of styrene to this macro-

initiator.[36]

2) Terminal peroxide groups

Smets[37,38] and co-workers have reported the formation of poly(styrene-b-methyl methacrylate) and poly(vinyl acetate-b-styrene) by using polymeric phthaloyl peroxide as the initiator.

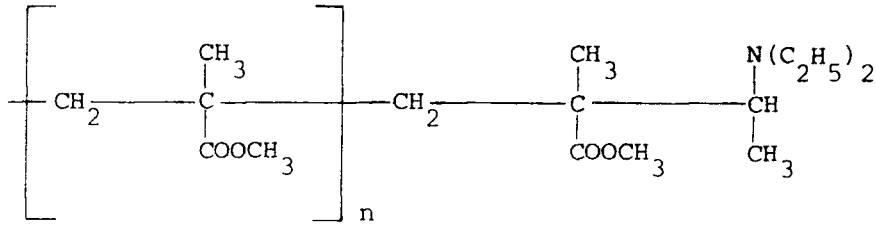


Monomer A is polymerized at low temperature to a low degree of polymerization, thus incorporating the initiator into the polymer backbone; monomer A is replaced by monomer B, and the copolymerization is initiated by heating. Block copolymers formed in this manner are contaminated with homopolymers. Another method for introducing terminal peroxy groups into homopolymeric blocks involves the polymerization of the monomer, styrene, in the presence of t-butyl hydroperoxide and Cu^{2+} ions.[39] The decomposition of t-butyl hydroperoxide in the presence of Cu^{2+} ions leads to the formation of $(CH_3)_3COO\cdot$ and $(CH_3)_3CO\cdot$ radicals, the first of which, probably as a result of recombination with the growing polystyrene macroradical, forms active terminal peroxide groups capable of initiating subsequent block copolymerization. Ceresa[40] has prepared block copolymers of methyl methacrylate with styrene and with acrylonitrile by first polymerizing methyl methacrylate in the presence of oxygen, thereby incorporating oxygen in the polymer, and then heating the resulting peroxide containing homopolymer in the presence of the second monomer. Similarly, block copolymers of cis-1,4 polybutadiene and acrylonitrile have been prepared by introducing peroxidic functionality into the polybutadiene by ozonolysis followed by heating in the presence of acrylonitrile.[41] Finally, α-w peroxypolystyrene, prepared anionically using

lithium-naphthalene and terminated with carbon dioxide yielding carboxylic groups which were then converted to peroxy groups, has been used to prepare A-B-A terpolymers by polymerization with acrylonitrile.[42]

3) Terminal amino groups

Bamford and White[43] showed that to obtain a block copolymer of the A-B type it is best to carry out the homopolymerization of the monomer A in the presence of triethylamine; chain transfer takes place through the latter with the formation of a compound of the type:



This polymeric product was used as macromolecular chain transfer agent in the homopolymerization of the monomer under conditions ensuring a high degree of chain transfer by the growing radical. Poly(methyl methacrylate-b-acrylonitrile) was prepared using this method.

4) Terminal groups containing halogen

Homopolymeric blocks with terminal halogen atoms absorb light of wavelength 2880-3500Å are raised to an excited state, and dissociate into free reactive polymeric radicals which can be used as macromolecular initiators in block copolymerizations. The macromolecular halides are usually prepared by the thermal or photolytic polymerization of styrene[44] or methyl methacrylate[45] in the presence of CBr_4 or $CBrCl_3$ which terminate the chain by a chain transfer reaction. In the second stage of the synthesis of the block copolymer, the macrohalide is irradiated with ultraviolet light in the presence of a vinyl monomer. Block copolymer formation by this

method has also been described by Bamford et al.[46] and by Guyot et al.[47] Hydrophilic block copolymers are obtained by copolymerizing acrylic acid in the presence of organic bromine containing compounds with three or four carbon atoms and three bromine atoms. The resulting bromine containing acrylic acid homopolymer is dissolved in an inert aqueous medium with another vinyl monomer, for example acrylonitrile, and the mixture is irradiated with ultraviolet light to give the block copolymer.[48]

5) Terminal groups containing sulphur

Organic compounds containing sulphur atoms,[45,46] which have the ability to undergo chain transfer reactions, may be used to initiate the polymerization of the primary monomer. Block copolymerization can be achieved by irradiation with ultraviolet light in the presence of vinyl monomers. Block copolymers of styrene with methyl methacrylate,[50] and with vinyl acetate[51] have been prepared by using this technique.

6) Terminal groups consisting of acid hydrazides

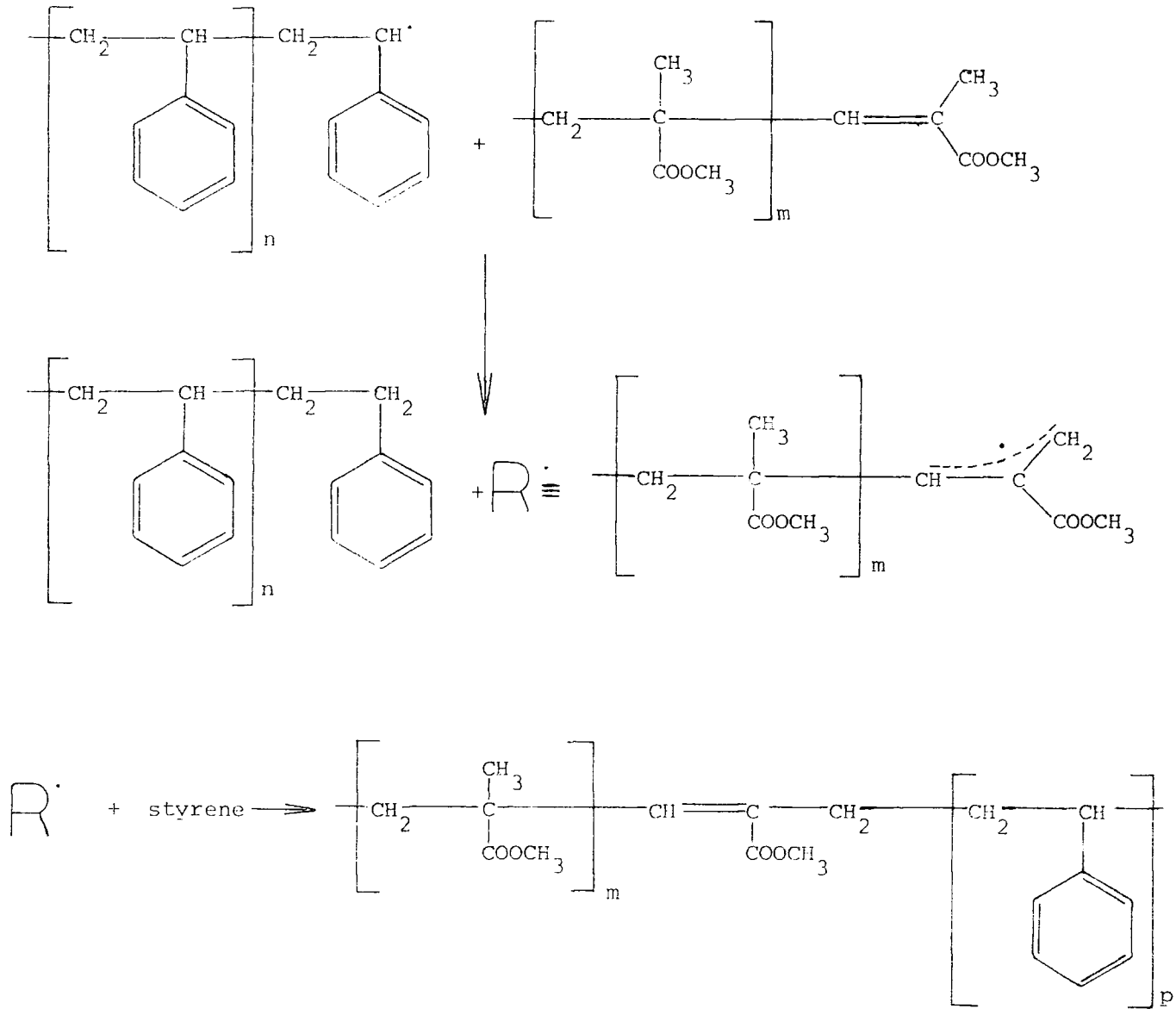
Acrylonitrile is capable of undergoing polymerization in the presence of a redox system consisting of acid hydrazides and Fe^{3+} ions. The polymerization of acrylonitrile can be initiated in analogous fashion by using polymeric blocks containing acid hydrazides as terminal groups. This method has been used to prepare block copolymers of polyaminotriazole with polyacrolein, the product exhibits a high afinity for acid dyes.[52]

b) Radical attack on unsaturated polymers

Free radical transfer reactions with unsaturated polymers commonly occur through the abstraction of allylic hydrogen atoms. Schulz et al.[33] studied the formation of such resonance stabilized macroradicals. They used polymethyl methacrylate containing terminal double bonds obtained from termination by disproportionation. Polymerization of styrene in the presence

of such a polymer lead to block copolymer formation, due to the preferred reactivity at the chain ends.

The mechanism of the formation of the stabilized macroradical, and for block copolymer formation are shown below.



1.2.(v) Synthesis via the living macroradical technique

Relatively little research has been carried out on the synthesis of block copolymers via stable macroradicals, although the anionic analogue of this process is, of course, well established. Under most circumstances

termination predominates and the "living macroradical technique" is consequently not easily applied. However, it has been shown that a polymer will precipitate as a coiled macroradical under some circumstances and that the precipitated macroradical has a relatively long life time. Many of the radical chain ends are trapped within the precipitated coils, consequently inhibiting termination reactions. A second monomer which can diffuse into the precipitated macroradical coil may be introduced and under favourable circumstances block copolymers may be formed. Some of the earlier work in this field has been referred to earlier (Bamford et. al. loc. cit.).

Seymour and co-workers have extensively developed this field and have established that a polymer will precipitate as a coiled macroradical when a monomer is polymerized in a solvent whose solubility parameter differs from that of the polymer by at least 1.8 Hildebrand units (H).[53] There must also be a difference of at least 1.8H but not more than 3.1H between the solubility parameters of the monomer and polymer.[54] Introduction of the second monomer results in block copolymerization provided that the coiled macroradical is sufficiently swollen and consequently penetrated by the new monomer and/or solvent; this condition is met when the solubility parameters of the macroradical and of the new monomer are similar. Further, macroradicals are present as statistical coils at the theta temperature and it has been shown that block copolymers may be produced by the addition of vinyl monomers at any temperature below the theta temperature. The rate of block copolymerization increases as the reaction temperature approaches the theta temperature.

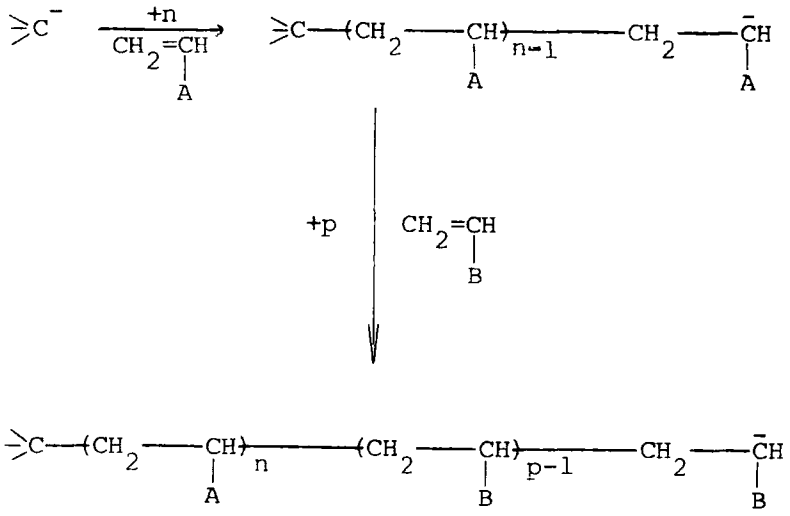
Several block copolymers have been prepared by the use of this technique. For example, block copolymers of vinyl acetate and other vinyl monomers have been produced in poor solvents,[55] viscous good solvents,[56] and in viscous poor solvents.[57] This technique was chosen for the work reported in this thesis.

