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THE SYNTHESIS AND PROPERTIES OF SOME FLUORINATED BLOCK COPOLYMERS.

Submitted by Malcolm Strange (Graduate Society)

A thesis submitted to the University of Durham for the degree of Master of Science.

1978.

SUMMARY.

Fluoroalkyl acrylate and methacrylate monomers were prepared by esterifying the appropriate acid chloride with the relevant fluoroalcohol and rigorously purified. The monomers were characterised by glc., infrared, mass spectral, elemental and nmr. analyses.

Homopolymers and random copolymers with methyl methacrylate were prepared by an emulsion technique and block copolymers were prepared via occluded methyl methacrylate macroradicals by precipitation of the growing polymer chains from a poor solvent, hexane. Fractionation of some of the block copolymers was effected by soxhlet extraction with methanol. The polymers were characterised by elemental analysis, infrared and nuclear magnetic resonance spectroscopy, solution viscosity and gel permeation chromatography together with surface free energy investigations by contact angle measurements.

It was established that block copolymers had a surface which was essentially composed of fluoroalkyl residues, even when the bulk composition was as low as 1.6 mole % of fluorinated monomer.

ACKNOWLEDGEMENTS.

My sincere thanks must be voiced to the members of the academic and technical staff of Durham University to whom I am endebted, not least to my supervisor Doctor W.J.Feast, who has supported, directed and encouraged this effort throughout the year. Finally, I must thank Ms.J.E.Reakes,B.A. for typing this thesis.

MEMORANDOM.

The work contained in this thesis was carried out in the Chemistry Laboratories of Durham University between November and September of the academic year 1977-'78. It has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

Note to the reader.

Due to the unwieldy length of the systematic names of the monomers and polymers discussed in this work, abbreviations have been made, and the systems adopted are described below.

2,2,2-Trifluoroethyl acrylate may appear simply as trifluoroethyl acrylate, or in some tables, as tfea. For the other monomers, the numbering system giving the positions of the fluorine atoms in the alkyl side chain has been ommitted in some cases, for example, trifluoroethyl methacrylate instead of 2,2,2-trifluoroethyl methacrylate. Other abbreviations used are:

2,2,2-trifluoroethyl methacrylate (tfem)
1,1,1,3,3,3-hexafluoroisopropyl acrylate (hfpa)
1,1,1,3,3,3-hexafluoroisopropyl methacrylate (hfpm)
2,2,3,3,4,4,5,5-octafluoropentyl acrylate (ofpa)
methyl methacrylate (mma)

Block copolymers are designated in the usual IUPAC method, i.e.

poly(methyl methacrylate-b-2,2,2-trifluoroethyl acrylate) is a copolymer comprised of a block of methyl methacrylate and a block of 2,2,2-trifluoroethyl acrylate, and may appear in the script as poly(mma-b-tfea).

Similarly,

poly(methyl methacrylate-r-2,2,2-trifluoroethyl acrylate) denotes a copolymer of randomly dispersed methyl methacrylate and 2,2,2-trifluoroethyl acrylate units, and the name has been shortened to poly(mma-r-tfea) for convenience.

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CHAPTER I

BACKGROUND TO BLOCK COPOLYMERS.

1.1. Introduction.

One method of modifying the physical and chemical properties of a given polymer is by the incorporation of a second monomer within the parent polymer structure.

The classic method of combining properties of two homopolymers in one product is that of random copolymerisation. This method, however, frequently results in products that have quite different properties from the parent homopolymers. For example, polyethylene has a suitably low brittle point for many applications, but a relatively poor surface hardness and a lowish melting point. Polypropylene, on the other hand, has good hardness and a higher melting point, but an unsuitably high brittle point. Mixtures of the two polymers exhibited demixing phenomena in a broad range of mixing ratios and were also particularly brittle; likewise, random copolymers of the two monomers gave inferior products. A further method of combining two monomers in a polymer was described by Melville.[1,2] He reported the first synthesis of a block copolymer in a photoinitiation study of the vapour phase polymerisation of monomers. Block copolymers are comprised of A and B constituent monomers arranged in blocks or long sequences,

i.e. A---A---A---A---A---B---B---B---B---B

Since the pioneer work by Melville, the intervening forty years have seen rapid development in both the theory and practice concerning block copolymers and applications of such resins are becoming more widespread. For example, returning to the case mentioned earlier of polyethylene and polypropylene, it has now become an accepted fact that copolymerising the two monomers, ethylene and propylene, under conditions that favour block formation will give products with superior properties to those obtained by random copolymerisation.[3]

The work contained in this thesis concerns the block copolymers of methyl methacrylate with fluoroalkyl acrylates or methacrylates. Particular interest lies in the surface properties of such resins.

It should be noted at this point that the properties of block copolymers themselves can be widely varied by altering the precise details of their production. Therefore, it must be stressed that the properties of the block copolymers synthesised in this work may have different characteristics from the similar type of block copolymer prepared by a different method and/or under different conditions.

1.2. Applications of block copolymers.

Block copolymers are currently finding many uses,[4-10] and illustrative examples are given below:-

1.2a. As reinforcements for natural rubbers.