1.3. The synthesis of block copolymers via ionic mechanisms

1.3.(i) Block copolymers via anionic polymerization

Anionic polymerizations, carried out in aprotic solvents, lead to the syntheses of "living" polymers which contain one or two organometallic sites per chain which can promote polymerization[58] or react with various electrophilic functions. The absence of spontaneous termination reactions is the factor which makes the use of the "living" polymer technique possible for the preparation of block copolymers. Living polymers are generally prepared by initiating vinyl monomer polymerization with alkali metals or alkali metal alkyls or aryls. Generally, block copolymers can be formed from "living" polymers by:

1) Simple addition of a monomer to a living homopolymer



By adding more $CH_2=\underset{\displaystyle A}{\underset{|}{C}}H$ an A-B-A triblock or sandwich copolymer will be formed. The order of monomer addition is an important factor in determining the formation of block copolymers by this technique. Polystyryl anions will initiate the polymerization of methyl methacrylate, but polymethyl methacrylate anions can not initiate the polymerization of styrene.[59] Likewise, living polystyrene will add to ethylene oxide to yield a block copolymer,

but the alkoxide will not add to styrene.[60] Such reactivities have been related to Q-e values[61] and suggest that the reaction of a living polymer is qualitatively related to the e value of the monomer from which it is formed. The anion of a monomer with a low e value initiates the polymerization of a monomer with a higher e value, but not vice versa.

Minimization of termination by impurities and of chain transfer has lead to the successful synthesis of block copolymers of styrene-butadiene having up to seven successive increments.[62] Monofunctional initiators (butyl-lithium, cumyl-potassium,...) usually lead to A-B block copolymers. Triblock copolymers can be prepared by using difunctional initiators, monomer adds to both ends of the difunctional initiator giving doubly ended living polymers. Addition of a second monomer yields a B-A-B triblock copolymer.

In certain cases, block copolymers can be prepared by polymerizing monomer mixtures. In the butyl-lithium initiated polymerization of styrene and butadiene in hydrocarbon solution,[63] a styrene-butadiene copolymer having predominant block character is formed. The segments are not completely pure and have been referred to as tapered blocks.[64] Although the homopolymerization rate of styrene is much faster than that of butadiene, the butadiene is essentially all depleated before any of the styrene is polymerized. The explanation usually offered for this unusual behaviour is that the polymerization kinetics very strongly favour the addition of polystyryl anion to butadiene monomer rather than to styrene monomer. Polybutadienyl anion also adds to butadiene monomer more rapidly than to styrene monomer.[65]

An interesting case of block copolymerization formation was observed by O'Driscoll and Tobolsky[66] in the lithium initiated copolymerization of styrene and methyl methacrylate. It was suggested that initiation occurs by an electron transfer from lithium to one of the monomers followed by growth at both ends of the ion radical. The methyl methacrylate would add to the

anionic end, and an alternating copolymer would be formed on the radical end. The relative lengths of the blocks would be determined by the relative rates of radical and anionic growth.

2) Coupling of living polymers

Reactions of "living" polymers with multifunctional electrophiles were studied by Finaz et al.[67] and Rempp et al.[68] They treated dicarbanionic "living" polystyrene, prepared with sodium-naphthalene initiator, with diacid chlorides, diesters, or dihaloalkanes. A poly-condensation reaction occurs resulting in a large molecular weight increase. The number of polystyrene blocks joined together by this method can be estimated from the molecular weight increase of the polymer. Block copolymers may also be prepared by coupling macroanions by difunctional halides,[69] bis(chloromethyl) and bis(bromomethyl) ether,[70] dibromobutane,[71] α,α'-dichloro-p-xylene,[71] phosgene,[72] and divinylbenzene.[73] Block copolymers have also been obtained by the coupling of styrene macroanions with THF macrocations.[74]

In general, the termination step in anionic polymerization is easier to control than in free radical syntheses, so that the possibilities of commercial ionic syntheses of block copolymers are very real. The patent literature is very rich in anionic polymerization methods that appear capable of being adapted to yielding segmental block and graft copolymers. Work in the field of commercialization of ethylene-propylene block copolymers has been carried out by the Texas Eastman Company with the introduction of "polyallomers",[75] which are crystalline block copolymers of ethylene and propylene, quite different from the commercially available ethylene-propylene rubbers.

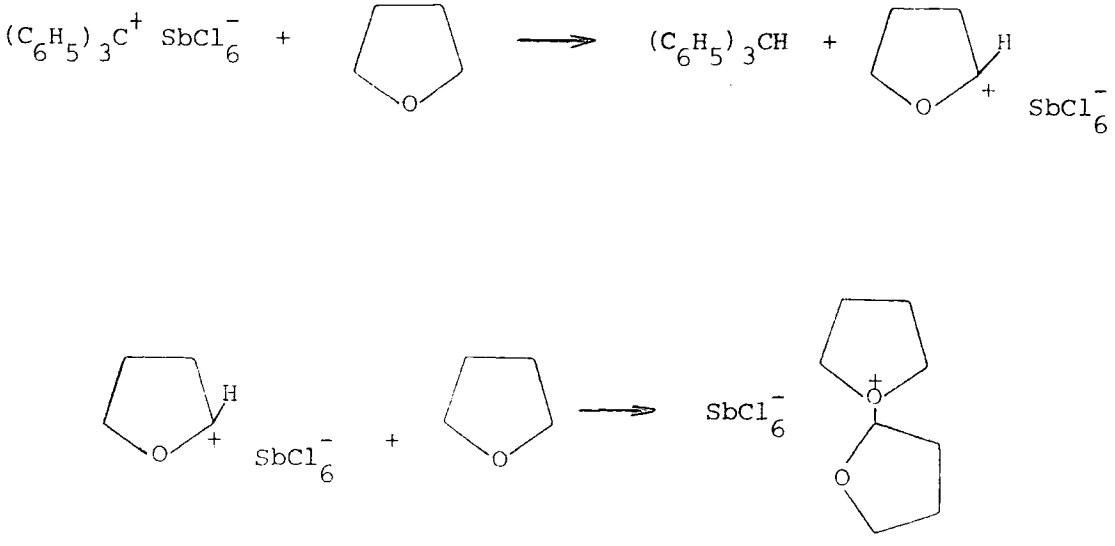
Anionic polymerization is also used to prepare stereo-block copolymers consisting of relatively long segments with different spatial configurations. For example, polystyrene having blocks of isotactic and atactic segments can

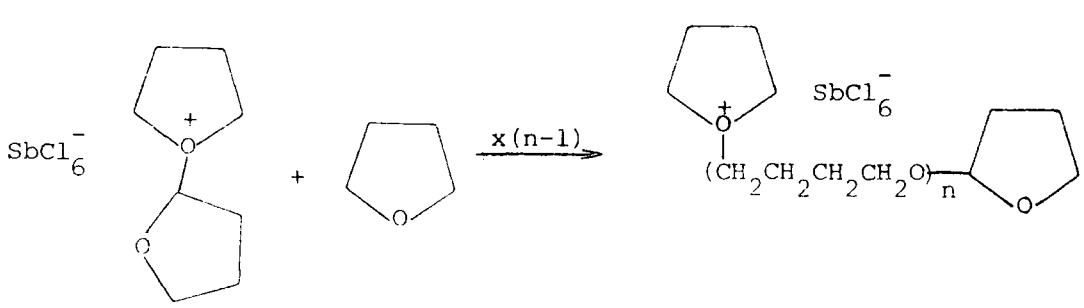
be formed using butyl-lithium as the initiator. The polymerization is conducted in hydrocarbon medium and the stereoregularity is altered by cycling the polymerization temperature between -30°C and -5°C.[76]

1.3.(ii) Block copolymers via cationic polymerization

Several workers have claimed that, under proper conditions, "living" cationic polymers can be prepared, since the rate of self-termination is very slow compared to the rates of initiation and propagation. The short life time of macrocations may be prolonged by using high concentrations of special initiators and, chain transfer is suppressed by using low solvent-monomer ratios.

Bawn and co-workers[77] showed that triphenylcarbonium hexachloroantimonate initiates the cationic polymerization of THF. They proved that the process involves a proton transfer followed by the formation of an oxonium ion which is the active site in the propagation:





The lack of termination was demonstrated by thermodynamic studies, by an increase in the molecular weight of the product on monomer addition, and through formation of block copolymers.[78]

Kennedy and Melby[79] reported the preparation of block copolymers of styrene and isobutylene via a cationic mechanism. A bromine terminated polystyrene oligomer was reacted with isobutylene in the presence of diethylaluminium chloride. Berger et al.[74] synthesized a THF-styrene-THF block copolymer by coupling a dianionically terminated polystyrene with cationically terminated polyTHF "living" polymers. The dianionic polystyrene was prepared in THF solution using α-methylstyrene tetramer dianion as the initiator, and the cationic THF polymer was synthesized using Meerwein's catalyst, $(C_2H_5)_3OBF_4$, at ice-bath temperature for 2 hours, combination of the two oligomers gave the product.

Zimmerman[80] claims the synthesis of a styrene-THF-styrene block copolymer by the combination of a polyTHF oligomer with two cationic end groups, polymerized via a "living" cationic process using trifluoromethane sulphonic anhydride, $(CF_3SO_2)_2O$, as the initiator for 1-4 hours at 25°C, with a monoionically terminated polystyrene, prepared via butyl-lithium initiation.

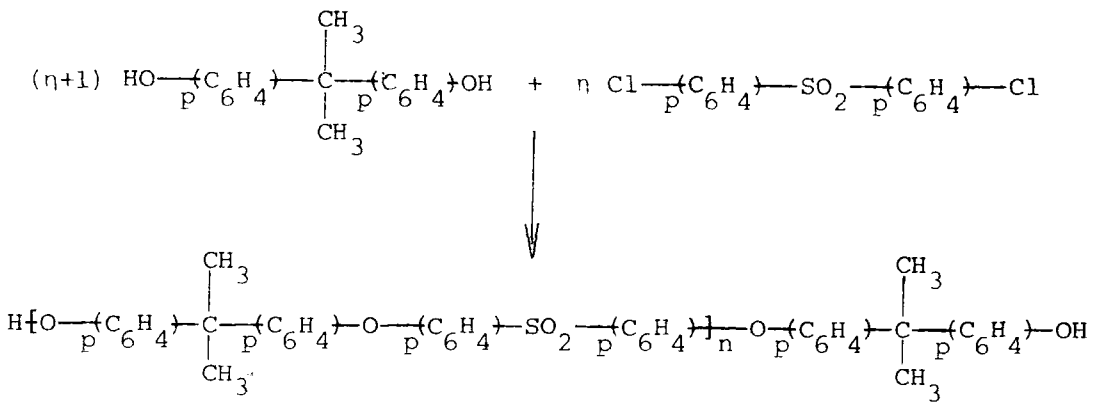
1.4. The synthesis of block copolymers from coordination catalysis

Coordination catalysts have been used in the preparation of block copolymers.[81] A requirement in the synthesis of these polymers with Ziegler-Natta type catalysts is that the growing olefin chain be sufficiently long lived so the copolymer can be formed by sequential monomer addition.[82] Coordination catalysts based on the $TiCl_3$-Et_2AlCl system have been the most widely used. The preparation of block copolymers of propylene/4-methylpent-1-ene,[83] propylene/1-butene,[84] and ethylene/α-methylstyrene,[85] have been reported.

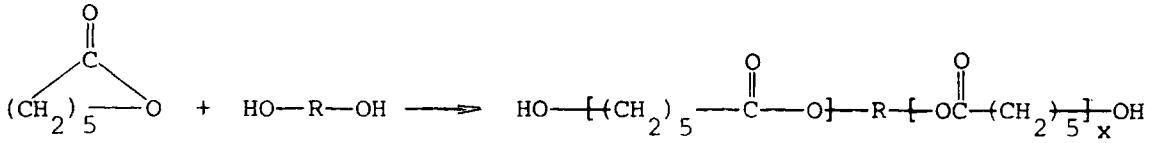
Styrene-isobutylene block copolymers have been prepared by combining anionic and coordination catalysis mechanisms.[86] Living polystyryl-lithium was terminated with α,α'-dibromo-p-xylene, complexed with titanium tetrachloride and reacted with isobutylene to yield poly(styrene-b-isobutylene) having a 91.5-8.5 composition.

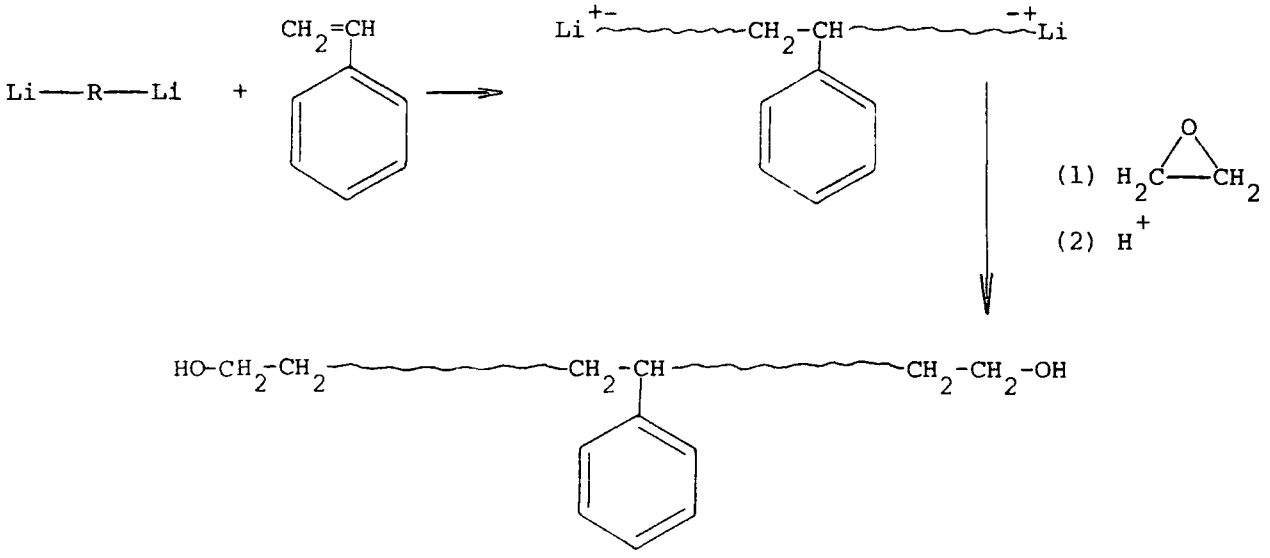
1.5. The synthesis of block copolymers via coupling or condensation reactions

The interaction of functionally terminated homopolymers is a versatile method for preparing block copolymers. Only the intersegment linkage is formed during these reactions. The preformed homopolymers can be prepared either by step-growth reactions, in which the end groups are a natural consequence of the polymerization chemistry,



or by appropriate additions or ring opening polymerizations, in which the end groups can be predetermined via initiator choice or by end capping.





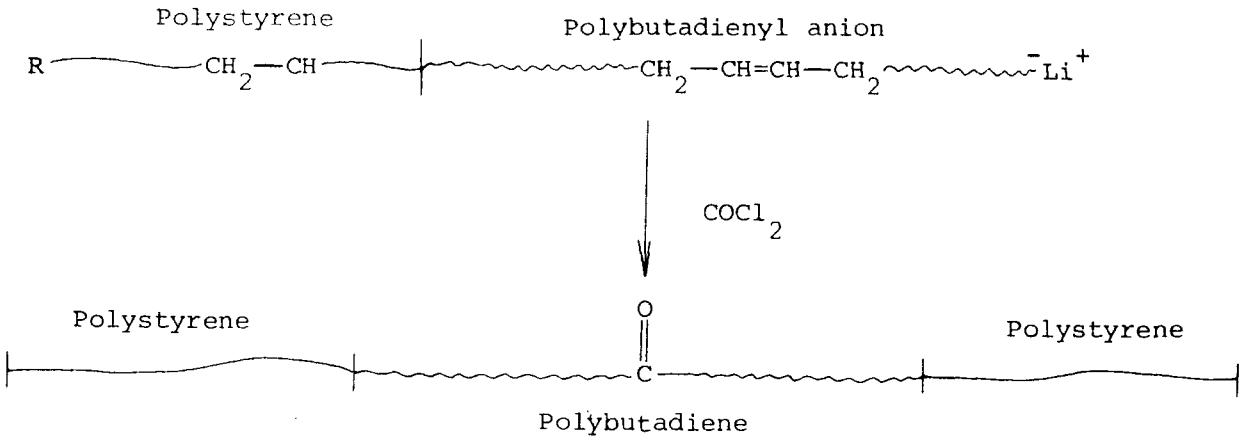
Useful end groups other than hydroxyl include amines, isocyanates, acid halides, silyl halides, carboxyl, thiol, and certain ester groups, the only major requirement is that they interact in a highly efficient manner.

Block copolymers with perfectly alternating distributions are obtained when homopolymers bearing reactive end groups are used. The literature contains many illustrations, for example, polydecamethylene terephthalate with hydroxyl end groups has been reacted with polydecamethylene isophthalate having acid chloride end groups to yield a block copolymer.[87]

In contrast, block copolymers with less control of segment sequence are obtained when two homopolymers with the same functional end groups are coupled via reaction with a third component. An example of this technique is the coupling of hydroxyl terminated polyethylene oxide and bis-phenol-A polycarbonate homopolymers by phosgene.

It is also possible to couple block copolymers themselves to alter their

architecture. A-B and A-B-A structures can be coupled to produce A-B-A or $\{A\text{-}B\}_n$ systems, respectively. An illustrative example is the linear coupling of polystyrene-polybutadiene,



The so-called radial block copolymers are prepared by a similar technique using a polyfunctional coupling agent such as silicon tetrachloride yielding a star-shaped structure.

Because of its low glass transition temperature, high gas permeability, incompatibility with many organic polymers, and excellent resistance to elevated temperatures, the siloxane domain has been introduced into many block copolymers.[88-90]

A review of the preparation of synthetic block copolymers by coupling and condensation reactions is given by Noshay and McGrath in their book "Block Copolymers".

1.6. The separation and purification of block copolymers

All polymer syntheses lead to the production of mixtures of molecules of different molecular weight. In the syntheses of block copolymers listed above the actual product will consist of some block copolymer and some homopolymer(s). There will be a distribution of molecular size for both the

homopolymer(s) and the block sequences. To characterize the reaction completely it is usually necessary to separate the various components of the reaction product, this is usually done by methods based upon differences in solubility. Although there are some guidelines for developing a separation procedure each particular case has to be worked out by essentially empirical methods. The methods used singly or collectively to achieve such separations are described below.

1.6.(i) Separation by precipitation

To employ precipitation techniques a common solvent for all the species must be used, preferably one which is effective at ambient temperature. The precipitant should be chosen so that the precipitation ranges of the homopolymers are as widely separated as possible, since the block copolymer will probably be precipitated somewhere in between these two ranges. There are two methods of separation by precipitation;

1) Fractional precipitation

This method involves the stepwise addition of nonsolvent to a solution of the polymer mixture.[38,39] The precipitated polymer fractions are isolated and characterized

In a solution of homopolymers mixed with a block copolymer the progressive addition of precipitant first collapses the molecular chains of the least soluble polymer species, causing it to precipitate. As precipitation continues, the solution generally develops a characteristic turbidity due to the scattering of light from the copolymer. The least soluble segments of the copolymer are precipitated and coagulated on a microscale but are retained in apparent solution by the solvated segments of the more soluble species. Such turbidity may not be apparent if the refractive index of the swollen aggregate does not differ greatly from that of the solution; although the presence of a stable turbidity is an almost certain

indication of the presence of a block copolymer fraction.[19]

2) Selective precipitation

This is a useful variant of the general fractional precipitation technique[37,38] which invariably gives the "cleanest" separation. This method is more frequently used when solvent-precipitant systems from which only one homopolymer can be precipitated at each stage are employed, the copolymer and the other homopolymer remaining in solution even when excess precipitant is added. Under these conditions coprecipitation can be avoided.

1.6(ii) Separation by extraction

In this method the polymeric material is subjected to extraction at low or elevated temperatures with successive mixtures of nonsolvent and solvent containing increasing fractions of the solvent component for the polymeric species. If a solvent is available that dissolves only one kind of polymer from the mixture, selective extraction can be carried out.[17,19] A block copolymer rich in one of the homopolymers may dissolve partly or wholly in the solvent for that polymer, and the copolymer can then be separated from the solution by a precipitation technique. Coextraction of the block copolymer invariably results in a nonprecipitable turbidity, which may disappear when the solution is heated but which reappears on cooling. This extraction of the block copolymer may not be apparent if selective extraction is carried out in a soxhlet apparatus unless the extracting solvent is cooled to room temperature.

Separation by extraction is effectively the reverse of the fractional precipitation procedure, but it requires smaller quantities of solvents and nonsolvents than the precipitation technique and it is more easily applied to large scale separations.

1.7. Characterization of block copolymers

During the purification of a block copolymer considerable information can be obtained as to the probable structure of the polymeric species present. For instance, the presence of homopolymeric fractions virtually eliminates the possibility of the copolymer fraction being a simple random or regular copolymer and suggests a block or graft copolymer structure.

Many of the analytical tools used to elucidate the structure of homopolymers[91] can also be used for the characterization of block copolymers. However, no single method is capable of describing the nature of these macromolecules; but a combination of several methods, and a knowledge of the mechanism of polymerization, must be used in concert.

Several authors have reported in the literature that elemental analysis,[92] infrared and raman spectroscopic,[93] nuclear magnetic resonance,[94] and thermal gravimetric analysis,[95] as well as, crystallographic studies,[96] fractional precipitation and extraction by selected solvents,[97] solution turbidimetry,[98] density gradient ultracentrifugation,[99] pyrolytic gas chromatography,[100] gel permeation chromatography,[101] optical properties,[102] and physical tests related to mechanical properties[81] have been used as analytical techniques for block copolymer characterization. However, it is not the intention of the author to give here a detailed description of all the analytical techniques available for the characterization of block copolymers, but to point out those techniques that can help in the elucidation of the segmental structure of these complex macromolecules. Thus, the five questions that need to be answered in characterising the products of a block copolymerization, are used as sub-titles for the sections below.

1.7.(i) Is the product a block copolymer or a homopolymer blend?

An important technique which has been used to differentiate between a block copolymer and a homopolymer blend is the solubility behaviour of the polymeric products. Sequential extraction with solvents selective for each component,

of a homopolymeric mixture, results in complete dissolution of the blend, leaving no insoluble residue. Extraction of block copolymers results in a distribution of fractions of varying compositions. Thus, an A-B block copolymer which is comprised predominantly of segment A will be soluble in segment-A selective solvents. Another method used to differentiate between block copolymers and homopolymer blends is film clarity, since the former produce transparent films because the domains of the different components are too small to scatter visible light, and the latter form opaque films due to a high degree of light scattering at the interface between the different phases. An exception to the generality of this technique occurs when the refractive index of the two homopolymers are similar; also the film clarity test may not detect minor amounts of homopolymer contamination.

Solubility compatibility is also used to differentiate between block copolymers, which produce single-phase solutions, and homopolymer blends, which result in incompatible cloudy solutions that eventually separate into two liquid layers due to inmiscibility phenomena.

Molecular weight distribution is another tool in the elucidation of the answer since block copolymers, which represent a single chemical species, display single-mode behaviour and homopolymer blends are more likely to exhibit bimodal characteristics. Density gradient ultracentrifugation and gel permeation chromatography are the techniques used to investigate this phenomenon. Finally, certain rheological tests, such as melt viscosity, can be used to differentiate between block copolymers and homopolymer blends.

1.7.(ii) Is the product a block copolymer or a random copolymer?

In favourable cases infrared spectroscopy and nuclear magnetic resonance spectroscopy can be used to quantitatively measure the distribution of the sequence types; on the other hand, dynamic mechanical behaviour and differential scanning calorimetry can show the presence of the two-phase

morphology present in most block copolymers. Block copolymers usually display two separate glass transition temperatures (Tg) characteristic of each segment, while random copolymers display only one Tg which lies in between the Tg values of the homopolymers. An exception occurs when the segments of a block copolymer are mutually compatible and thus single-phase behaviour is displayed. Morphological techniques such as transmission electron microscopy, scanning electron microscopy and small-angle X-ray scattering are particularly effective. The homogeneous single-phase copolymer appears relatively featureless, whereas in block copolymers the coexistence of two types of domains can usually be detected with the aid of selective staining. Mechanical and rheological properties such as elastic recovery and melt viscosity, and in particular light scattering from solution can add information regarding the block-like nature of a copolymer.

Once it has been established that a macromolecule is a block copolymer, the third question follows.

1.7.(iii) What is the molecular size of the block copolymer and its segments?

Macromolecular structural characteristics, such as molecular weight and molecular weight distribution, can be investigated by the use of those techniques that are established for homopolymers; like membrane and vapour pressure osmometry, solution light scattering, ultracentrifugation, gel permeation chromatography, and solution viscometry. Much of the data obtained by these techniques can be analyzed in the same way as that for homopolymers, but interpretational uncertainties can occur with solution light scattering data if a knowledge of the true theta conditions for both segments is lacking. Problems also exist in the interpretation of GPC data.

Complete and exclusive selective degradation of one segment of the block copolymer which leaves the other segment intact for subsequent analysis is

another method of studying the molecular structure of the segments; the limitation of this method is obvious and therefore it can only be applied to a small number of block copolymer systems.

1.7.(iv) What is the detailed molecular structure of the block copolymer and its segments?

A knowledge of the polymerization technique is an advantage in elucidating the architecture and purity of a block copolymer. Elastic recovery can be used to distinguish between elastomeric A-B structures, which will display poor elastic recovery properties, and A-B-A and $\{A-B\}_n$ structures which, due to the presence of a physical network, will display good recovery properties. Also, triblock and multiblock structures generally display higher melt viscosities than diblock structures, due to the partial retention of the physical network even in the melt.