Natural rubber can be modified by copolymerising with methyl methacrylate. Little difference has been found between latex and solid phase block copolymerised materials. Both show a marked stiffening but the thermoplastic characteristics of the vulcnaizates impede hot injection from moulds. The presence of 10% or more of block copolymerised monomer in a natural rubber vulcanizate prevents the growth of bacteria on the surface. This somewhat unexpected property has led to its use as a chopping and cutting block material for butchers and meat handlers.

1.2b. High impact strength polymers.

According to theory, the introduction of discontinuities or nuclei in the incipient path of a fracture surface would increase the resistance to the impact causing such a fracture. If discrete particles of a different phase could be dispersed uniformly in glass-like polymers such as polystyrene then the impact resistance would be increased. However, the introduction of microparticles of rubber gives products that are structurally weak due to incompatability and consequent microphase separation. This problem is overcome by using block copolymers. In fact, it is only necessary to introduce into polymer A a mixture of block copolymer AB and homopolymer B to achieve the desired effect. In other words, polystyrene can be given high impact properties by blending it with a mixture of polybutadiene or other rubber and a block copolymer of the rubber with polystyrene.

The manufacture, properties and testing of high impact materials, including toughened polystyrene, ABS copolymers and high impact poly(vinyl chloride) prepared by milling poly(vinyl chloride) with butadiene copolymers and terpolymers have been reviewed.[11]

1.2c. Surface active agents.

The basic structure of block copolymers should impart exceptional surface active properties to these materials in appropriate cases, since polymeric segments that are water soluble and others that are oil soluble may be incorporated into the same macromolecule. The effectiveness of the "Pleuronics"and "Tetronics" surface active agents is a consequence of this particular property.

Block copolymers of ethylene and propylene oxide have been commercially produced for many years and have found widespread use as emulsifiers. The critical micelle concentration of these surfactants was found to be lower than that obtained for other non-ionic surfactants.[12]

The stability of emulsions and dispersions is generally enhanced by block copolymers producing more uniform materials, usually with improved properties. For example, Berlin and Berkman[13] found that the addition of methoxy-cellulose during the suspension polymerisation of methyl acrylate provided stabilisation of the suspension, but similar additions to a polymeric dispersion did not enhance stability. From this and other experiments it was concluded that a methoxy cellulose-acrylate block copolymer was formed during the polymerisation and stabilised the acrylate homopolymer molecules.

It has also been found that such materials as starch-b-poly(methyl methacrylate), casein-b-poly(vinyl acetate) and poly(ethylene oxide-b-styrene) at concentrations less than 0.5% are very effective surface active agents in emulsion and suspension polymerisations.

1.2d. Fibres.

Many new fibres, such as acrylonitrile, present dyeing and dye retention problems. The problem can be overcome by grafting or block copolymerising with a monomer, the polymer of which readily accepts the dyestuff it is required to use.

1.2e. Film forming polymers.

The Dow Chemical Company and BX Plastics have patented transparent block copolymer films for food packaging and other applications. It is generally accepted that high energy linear accelerators are used in the synthesis of these materials.[14-16]

1.2f. Adhesives, caulks, sealants and coatings.

The elastomeric block copolymers themselves are tack-free, but can be made tacky by compounding with an appropriate resin. For example, styrene-butadiene block copolymers have been used with terpene resins as hot melt pressure sensitive adhesives.[17] The adhesion of metal films to block copolymers is often greater than to random copolymers of the same composition.[18]

Block copolymers can be compounded with other materials such as inorganic fillers, petroleum oils, asphalts and reactive monomers to develop desirable properties. Examples are:-

Kraton 1101	poly(styrene-b-butadiene-b-styrene),
Kraton 1107	poly(styrene-b-isoprene-b-styrene).

These are thermoplastic elastomers introduced by the Shell Chemical Company. They have high tensile strength, high resiliance and reversible elongation. Their stress-strain properties are essentially unaffected by repeated melting or dissolution, they also retain their elastomeric properties at low temperatures and can be injection moulded or extruded,[6] and have a wide range of applications.[4]

A series of styrene-butadiene diblock copolymers is produced by the Philips Petroleum Company under the trademark "Solprene". These find uses in moulded and extruded mechanical goods, shoe products, sealants and adhesives. The fabricated products generally must be vulcanised to obtain good mechanical properties.

1.2g. Extrusion and moulding.

Elastomeric block copolymers are available in pellet form which may be directly fed into conventional plastics processing equipment. Premixing with other substances is eliminated since the materials are in ready-to-use form. They find application where the processing advantages of the thermoplastics are desired in combination with rubbery properties such as elasticity, low temperature flexibility, high friction abrasion resistance etc. Examples are:-

Kraton 2104	for pharmaceutical uses, films, disposable syringe bulbs.
Kraton 2109	for special tubing.
Kraton 3125	for films, laminates and wire insulation.

1.2h. Cosmetics.