Gel permeation chromatography and density gradient ultracentrifugation techniques can be used to detect impurities, if these differ sufficiently in either molecular size or density. The analytical techniques used to establish detailed chain structure (i.e. structural isomerism, geometrical isomerism, and tacticity of monomer placements) for homopolymers can equally be applied to block copolymers, although the interpretation of the data would usually be more complicated than is the case for the homopolymers.

1.7.(v) What is the supermolecular structure of the block copolymer?

The distinctive behaviour of block copolymers as supermolecular structures results from the aggregation of like segments to form complex morphological systems, which are comprised of two normally incompatible phases forced to coexist with each other. The three critical characteristics of the segments on which microphase separation is dependent are:

a) Compositional dissimilarity. Mutual incompatibility of the segments due to appreciable differences in chemical composition leads to two-

phase systems, while single-phase morphology results when the segments are compatible due to similar composition and/or short length of one segment.

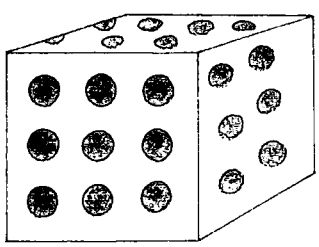
b) Molecular weight. In amorphous block copolymers a pair of low molecular weight segments will display two-phase behaviour only if the differential solubility parameter (Δ) value is relatively large, although two high molecular weight segments can produce two-phase systems even when the Δ values are small. Δ is defined as the difference in the solubility parameters of the segments.

c) Crystallizability. This characteristic provides a new dimension, since crystallization, by definition, is a strong driving force for phase separation even when the blocks are similar in chemical nature and low in block molecular weight.

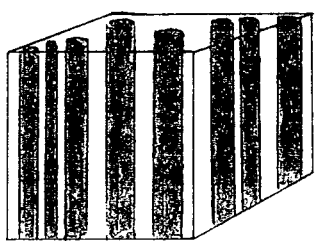
The kind of morphology obtained from two-phase amorphous block copolymers depends upon the volume fraction of segments A and B and on the method of synthesis. The major component will usually exist as the continuous phase with the minor component present as discrete domains, which assume spherical shapes at very low volume fraction levels, rod-like forms at higher levels, and lamellar structure when the two phases are present in nearly equivalent volume fractions, as shown below. The casting of films from selective

Block copolymer morphology

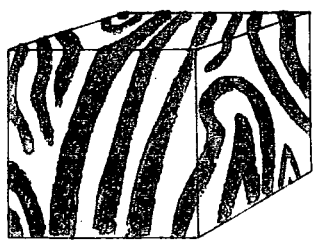
(white = continuous phase)



spheres, at low concentration of second component.



rods, at intermediate concentration of second component.



lamellae structure at ca. 50:50 composition.

solvents is a particularly effective method for controlling morphology.

The following techniques can be used to investigate the supermolecular structure of block copolymers:

Thermal analysis, differential scanning calorimetry and rheological measurements can detect the presence of supermolecular structures but can not readily distinguish between morphological types. Transmission and scanning electron microscopy can reveal the shape and size of domains on the surface of a block copolymer; before being examined some block copolymers must be exposed to selective staining procedures, due to the low differences in the electron density of the segments. Wide- and small-angle X-ray scattering have been used to study the morphology of crystalline and amorphous block copolymers. The later technique is also used to investigate interdomain spacing and subsurface morphological characteristics. Finally, small-angle light scattering and birefringence have been used to identify the sizes and shapes of domains.

1.8. Uses and applications of block copolymers.

Block copolymers, apart from being scientifically interesting, are a new class of materials, several of which are now commercially available. Their main applications fall into three categories, as follows:

(i) Elastomers

The first styrene-diene elastomeric block copolymers to be offered commercially were a styrene-butadiene diblock copolymers, produced by the Phillips Petroleum Co. under the trademark of Solprene. These find uses in molded and extruded mechanical goods, shoe products, adhesives, floor tile foam, wire and cable, and artificial leather.

The two-phase block copolymer elastomers that have been commercialized are of three structural types:

a) Styrene-diene A-B-A block copolymers, for example, the Kratons of Shell Chemical Co. The main applications of these triblock structures are as components for adhesives, latex films, elastic filaments, caulkings and sealants, coatings, and injection molding or extrusion, as well as to form alloys with other materials to improve specific properties like strength, toughness, and weather and ozone resistance.

b) Ester-ether $\{A\text{-}B\}$ block copolymers, for example, the Hytrels of DuPont Co., which are based on the tetramethylene terephthalate-tetramethylene oxide block copolymer structure. These macromolecules are useful in rotational molding, powder coating, injection molding, and casting applications. The polyether soft blocks provide the flexibility by virtue of their low glass transition temperatures, and the polyester hard blocks provide the physical cross-linking effect due to their crystallizability.

c) Urethane-ester $\{A\text{-}B\}_n$ block copolymers, for example, the Estanes of B.F. Goodrich Co.. Elastomeric polyurethane fibres are characterized by a very high elongation at break, very low modulus, and high recovery from large deformations. The well-known Spandex elastomeric fibres are also based on polyurethanes.

All of the A-B-A and $\{A\text{-}B\}_n$ commercial elastomeric block copolymers have a physical network structure. The thermoplastic elastomeric behavior of these materials make them useful in a variety of applications listed below.

1) Automotive; replacing the plasticized vinyls used currently in interior flexible applications.

2) Mechanical goods; this market includes articles such as flexible couplings, O-rings, seals, gaskets, and extruded hydraulic and industrial hoses.

3) Electrical and electronic; which include wire and cable insulation and transformer encapsulation.

4) Sealants, caulks, and adhesives; important advantages for these materials over conventional adhesives are the ability to apply them either via solution or melt techniques and their ability to subsequently develop high strength and recovery characteristics without the need of a curing step.

5) Footwear; the combination of melt processability, good elastomeric properties, high dynamic coefficient of friction, and excellent abrasion resistance make block copolymer elastomers especially attractive for footwear applications.

The total market for all thermoplastic elastomer materials in the mid-1980's is predicted to be one billion pounds per year.[103]

Elastomeric block copolymers can be economically fabricated into end-use articles by processes similar to those used for thermoplastics, for example, injection or blow molding, extrusion, vacuum forming, and solution casting.

(ii) Toughened thermoplastic resins

The impact modification of a rigid but brittle polymer can be achieved by the production of block copolymers containing a high volume fraction of a hard block and a minor concentration of a soft block. Styrene-rich resins have been commercialized under the trade name KResins. These materials are almost as tough as conventional rubber-modified polystyrene and have the advantage of optical clarity due to the small domain size of the polybutadiene phases, making them suitable for many packaging applications.

Crystalline block copolymers of propylene with ethylene (and an ethylene-propylene random copolymer) have been reported to have several property advantages over ethylene and propylene homopolymers.[81] The most dramatic effect is that brittleness temperature decreases and impact strength

increases with increasing ethylene content. These materials are used in place of polypropylene homopolymer in applications that require improved toughness and that can tolerate the somewhat lower modulus levels of the block copolymers, such as in fabricating containers, blow molding bottles, films, tubbing, wire coatings, paper coatings, and molded objects in general. They have also been claimed to be useful as adhesives for bonding polyethylene to polypropylene.

(iii) Surfactants

Block copolymers of ethylene oxide and propylene oxide have been commercial products for many years. A series of these nonionic surface active agents has been manufactured since 1957 under the trademark Pluronic by the Wyandotte Chemical Corporation. The properties of these surfactants make them useful in applications requiring the emulsification of aqueous and nonaqueous components and/or the wetting of substrate surfaces.

Block copolymers of siloxanes and alkylene ethers are widely used as surfactant additives for urethane foams. When added at the ~1% level to foam formulations they enable cell size and uniformity to be controlled during the foam-forming process. This is because the alkylene ether segment is soluble in the urethane matrix, while the siloxane segment resides at the gas-urethane interface. These copolymers are also claimed to be useful in fibre antistatic, antifoam, mold release, lubricant, and wetting agent applications.

The use of block copolymers in the surface coatings area, in the production of new alloys, to enhance the performance of adhesives, and in semipermeable membrane and biomedical areas are some of the conceivable new applications that would take maximum advantage of their inherent capabilities. The uses and applications described in this section are extensively documented in the book "Block Copolymers", by Noshay and McGrath.

CHAPTER 2

Experimental

2.1. Monomer synthesis

2.1.(i) Introduction

a) Vinyl acetate

Vinyl acetate, $CH_3COOCH{:}CH_2$, was probably first synthesized by Miasnikoff[104] in 1860, although he did not publish any physical property data at the time. Today most vinyl acetate is produced by processes which involve the reaction of either ethylene or acetylene with acetic acid.[105] Vinyl acetate is an important commercial material and many alternative syntheses have been reported. For example, the Celanese Corporation have a process involving the reaction of acetic anhydride with acetaldehyde to give ethylidene diacetate which is pyrolytically decomposed.[106]

$$(CH_3CO)_2O + CH_3CHO \longrightarrow CH_3CH(OCOCH_3)_2 \longrightarrow CH_3COOCH{:}CH_2 + CH_3COOH$$

Amongst other methods of synthesis for vinyl acetate are the reaction of ketene with acetaldehyde,[107] the pyrolysis of glycol diesters[108] and dehydration of the adduct between acetic acid and ethylene oxide.[109]

Vinyl acetate is a widely used monomer in both homopolymerizations and copolymerizations. The homopolymer is the precursor of poly(vinyl alcohol) which in its turn is the parent of a large range of important materials. There is a very extensive literature concerning the synthesis and applications of vinyl acetate; see, for example, Encyclopaedia of Polymeric Science and Technology, 15, 531-677, (1977).

b) Fluorinated alkyl acrylates and methacrylates

Fluoroalkyl methacrylate esters were prepared by Crawford and Slanley[110] by reacting primary or secondary saturated alcohols containing 2, 3, or 4 carbon atoms and 1 or more fluorine atoms with methacrylic acid, its anhydride, acid chloride or methyl ester in the presence of an inhibitor.

Thus, trifluoroethyl methacrylate (TFEM) was made by refluxing 2,2,2-trifluoroethanol with methacrylic chloride in the presence of pyrogallol for 3 hours at 80-90°C. Albrecht[111] prepared 1,1-dihydroperfluorobutyl acrylate using a mixture of acrylic acid and perfluoroacetic anhydride with the fluoroalcohol. Codding and co-workers[112] reported that direct esterification of a fluorinated alcohol using acrylic acid, in the presence of strong acids, was impractical due to the low reactivity of the fluoroalcohols used. In the same paper a more useful procedure was described involving the reaction of fluorinated alcohols with acrylyl chloride.

$$CH_2{:}CHCOCl + R_fCH_2OH \longrightarrow CH_2{:}CHCOOCH_2R_f$$

A side reaction resulting in the formation of 1,1-dihydroperfluoroalkyl β-chloropropionate esters was minimized by heating the acrylyl chloride to the desired reaction temperature before addition of the alcohol. Halpern and Karo[113] also reported the synthesis of trifluoroethyl acrylate (TFEA) by reacting trifluoroethanol with acrylyl chloride in the presence of triethylamine. Hexafluoroisopropyl acrylate and methacrylate (HFPA,HFPM) were prepared by Hollander and Woolf[114] by refluxing a mixture of the fluoroalcohol with acrylyl and methacrylyl chlorides for 12 hours and then adding pyridine and heating for a further 5 hours at 70-100°C. Karo and Kline, in a patent,[115] described the preparation of TFEA by reacting trifluoroethanol with acrylic acid complexed or dissolved in polyphosphoric acid using phenothiazine as inhibitor. A different approach to the synthesis of fluorinated acrylic esters involves the reaction of a perfluoroalkoxide (a perfluoroketone - metal fluoride adduct) with an appropriate acid chloride.

$$(CH_3)_2CO + KF \rightleftharpoons (CF_3)_2CFO^- K^+ \xrightarrow{CH_2{:}CHCOCl} CH_2{:}CHCOOCF(CF_3)_2$$

Such perfluoroalkoxides have also been used to introduce fluoroalkyl groups into acrylic esters by nucleophilic displacement of bromide, for example, from ω-bromo esters.[116]

The polymers obtained from fluoroacrylic esters are not produced in high tonnage as is the case for vinyl acetate; nevertheless the low surface energies exhibited by these materials have been exploited in several applications. Poly(fluoroalkyl acrylates) have been used in surface treatments of fabrics, leathers and paper products to impart oil and water resistance.[117,118] During the 1950's these materials were intensively investigated as potential solvent resistant elastomers,[112,119-121] and although materials with many of the properties required (low Tg, solvent resistance) were obtained their limited thermal and hydrolytic stability prevented their development as useful commercial materials. Another important disadvantage of these materials is their relatively high cost; as a consequence they tend to find use in applications where trace amounts have a significant effect on the performance, a typical example is the addition of 0.001 → 6% fluoroalkyl (methyl) acrylate polymers to some shampoos as an aid to rapid hair drying.[122] Fluoropolymers are often biologically inert materials and this has lead to applications such as the use of copolymers of fluoroacrylic monomers in dental restoratives.[123]

2.1.(ii) Experimental

a) Materials

Acrylic acid stabilised with 20 p.p.m. hydroquinone monomethyl ether and methacrylic acid inhibited with 1000 p.p.m. hydroquinone and 250 p.p.m. hydroquinone monomethyl ether (Aldrich Chemical Co. Ltd.), benzoyl chloride (Aldrich Chemical Co. Ltd.), hydroquinone (B.D.H. Chemicals Ltd.), and 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol (Bristol Organics Ltd.) were obtained from the manufacturers and used without further purification.

b) Synthesis

The synthetic route used for the preparation of the fluorinated acrylates and methacrylates was the one described by Codding and co-workers[112] that is, reacting acrylyl or methacrylyl chloride with the fluoroalcohols, as summarized below:

$$PhCOCl + CH_2{=}{=}C(Y)COOH \longrightarrow PhCOOH + CH_2{=}{=}C(Y)COCl$$

$$CH_2{=}{=}C(Y)COCl + RfCH_2OH \longrightarrow CH_2{=}{=}C(Y)COOCH_2Rf + HCl$$

where Y is H in the case of acrylates, and $-CH_3$ for methacrylates.

In practice, it was found most convenient to use the acid chlorides immediately after synthesis; a standard procedure was adopted which is given below for the case of 2,2,2-trifluoroethyl acrylate. The details for the syntheses of the other monomers are recorded in table 2.1.

The apparatus used consisted of two reaction flasks. The first (500c.c.; 2 necked) was fitted with a nitrogen inlet and a fractionating column (20 cms. long; 1 cm. internal diameter, containing glass helices). This was connected to the second flask (500c.c.; 3 necked) via the column by a still head and condenser. The remaining necks of the flask were fitted with a reflux condenser with a nitrogen inlet, and a pressure equilibrated dropping funnel, connected to a dry nitrogen supply. The entire apparatus was oven dried at 140°C for two hours and then assembled hot whilst purging with dry nitrogen. Acrylic acid (108g.; 1.5 moles) and benzoyl chloride (315 g.; 2.25 moles) were introduced into the two necked flask. A small quantity of hydroquinone (about 1.24 g.) was placed in the receiving flask to act as inhibitor. The mixture in the flask was heated by electric mantle and acrylyl chloride was distilled (b.pt. 76°) and condensed into the second reaction vessel. When no more acid chloride distilled, the condensing

system was removed from the three necked flask and the neck sealed with a previously dried thermometer well and thermometer. The acrylyl chloride was heated to 60°C using an electric mantle before 2,2,2-trifluoroethanol (150 g.; 1.5 moles) was added rapidly. The mixture was refluxed for 15½ hours at 75°C, the hydrogen chloride evolved being removed in the nitrogen sweep. The contents of the flask included the desired fluorinated acrylate, together with excess alcohol (as demonstrated by both infrared and glc analysis). The latter was removed by washing thoroughly with 6x200 cm^3 aliquots of deionised water. The acrylate was dried ($MgSO_4$) and distilled (Spaltrohr concentric tube fractionating column, HMS 500, 75 theoretical plates). The fraction distilling at 47.00-47.25°C at 126.5 mm.Hg was collected at a reflux ratio of 10:1 and examined by glc (column A at 100°C), and infrared spectroscopy. Some fractions obtained from the distillation were purified by preparative glc (column A).

The monomers thus formed were stored at -25°C over hydroquinone inhibitor.

c) Characterization

i) Gas-liquid chromatography

Analytical gas chromatography using a Pye Series 104 Chromatograph, incorporating a di-n-decylphthalate/celite (1/2) column, a flame ionization detector, and a Honeywell precision integrator indicated that the products obtained were single compounds with a purity $\geq$ 99.99%

ii) Spectroscopy

All the monomers are known materials and the mass and infrared spectra displayed were identical with those of authentic samples.

Table 2.1.

Acid	Benzoyl chloride	Alcohol	Product	b.pt.°C/mm.Hg.	Yield
Acrylic acid (108 g.; 1.5 moles)	315 g.; 2.25 moles	2,2,2-trifluoro-ethanol. (150 g.; 1.5 moles)	2,2,2-trifluoro-ethyl acrylate. (118 g.; 0.76 moles)	47.00 - 47.25/116.5	51%
Methacrylic acid (129 g.; 1.5 moles)	315 g.; 2.25 moles	2,2,2-trifluoro-ethanol. (150 g.; 1.5 moles)	2,2,2-trifluoro-ethyl methacrylate. (121 g.; 0.72 moles)	47.00/105	48%
Acrylic acid (108 g.; 1.5 moles)	315 g.; 2.25 moles	1,1,1,3,3,3-hexa-fluoropropan-2-ol. (252 g.; 1.5 moles)	1,1,1,3,3,3-hexa-fluoroisopropyl acrylate. (193 g.; 0.87 moles)	36.25/98.5	58%
Methacrylic acid (129 g.; 1.5 moles)	315 g.; 2.25 moles	1,1,1,3,3,3-hexa-fluoropropan-2-ol. (252 g.; 1.5 moles)	1,1,1,3,3,3-hexa-fluoroisopropyl methacrylate. (212 g.; 0.9 moles)	46.25/98.5	60%

iii) Elemental analysis

The elemental analyses, table 2.2., were satisfactory.

Table 2.2.

Monomer	Element	Calculated	Found
2,2,2-trifluoroethyl acrylate	Carbon	38.97	39.20
	Hydrogen	3.27	3.48
	Oxygen	20.77	20.47
	Fluorine	36.99	36.85
2,2,2-trifluoroethyl methacrylate	Carbon	42.86	43.01
	Hydrogen	4.17	4.54
	Oxygen	19.05	18.85
	Fluorine	33.93	33.60
1,1,1,3,3,3-hexafluoro-isopropyl acrylate	Carbon	32.43	32.14
	Hydrogen	1.80	1.79
	Oxygen	14.41	14.47
	Fluorine	51.35	51.60
1,1,1,3,3,3-hexafluoro-isopropyl methacrylate	Carbon	35.59	35.62
	Hydrogen	2.54	2.28
	Oxygen	13.56	13.67
	Fluorine	48.30	48.43

2.2. Polymer Synthesis

2.2.(i) Introduction

Homopolymerizations and copolymerizations of the monomers described in the previous section have been the subject of several investigations; bulk, solution, and emulsion techniques have been used.

In this work the synthesis of block copolymers was the objective and as described in Chapter 1 the chosen route was via the "living" macroradical technique initially suggested by Swarc and developed by Seymour and co-workers.

A number of limitations have been established by Seymour and his group for the application of this technique. The essential features of the method are as follows: the radical polymerization of the first monomer is conducted in a poor and/or a viscous solvent and when the molecular weight of the growing chain exceeds a particular value the living polymer radical precipitates from solution. This first stage of the process is carried on until most (ideally all) of the monomer and the radical initiator have been consumed. The monomer for the second block is now introduced and provided that it can penetrate the coil of the precipitated macroradical the polymerization process can continue using the macroradical as the initiator for this second stage. There are clearly a number of problems which can prevent the successful application of this method. In the first stage it is important to avoid all termination reactions, in as far as this is possible. Solvents must be chosen for which transfer to solvent is limited and impurities which can act as chain transfer or termination agents must be rigorously excluded. It is also important that transfer to monomer should not be significant in either stage of the process. If these conditions are met block copolymer synthesis will predominate and only small amounts of homopolymers will be produced.

In earlier work on the formation of block copolymers from precipitated vinyl acetate macroradicals tertiary-butanol and cyclohexane were chosen as good and poor solvents respectively because of their low chain transfer reactivity with vinyl acetate macroradicals.[124] In this work cyclohexane has been the solvent used predominantly and some polymerizations have been conducted in tertiary-butanol for comparison purposes. We also aimed to produce polymers with a short fluoroacrylate block attached to vinyl acetate blocks of different lengths, those macroradicals produced in the poor solvent (cyclohexane) should be significantly smaller than those produced in the viscous good solvent (tertiary-butanol).

The penetration of the second monomer into the macroradical coil requires that the difference between the solubility paramenters of the macroradical and the monomer must not be greater than 3.1H units. The solubility parameter for poly(vinyl acetate) is 9.4H and consequently the fluoroalkyl monomers should have solubility parameter values lying between 12.5 and 6.3H units. The actual values have been calculated by Strange,[125] and are tabulated below.

Monomer	δ
2,2,2-trifluoroethyl acrylate	8.06
2,2,2-trifluoroethyl methacrylate	7.94
1,1,1,3,3,3-hexafluoroisopropyl acrylate	7.27
1,1,1,3,3,3-hexafluoroisopropyl methacrylate	7.10

As was mentioned in chapter 1 (section 1.2.(v)) temperature of reaction is also an important determinant of success or failure in this method of making block copolymers.

With the foregoing considerations in mind the synthesis of block copolymers using vinyl acetate macroradicals and fluoroalkyl acrylates was tempted as described below.

2.2.(ii) Experimental

a) Materials

Vinyl acetate, inhibited with 4p.p.m. hydroquinone and 300p.p.m. diphenylamine, was obtained from Aldrich Chemicals Co. The monomer was purified by drying it overnight over $MgSO_4$ and then fractionally distilled under an atmosphere of dry nitrogen. The fraction b.pt. 72.5°C was collected and stored over activated molecular sieve (4A) under nitrogen at -25°C until required.

The fluoroalkyl acrylate and methacrylate monomers were prepared as described in the previous section, and used without further purification.

Cyclohexane (analar was refluxed over sodium and then fractionally distilled under an atmosphere of dry nitrogen; the fraction distilling between 80.6 and 80.8°C was collected.

Tertiary butanol obtained from Kock-Light Laboratories was refluxed over lime for 4½ hours and then fractionally distilled under an atmosphere of nitrogen. The fraction b.pt. 82.0°C was collected and used as required.

2,2'-a-Azo-bis-isobutyronitrile (AIBN), obtained from B.D.H. Chemicals Ltd. was recrystallized twice from methanol (maximum temperature 35°C), filtered, dried under vacuum (0.005 mm. Hg; 8 hours) and stored in a sealed container at -25°C.

b) Homopolymer preparation and isolation

The polymerization of vinyl acetate will be described; the technique used was the same for all other homopolymer syntheses; the exact amounts of chemicals used are recorded in table 2.3.

The apparatus consisted of a round-bottomed flask (500 c.c.; 2 necked) containing a magnetic stirrer and attached to a conventional vacuum line via a condenser. The glassware was oven dried at 140°C overnight, assembled hot and allowed to cool under vacuum; the system was then let down to an atmosphere of dry nitrogen. 190 g. of solvent, 0.6 g. of AIBN and about 10 g. of monomer were introduced in the reaction flask against a counter-current of dry nitrogen. The reactants were degassed by at least five freeze and thaw cycles, to remove any traces of dissolved oxygen, and then heated in an oil bath at 50°C while being stirred slowly under an atmosphere of dry nitrogen for 96 hours. At this stage about 1 c.c. of MeOH (analar) was introduced in the reaction flask to quench the precipitated living macroradicals.

The bulk of the solvent was decanted and the polymeric products were recovered by dissolving in acetone, transferring to a wide necked flask, and evaporating the solvent using a rotary evaporator. The polymer was then dried under vacuum (0.01 mm. Hg.) at room temperature for at least 96 hours. Yields of the precipitated products are recorded in table 2.3.

c) Block copolymer preparation and recovery of the products

Vinyl acetate was polymerized as explained in the last section for 96 hours and then fluoroalkyl acrylates and methacrylates (see table 2.4. for amounts of reactants) were vacuum transferred into the reaction flask and allowed to react under an atmosphere of dry nitrogen for a further 96 hours while being heated by an oil bath at 50°C, and stirred slowly. The macroradicals were quenched with 1 c.c. of MeOH (analar) and the recovery procedure for the polymeric products was the same as that described for the homopolymers. Yields of the precipitated products are recorded in table 2.4.

The characterization of these products is described in the next chapter.

Table 2.3.

Run Number	Monomer grs.	Monomer moles	Initiator grs.	Initiator moles.	Solvent grms.	Temp. Duration	Yield
1	vinyl acetate 9.78	0.1137	AIBN 0.5909	0.0036	t-Butanol 190	50°C 96 hours	89.8%
2	vinyl acetate 9.78	0.1137	AIBN 0.6059	0.0036	t-Butanol 190	50°C 96 hours	89.0%
3	vinyl acetate 9.78	0.1137	AIBN 0.16225	0.00098	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	95.0%
4	vinyl acetate 9.78	0.1137	AIBN 0.3012	0.00183	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	93.0%
5	vinyl acetate 10.25	0.119	AIBN 0.5991	0.00365	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	85.0%
6	vinyl acetate 10.25	0.119	AIBN 0.6047	0.00368	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	91.0%
7	TFEA 10.114	0.0656	AIBN 0.6064	0.00369	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	92.3%
8	TFEM 9.37	0.0557	AIBN 0.33135	0.002018	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	96.7%
9	HFPA 9.54	0.0429	AIBN 0.2346	0.001428	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	78.9%
10	HFPM 10.368	0.0439	AIBN 0.6045	0.00368	$c\text{-}C_6H_{12}$ 190	50°C 96 hours	68.0%
11	HFPM 10.368	0.0439	AIBN 0.6011	0.00366	t-Butanol 190	50°C 96 hours	79.0%

Table 2.4.

Run Number	Monomer 1 moles	Monomer 2 moles	Initiator moles	Solvent grms.	Temp. Duration	Yield
12	Vac .11905	TFEA .00737	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	90.53%
13	Vac .11905	TFEA .01978	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	93.26%
14	Vac .11905	TFEA .03975	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	92.88%
15	Vac .11905	TFEM .00734	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	91.11%
16	Vac .11905	TFEM .01451	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	88.01%
17	Vac .11905	TFEM .01331	AIBN .0036	c-C_6H_{12} 190	60°C 192 hours	85.66%
18	Vac .11905	TFEM .00782	AIBN .0036	c-C_6H_{12} 190	76°C 192 hours	59.06%
19	Vac .11905	TFEM .02891	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	95.05%
20	Vac .11905	HFPA .00740	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	87.05%
21	Vac .11905	HFPA .01500	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	81.87%
22	Vac .11905	HFPA .03025	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	94.23%
23	Vac .11905	HFPM .00716	AIBN .0036	c-C_6H_{12} 190	50°C 192 hours	85.29%
24	Vac .23268	HFPM .03102	AIBN .0073	c-C_6H_{12} 380	50°C 192 hours	84.20%
25	Vac .23268	HFPM .07775	AIBN .0073	c-C_6H_{12} 380	50°C 192 hours	83.56%
26	Vac .23268	HFPM .02499	AIBN .0072	t-butanol 380	50°C 192 hours	83.44%
27	Vac .23268	HFPM .08334	AIBN .0073	t-butanol 380	50°C 192 hours	82.37%

CHAPTER 3

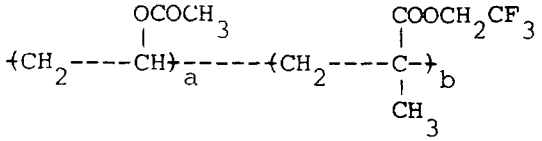
Characterization of Polymeric Products

3.1. Introduction

The materials produced in this work displayed bulk physical properties varying from dry white powders to sticky elastomeric products. The objectives of the investigation described in this chapter were to establish the compositions of the products and in particular whether the expected block copolymers had been formed. The methods used in the investigation were: elemental analysis; infrared, ^{1}H and ^{19}F n.m.r. spectroscopy; solvent extraction; gel permeation chromatography; and film opacity. These methods used in combination provide convincing evidence that the route selected for the synthesis gives a viable method of producing block copolymers.

3.2. Elemental analysis

All elemental analyses were obtained through the Departmental service. Carbon, hydrogen, and nitrogen values were obtained by combustion analysis. Fluorine values were obtained using the potassium fusion method which depends on determining KF by ion exchange. The molar composition of copolymers can be determined from the elemental analyses figures, and in this case the use of carbon, hydrogen and fluorine values should in theory produce an internally consistent set of determinations. The error on the small hydrogen value means that compositions determined from percentage of hydrogen are unlikely to be accurate. In principle, agreement between the compositions determined from the larger carbon and fluorine values should be reasonably good. In practice, this was not the case, take as an example a copolymer between vinyl acetate and trifluoroethyl methacrylate,



It is straight forward exercise to calculate molar incorporation ratios, that is a:b, from the elemental analysis figures. For a typical product the measured values for carbon, hydrogen and fluorine percentage are shown below together with the computed incorporation ratio.

	a : b
C % - 52.15	1 : 4.96
H % - 6.97	1 : 812
F % - 13.57	1 : 2.93

As expected the hydrogen figure differs widely from the other two. However, it is clear that the use of elemental analysis requires extremely accurate composition determination if a useful measure of incorporation ratios is to be obtained.

It should be emphasized that these discrepancies do not reflect the competence of the analyst, but rather point to the limitation of this method. Very small variations from the correct figure for the elemental composition result in quite wide variations in the calculated incorporation ratio and the presence of minor impurities, such as traces of solvent or, for low molecular weight materials, initiator fragments completely invalidate the procedure. Nevertheless where compositions vary over a range of values the trend will be revealed by variation in the elemental analysis figures.

Another reason for caution when using elemental analyses figures stems from the fact that the nitrile initiator residues will be determined as "fluoride" in the potassium fusion method. In practice, for both homopolymers and copolymers agreement between calculated and measured elemental analysis figures were usually within the error limits of the method for carbon and hydrogen, whereas fluorine figures were almost invariably too high.

Elemental analysis figures are recorded were appropriate throughout the remainder of the chapter.

3.3. Infrared spectroscopy

Since all the polymers involved in this work could be cast as films from acetone it was a straight forward matter to record their infrared spectra. There was no requirement for solvent or mulling agents and consequently no complications to the interpretation of the spectra.

For the homopolymers comparison of monomer and polymer spectra showed the expected trends. For example, on polymerization of vinyl acetate the stretching vibration of the carbon-carbon double bond at 1644 cm^{-1} in the monomer is not found in the polymer, and the monomer carbonyl band at 1760 cm^{-1} is shifted to 1740 cm^{-1} in the polymer, which is consistent with the change in its environment. The infrared spectrum of poly (vinyl acetate) has been the subject of several studies[126,127] and, in particular, bands at 1090 cm^{-1} and 1125 cm^{-1} have been associated with respectively syndiotactic and atactic sequences. In the homopolymers produced in this work a band at 1125 cm^{-1} was always visible, but no significant absorption at 1090 cm^{-1} was seen; thus, as expected, the poly(vinyl acetate) produced is atactic; this is also consistent with its solubility behaviour since syndiotactic poly(vinyl acetate) is insoluble in acetone.

The fluoroacrylate homopolymers showed similar trends, all the monomers displayed carbon-carbon double bond stretching frequencies at 1640 cm^{-1} which were not present in the polymers. The ester carbonyls in all these polymers were found at frequencies 10 to 20 cm^{-1} higher than the monomer ester carbonyls, which is consistent with the loss of conjugation on polymerization. All spectra showed the expected C-H and C-F absorptions.

The infrared spectra of the monomers and homopolymers have been recorded previously,[123,125] and are not repeated here. Since the spectra of

poly(vinyl acetate) and the fluorinated acrylate esters differ significantly, infrared spectroscopy can be used for qualitative analysis of the composition of samples (see Section 3.5.).

3.4. ^{1}H and ^{19}F N.M.R. spectroscopy

N.m.r. spectroscopy has been widely used for the quantitative determination of the composition of copolymers, and investigation of the details of structure. In this work this technique was used in an attempt to provide evidence for the "blockiness" of the polymers synthesized as well as to determine the monomer incorporation ratios. The spectra of homopolymers were also recorded as part of their characterization and as reference data for copolymer studies. The spectra were obtained through the Departmental service, which uses a Brücker HX90E modified for FT operation.

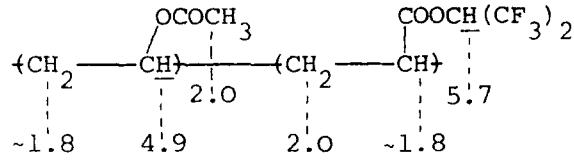
It has previously been demonstrated that the ^{19}F n.m.r. chemical shift is sensitive to the environment of the fluorinated group in copolymers. Thus, Strange has shown that for poly(hexafluoroisopropyl methacrylate) and poly(methyl methacrylate-b-hexafluoroisopropyl methacrylate) the ^{19}F n.m.r. chemical shifts are the same whereas for a random copolymer of the same two monomers the ^{19}F signal is shifted downfield by 0.56 p.p.m.[125] For the polymers prepared in this work the ^{19}F n.m.r. signals for homopolymers and copolymers were single sharp resonances and were observed at the same chemical shift (72.89 ± 0.01 p.p.m. downfield from internal $CFCl_3$ in $CDCl_3$ solution, for hexafluoroisopropyl methacrylate). This is evidence which is consistent with the proposal that the fluorinated monomer residues occur as homogeneous blocks and not as random copolymers with vinyl acetate; although this evidence by itself is not the basis for an unambiguous structure assignment it does provide support for the conclusions drawn from other items of evidence.

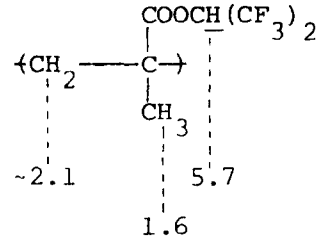
The ^{1}H n.m.r. spectra were not particularly well resolved and generally appeared as broad bands which often overlapped each other. However, for all

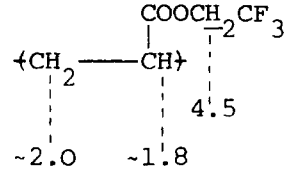
the copolymerization attempts it was possible to identify reasonably well resolved resonances which were associated with specific monomer features. These are listed in figure 3.1. below.

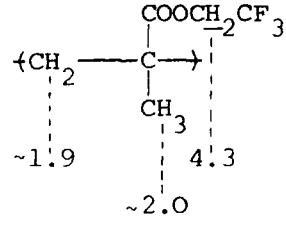
Figure 3.1. ^{1}H n.m.r. parameters for copolymers.(i)

Copolymer type

I 

II " 

III " 

IV " 

(i) as solutions in $CDCl_3$, shifts in p.p.m. from internal TMS. Approximate values (~) estimated from overlapping broad signals.

Monomer incorporation ratios were calculated from the integrated intensities of the signals associated with the protons underlined in the structures drawn in figure 3.1. These were compared with the incorporation ratios calculated from elemental analysis figures, and the results for a

representative set of samples are recorded in table 3.1. The conclusion to be drawn from the data presented in Table 3.1. is clearly that agreement between the various methods of determining monomer incorporation is almost

Table 3.1. Monomer imcorporation ratios

Copolymer type	Run	^{1}H n.m.r.	Monomer incorporation ratios (vinyl acetate : comonomer)		
			C %	H %	F %
I	21	3 : 1	6 : 1	10 : 1	2 : 1
I	22	6 : 1	2 : 1	111 : 1	2 : 1
II	25	9 : 1	3 : 1	9 : 1	3 : 1
II	27	10 : 1	10 : 1	110 : 1	4 : 1
III	14	2 : 1	3 : 1	11 : 1	---
III	13	7 : 1	2 : 1	85 : 1	---
IV	16	10 : 1	15 : 1	12 : 1	4 : 1
IV	19	6 : 1	5 : 1	812 : 1	3 : 1

(for experimental details on the runs see table 2.4.)

non-existant. The problems associated with calculations based on elemental analysis have been discussed earlier. The question which remains is which, if any, of these values is reliable. In theory the ^{1}H n.m.r. approach ought to give a satisfactory result but it depends on the accuracy with which the integration can be made and this in its turn depends on the sharpness of the signals and the flatness and electronic noise level of the base line. The spectra obtained were far from ideal, the base lines were usually quite

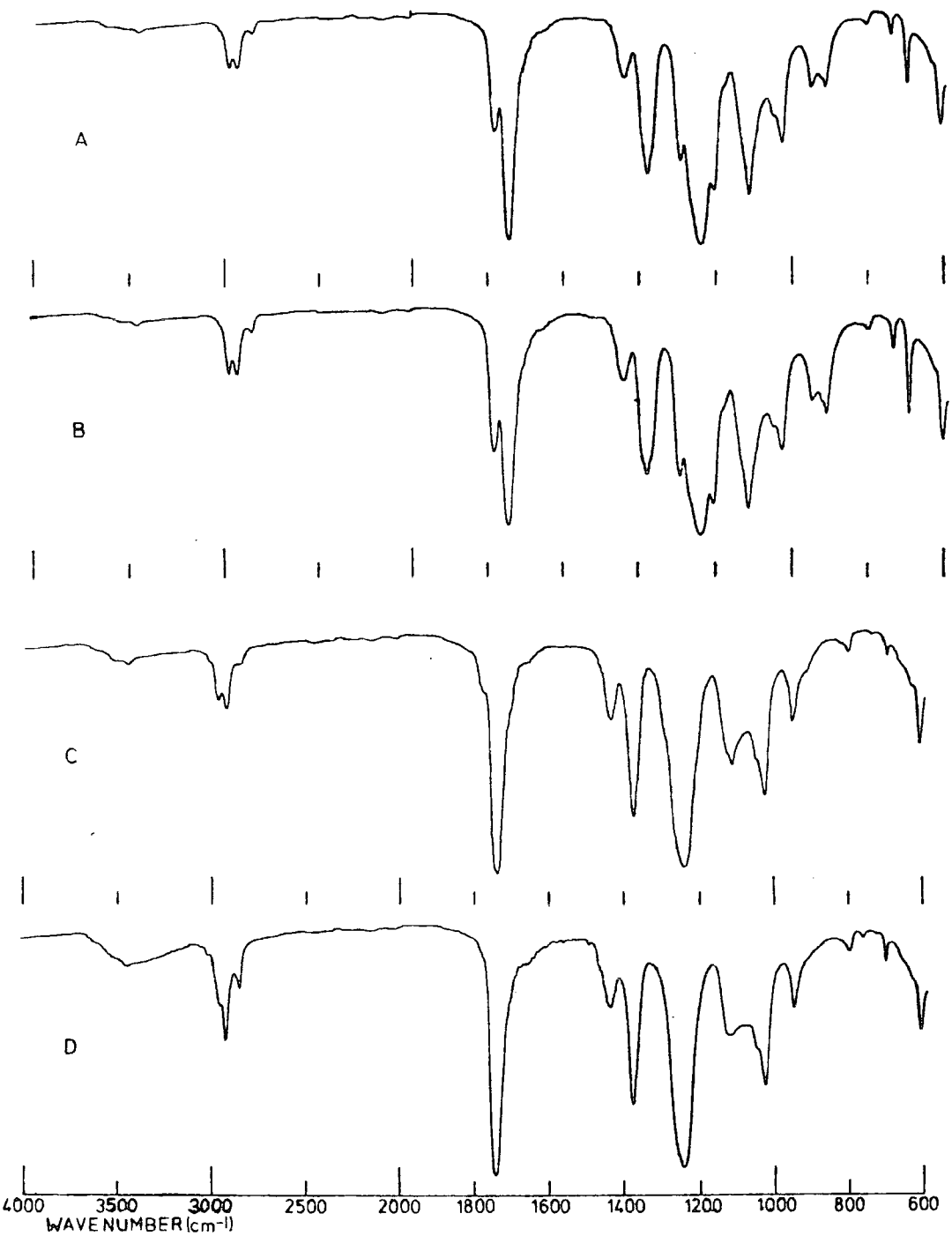
"noisy" and often not flat, also the signals observed were broad and deciding the point at which the signal associated with a particular peak emerged from the background noise was not easy. It was not possible to carry out internal checks on the consistency of the ^{1}H n.m.r. method because of considerable overlapping of resonances. Thus, the results of ^{1}H n.m.r. analysis can only be said to be in qualitative agreement with earlier assignments.

3.5. Solvent extraction and solution behaviour

Poly(vinyl acetate) and the poly(fluoroacrylates) have different solubility characteristics, thus the fluorinated polymers are all soluble in diethyl ether whereas poly(vinyl acetate) is not. There are other solvents which are exclusive to one kind of homopolymer, for example, poly(vinyl acetate) dissolves in methanol whereas the fluorinated methacrylates do not. Such sharp differences in solubility allowed the possibility of separation by extraction. In this work, diethyl ether was used, chiefly because of its low volatility and easy removal from samples by evaporation under vacuum.

As a typical example, consider the material produced in experiment 21, table 2.4. When the product of this attempted synthesis of a poly(vinyl acetate-b-hexafluoroisopropyl acrylate) was extracted with cold ether 82% of the material was dissolved. The residue was extracted in a soxhlet apparatus for a week giving a further 15% of extractable material, and a residue (3%) which was not dissolved even after a further week of continuous ether extraction. The infrared spectra of the raw product from experiment 21, the two fractions extracted with diethyl ether and the insoluble residue are shown in figure 3.2. In this particular case, the carbonyl frequencies of the vinyl acetate and hexafluoroisopropyl acrylate residues are quite distinct at 1740 and 1780 cm^{-1} respectively. Examination of the spectra

Figure 3.2. Infrared spectra of solvent extracted fractions from block copolymerization run 21, table 2.4.



A. Raw product

B. Material extracted with cold ether (82%)

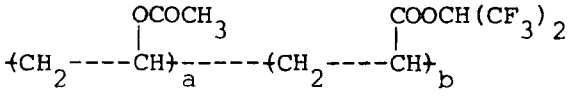
C. Material soxhlet extracted with ether for one week (15%)

D. Non-extractable residue after two weeks of soxhlet extraction with ether (3%)

in figure 3.2. shows that the fraction extracted with cold ether (B) contains a significantly higher proportion of the fluoroacrylate residue than the raw material (A). Fraction C obtained by extracting for one week also clearly contains some fluoroacrylate residue as the carbonyl absorption has a significant shoulder at 1780 cm^{-1}. Absorptions assigned to C-F bonds are visible in the spectra of samples A and B at 1290, 1205 and 1110 cm^{-1}, these bands are less evident in sample C and not detectable in sample D. The non-extractable residue (D) has a spectrum corresponding to virtually pure poly(vinyl acetate) with no trace of fluoroacrylate. This case is particularly clear, for other block copolymer samples the separation of the carbonyl frequencies is not so clearly marked but the same trends were observed.

The elemental analyses of samples A, B and C are presented in table 3.2. and confirm the trends seen in the infrared spectra. Although the

Table 3.2. Elemental analysis for samples A, B, and C (figure 3.2)



Sample	C %	H %	F %	a : b molar ratio		
				from C %	from H %	from F %
A	48.93	5.89	28.0	6 : 1	8 : 1	2 : 1
B	43.85	4.49	---	2.5 : 1	3 : 1	---
C	53.23	7.37	2.0	21 : 1	37 : 1	64 : 1

monomer incorporation ratios calculated from the elemental analysis figures for C, H and F are, as expected, not internally consistent the general trend supports the conclusions drawn from the infrared spectroscopic analysis.

There was insufficient sample for elemental analysis of fraction D but its ^{19}F n.m.r. spectrum showed no trace of fluorine, even on prolonged accumulation.

A number of conclusions can be drawn from the above data:

(i) It is clear that there is some homopoly(vinyl acetate) present in the products from the block copolymerization attempts. This is not unexpected since there will inevitably have been some termination of the vinyl acetate macroradicals. In the example presented above the amount of homopoly(vinyl acetate) is of the order of 3%. In the other experiments where cyclohexane was used as solvent the amount varied between 3 and 8%.

(ii) These extractions do not establish whether or not there is any homofluoroacrylate polymer present. In the case discussed the homopolymer (if present) would have been extracted in fraction B. Fraction C, on the other hand, is almost certainly block copolymer since it contains a substantial amount of vinyl acetate residues which are insoluble in ether and only a small proportion of fluoroacrylates.

(iii) Similar trends were found for the polymeric materials obtained from block copolymerization attempts (see table 2.4.). That is to say that using ether as the extraction solvent spectra similar to those in figure 3.2. were obtained.

When carbon tetrachloride was used as the extracting solvent poly(vinyl acetate) rich polymeric species dissolved first and after three weeks of extraction residues of less than 5% of the original material remained in the soxhlet thimble. Although these residues were fluoroacrylate rich materials their infrared spectra always contained carbonyl bands at 1740 cm^{-1} typical of poly(vinyl acetate). Thus it seems unlikely that any homopolymers were produced from the fluorinated monomers, either by transfer or by initiation with AIBN residues.

An unusual case of solution behaviour was observed when the product of polymerization 27 (table 2.4.) was dissolved in acetone, two distinct layers were formed. The top layer contained poly(vinyl acetate) rich polymer and the bottom layer poly(hexafluoroisopropyl methacrylate) rich polymer, as indicated by infrared and elemental analysis. Although this type of solution behaviour is usually associated with homopolymer blends rather than copolymers, the analysis of the contents of the two layers indicates quite unambiguously that they contained both monomer residues. This block copolymerization was one of only two carried out using t-butanol as solvent and in this case it is expected that there will be a significantly higher proportion of homopoly (vinyl acetate). To quote Seymour,[124] "while most of the products produced in tert. butanol was dead polymer, some stable vinyl acetate macroradicals were present because of the gel effect in the viscous solution of poly(vinyl acetate) in this good solvent". The data on which the above quotation is based together with the results obtained probably indicate that the product from experiment 27 contained a substantial amount of poly(vinyl acetate) homopolymer and some block copolymer. The homopolymer and part of the block copolymer with very short fluoromethacrylate blocks segregating into one layer and the block copolymer with long fluorinated sequences forming the other layer. This point was not followed up and tert. butanol was used as solvent for only two copolymerization experiments and some test runs with pure vinyl acetate and hexafluoroisopropyl methacrylate monomers.

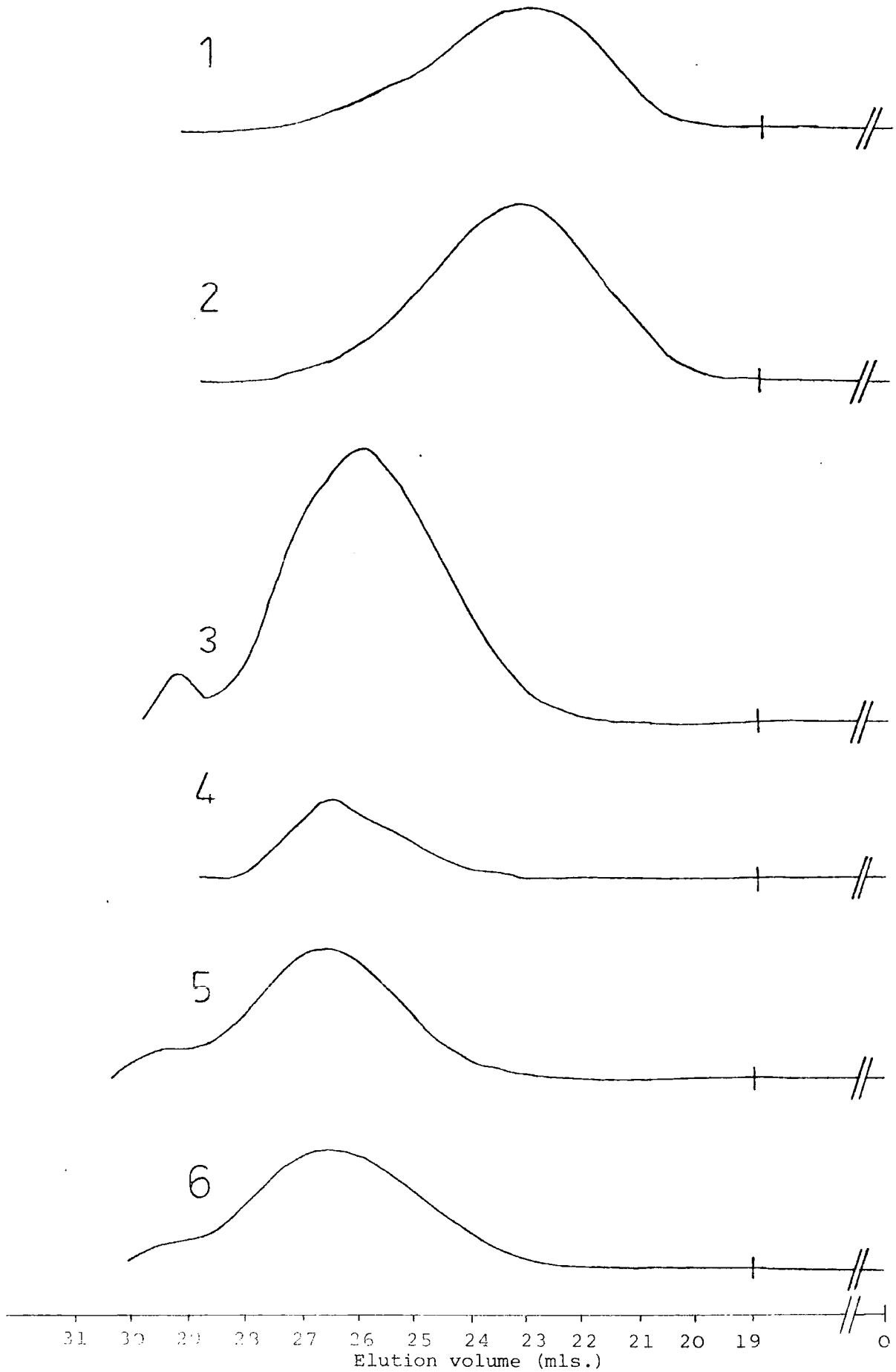
3.6. Gel permeation chromatography (GPC)

Gel permeation chromatography is a technique for separating molecules according to their hydrodynamic volume.[128] Polymers in dilute solution exist as statistical coils, the size of the coil being determined predominantly by a combination of chain stiffness, polymer-polymer and polymer-solvent interactions. The average coil size for a polymer of a particular

molecular weight in a specific solvent is its hydrodynamic volume. In practice a particular polymer solution will consist of a distribution of coils of different hydrodynamic volumes. The principle of GPC is that the polymer solution is passed through a chromatography column which sorts the constituents according to their hydrodynamic volumes, the largest coils emerging first. The columns are usually packed with a stationary phase of porous gel particles of different sizes, these packings are usually prepared from a cross-linked styrene-divinyl benzene copolymer. The apparatus consists of solvent pumping equipment, an injector system and a device for detecting the emerging sample, a variety of experimental configurations are possible. In the work reported in this section the equipment used was made available by Dr. A.F.Johnson, at Bradford University. This consisted of a Waters Associates High Speed Liquid Chromatograph using a loop injection system, three gpc columns (PLgel) in series, and a refractive index detector. The experimental procedures consisted of preparing an approximately 1% solution of the polymer in THF, this solution was filtered through a Millipore filter to remove any particulate matter and then injected (using the loop system) into the solvent stream. The solvent stream is split into two, one stream is used as reference in the detector system and the other carries the sample through the gpc columns and detector. The output from the instrument consists of a curve plotted on a potentiometric recorder, and typical examples for poly(vinyl acetate) homopolymers are shown in figure 3.3. The highest molecular weight components emerging first.

To obtain molecular weight information from the gpc data it is necessary to calibrate the apparatus and this had already been done for the columns and solvent system used using a series of samples of polystyrene of narrow molecular weight distribution. The molecular weights for the calibration samples had been measured by absolute methods, $\bar{M}w$ by light scattering and

Figure 3.3. GPC curves for poly(vinyl acetate) homopolymers



$\bar{M}n$ by osmometry.

The hydrodynamic volume is defined as the product of the intrinisc viscosity (η) and the molecular weight, and the intrinsic viscosity is related to the molecular weight by the Mark-Houwink equation,

$$\eta = K \cdot M^{\alpha}$$

multiplying each side by M,

$$(\eta) \cdot M = K \cdot M^{(\alpha+1)}$$

for any elution volume the hydrodynamic volumes will be equivalent and so the molecular weights of an unknown polymer (2) can be related to that of a well characterized reference polymer (1) by the following relationship:

$$(\eta)_1 \cdot M_1 = (\eta)_2 \cdot M_2 \qquad \text{by definition}$$

$$\therefore \quad K_1 \cdot M_1^{(\alpha_1+1)} = K_2 \cdot M_2^{(\alpha_2+1)}$$

$$\text{i.e.} \quad (\alpha_1+1) \log K_1 \cdot M_1 = (\alpha_2+1) \log K_2 \cdot M_2$$

$$\text{i.e.} \quad (\alpha_2+1) \log M_2 = (\alpha_1+1) \log M_1 + \log (K_1/K_2) \quad — \quad (1)$$

thus by calibrating with polymer 1 it is possible to obtain the molecular weight of material eluting at a specific elution volume providing K and α values for both polymers in the solvent used are known. Such values are known for many polymers and have been tabulated.[129] Since K and α values for polystyrene and poly(vinyl acetate) in THF are known it was possible to use equation 1 to convert the given calibration curve of polystyrene molecular weight vs) elution volume to a calibration curve for poly(vinyl acetate).

This calibration allows the interpretation of the GPC curves for the poly(vinyl acetate) homopolymers, a typical example is presented below. The height of the peak (h_i) is a measure of the number of molecules (N_i) with a given molecular weight (M_i); the molecular weight can be obtained from the elution volume vs) molecular weight calibration curve.

Sample from polymerization 4

Elution volume (mls.)	Peak height (mm.)	M_i	$N_i = h_i/M_i$ ($\times 10^{-3}$)	$N_i \cdot M_i^2$ ($\times 10^{-3}$)
22.0	0	140.000	0	0
22.5	0.1	110.000	.00090	$11 \cdot 10^6$
23.0	0.8	87.000	.00919	$69.6 \cdot 10^6$
23.5	1.5	70.000	.02142	$105 \cdot 10^6$
24.0	3.0	55.000	.05454	$165 \cdot 10^6$
24.5	5.0	44.000	.11363	$220 \cdot 10^6$
25.0	7.5	35.000	.21428	$262.5 \cdot 10^6$
25.5	10.5	28.000	.375	$294 \cdot 10^6$
26.0	13.5	22.000	.61363	$297 \cdot 10^6$
26.5	16.0	17.500	.91428	$280 \cdot 10^6$
26.95	18.8	14.400	1.30555	$270.72 \cdot 10^6$
27.0	18.5	14.000	1.32142	$259 \cdot 10^6$
27.5	14.8	11.000	1.34545	$162.8 \cdot 10^6$
28.0	10.0	8.733	1.14508	$87.33 \cdot 10^6$
28.5	4.8	7.000	.6857	$33.6 \cdot 10^6$
29.0	0	5.600	0	0
	124.8		8.12015	$2517.55\ 10^6$

$$\bar{M}n = \frac{\Sigma N_i M_i}{\Sigma N_i} = 15{,}369 \qquad \bar{M}w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = 20{,}173$$

$$\text{Polydispersity} = \bar{M}w/\bar{M}n = 1.3$$

For all the vinyl acetate polymerizations, $\bar{M}n$, $\bar{M}w$ and $\bar{M}w/\bar{M}n$ were obtained as shown above and are tabulated in table 3.3 below.

Table 3.3. Molecular weight determination for the products of the vinyl acetate polymerizations

Polymerization	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
1	65,000	81,100	1.24
2	63,700	146,000	2.30
3	14,200	37,700	2.65
4	15,400	20,200	1.31
5	9,300	18,000	1.90
6	11,500	22,200	1.93

Several conclusions can be drawn from the data presented in table 3.3. on the homopolymerizations of vinyl acetate carried out in this work:

(i) Keeping constant the polymerizations conditions (see Table 2.3.) it seems possible that macroradicals of poly(vinyl acetate) with similar molecular weight distributions can be obtained in cyclohexane and tert. butanol. That is to say the experimental procedures adopted appear to give reasonably reproducible results.

(ii) The effect of initiator concentration is small, as expected since the macroradicals are supposed to precipitate at a particular molecular weight and at this stage the continued growth of the polymer will be determined by the rate at which monomer reaches the active site. Also, since molecular weight in solution polymerization is proportional to the initiator

concentration to the power -1/2 only small effects would be anticipated. In polymerizations 3, 4 and 6 the initiator concentrations were in the ratio 1:2:4, all other variables being kept constant.

(iii) The effect of solvent in the molecular weight distribution is much more clear; polymerizations of vinyl acetate in tert. butanol (experiments 1 and 2) result in macromolecules with higher molecular weight than those produced in cyclohexane (experiments 3-6), due to the lower transfer constants for the former solvent.

For the homopolymers from fluorinated acrylates and methacrylates, and for the copolymers, the interpretation of GPC curves is much less certain since k and α values in THF are unknown. In these cases it is possible to calculate "poly(vinyl acetate) equivalent" molecular weights but since the influence of the fluoroalkyl groups on the hydrodynamic volume of the polymer coil is unknown the values obtained have to be treated with caution.

Only a preliminary examination of the GPC behaviour of the fluorinated homopolymers was possible, from this a number of points emerged; the first being that the refractive index difference between THF and the fluorinated acrylate polymers has the opposite sign to that between THF and poly(vinyl acetate). This poses no difficulty for interpreting the homopolymer GPC traces but may result in a simple cancellation effect for copolymers. This observation probably accounts for unsuccessful attempts to record GPC data for poly(methyl methacrylate-b-hexafluoroisopropyl methacrylate) samples.[125] Only poly(hexafluoroisopropyl methacrylate), experiment 10 in table 2.3., was investigated in any detail, and this sample showed a somewhat

unexpected GPC trace. There were three resolved peaks at elution volumes equivalent to poly(vinyl acetate) molecular weights of 140.000, 8.700, and 1.500. When the whole GPC trace was analyzed as described previously the values obtained were $\bar{M}n$ = 6.000, $\bar{M}w$ = 30.600, with a polydispersity of 5. It would seem therefore that the solution (or the polymerization) behaviour of these fluorinated systems is non-standard. The interpretation of the observations of this particular sample require more extensive work than was possible in the present study. It may be that the observation of resolvable peaks results from the association of individual polymer coils into "macrocoils",[130] if so the phenomenon should be time dependent.

The copolymer samples gave GPC traces which were qualitatively similar to those of poly(vinyl acetate), that is smooth curves with no resolvable peaks or shoulders. The data was treated as described previously and is presented in table 3.4. The results obtained are consistent with the hypothesis that the synthetic procedure used had produced the block copolymers

Table 3.4. GPC data for copolymers

Experiment number	Copolymer type	"Poly(vinyl acetate) equivalent" molecular weights $\bar{M}n$	$\bar{M}w$	Polydispersity $\bar{M}w/\bar{M}m$
12	III	11.900	17.700	1.5
13	III	14.400	23.100	1.6
14	III	17.200	30.300	1.8
15	IV	12.000	22.800	1.9
16	IV	13.300	17.700	1.3
17	IV	10.000	16.100	1.6
18	IV	7.000	12.900	1.65
20	I	9.100	13.700	1.5
21	I	10.100	16.400	1.5
22	I	11.700	17.000	1.5
23	II	10.200	17.200	1.7

desired. Thus, the sets defined by experiments 12, 13 and 14, experiments 15 and 16, and experiments 20, 21 and 22 result from a standard macroradical preparation followed by the addition of successively increasing amounts of comonomer. For all these sets of experiments the molecular weight of the final polymer increases in line with the increased amount of fluoromonomer added in the second stage of the copolymerization.

The set 16, 17 and 18 resulted from experiments carried out at respectively 50, 60 and 76°C, all other variables being fixed. In this case the product polymer molecular weights decreased successively, it should also be noted that the yield of polymer from these experiments decreased as the reaction temperature increased. These observations are consistent with an increasing proportion of dead poly(vinyl acetate). Unfortunately confirmation of this hypothesis by extraction (see section 3.5.) was not possible within the time available.

3.7. Film opacity

The films formed from the products of block-copolymerizations were always colourless and transparent. Films formed from mixtures of fluorinated homopolymers and poly(vinyl acetate) were, in contrast, never clear and transparent but varied from translucent to opaque. The observation of the different signs of the GPC peaks, obtained from a Refractive Index Detector, for fluorinated homopolymers and poly(vinyl acetate) establishes that there must be a large refractive index difference between the two types of polymer. In the light of the previous discussion of film clarity (Chapter 1, section 1.7.) it is clear that this observation is consistent with these products being block copolymers with at most small proportions of homopolymers.

CHAPTER 4

Conclusions and Suggestions for Further Work

In the work reported in this thesis homopolymers of vinyl acetate and of some fluoroalkyl acrylates were prepared and characterized. Block copolymerizations of vinyl acetate with different fluoroalkyl acrylates were carried out using the "living" macroradical technique. The investigation of the products obtained (Chapter 3), plus a knowledge of the synthetic procedure followed (Chapter 2) leads to the conclusion that block copolymers of vinyl acetate and some fluoroalkyl acrylates can be prepared using the polymerization method described.

The detailed characterization of the block copolymers qualitatively confirmed that they had the expected structures; however, a more quantitative characterization of the structure and molecular size of the products should be a priority in any continuation of this work. The lack of good agreement between the various methods of measuring copolymer composition was disappointing and although rationalizations for the differences were provided (Chapter 3) future work should examine this matter in order to establish more reliable quantitative analytical procedures; probably this will involve improving the reproducibility of presently available methods. The structure of the block copolymers could be further confirmed by use of differential scanning calorimetry, which should show the two Tg transitions characteristic for each block, and by ^{13}C n.m.r. spectroscopy which is a more sensitive probe of structure than either ^{1}H or ^{19}F n.m.r.; neither of these techniques were available to the author.

Phase separation could be investigated by electron microscopy and, in particular, surface segregation of the fluoroalkyl

substituents could be investigated by studying the wettability of the products with liquids of different surface tension.[116,131]

The observation of unusual GPC behaviour for poly(hexafluoroisopropyl methacrylate), section 3.6., suggests that the solution properties of this homopolymer may be unusual and merit further investigation.

Finally, the application of such materials should be investigated. The original intention was to examine their potential as paint resin components in the hope of introducing low surface free energy properties at a relatively low price; the author did not carry out any work on this point; however, it was observed that the block copolymers had the expected surface active properties and dilute solutions of the polymers showed a tendency to foam.

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