In a French Patent[19] appearing in 1973, the authors were in the process of developing cosmetically useful block copolymers. Trisequenced block copolymers, useful in oil-containing cosmetic emulsions are prepared by radical or redox polymerisation of one monomer, addition of a second monomer, continuing polymerisation, eliminating the first monomer and completing the polymerisation.

1.3. Methods of Synthesis of Block Copolymers.

Basically, the method of production of a block copolymer is by reacting a second monomer with a preformed polymer prepared in such a way that it is able to undergo such a second phase reaction. Methods of producing this reactive polymeric species are many and varied and there is a wealth of literature dealing with this topic, dating back to the 1940s. The major methods are described under the following methodology headings:-

1.3a. Block copolymerisations via free radical intermediates.

(i) Photochemical synthesis.

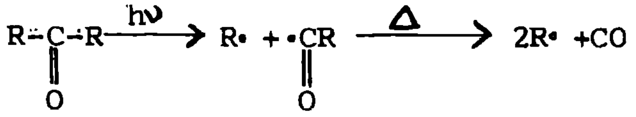
Photolysis of a preformed polymer can, under certain conditions, lead to the formation of macromolecular free radicals which, in the presence of a second monomer, can lead to block copolymerisation. Photosensitisers can be added to increase this effect.

Bolland and Melville[20] photopolymerised methyl methacrylate and found that poly(methyl methacrylate) which was deposited on the walls of the reaction vessel could be used to initiate the subsequent polymerisation of a second monmer. In fact, they block copolymerised poly(methyl methacrylate) with chloroprene or methyl isopropenyl ketone introduced to the reaction vessel in the vapour state. Termination of the poly(methyl methacrylate) macroradicals is prevented by chain entanglement, but the second monomer was able to diffuse to the unpaired electron site and undergo reaction.

Block copolymers can be obtained by the polymerisation of a water soluble monomer in which an oil soluble monomer is suspended.[21] When the polymer radicals, generated in the aqueous phase, diffuse across the water-oil interface, the second monomer block is formed.

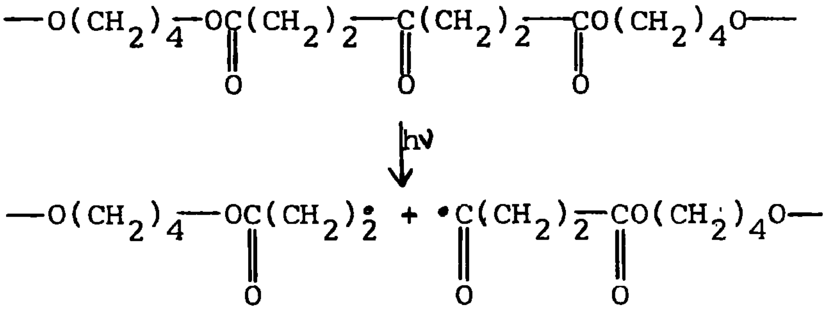
A more unorthodox technique for the photoinitiation of one monomer followed by block copolymerisation with a second monomer was suggested by Hicks and Melville.[22-24] They photoinitiated the first monomer plus a sensitiser mixture as it flowed through a capillary tube into a reservoir containing a second monomer. By adjusting conditions to minimise chain transfer or termination reactions before the growing chains reached the reservoir, reasonable yields of block copolymers were obtained. Butyl acrylate or acrylonitrile were the "flowing" monomers while styrene was employed in the reservoir. Other workers[25] have used a similar method to prepare block copolymers of butyl acrylate with 2-vinyl pyridine and styrene.

Photolysis of polymeric ketones give rise to free radicals by the Norrish type 1 mechanism.[26]



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

Block copolymers can be formed if the ketogroup is contained in the main chain of the polymer; when the ketogroup resides in the side chain, graft polymers may be produced. Towards this end, Guillet and Norrish[27] photolysed poly(methyl vinyl ketone) in the presence of methyl methacrylate. Irradiation of a copolymer poly(tetramethylene sebacate-co-γ-ketopimelate) containing 10 mole % of γ-ketopimelic acid at 300mμ, where only the ketogroups absorb, is accompanied by a rapid decrease in molecular weight. When a vinyl monomer is added to the solution, polymerisation occurs which is apparently initiated by macroradicals formed by the type 1 ketone cleavage.



$$—O(CH_2)_4—O\underset{\underset{O}{\|}}{C}(CH_2)_2—\underset{\underset{O}{\|}}{C}(CH_2)_2—\underset{\underset{O}{\|}}{C}O(CH_2)_4O—$$

$$\Big\downarrow h\nu$$

$$—O(CH_2)_4—O\underset{\underset{O}{\|}}{C}(CH_2)_2^{\bullet} + {}^{\bullet}\underset{\underset{O}{\|}}{C}(CH_2)_2—\underset{\underset{O}{\|}}{C}O(CH_2)_4O—$$

Later work in this field by Guillet[28] gave rise to polymers with controlled environmental lifetimes. Inclusion of ketone groups within the polymer structure gave the so-called "ecolyte plastics", which can be degraded by sunlight at wavelengths between 290 and 330 nms, further biochemical degredation ultimately yields carbon dioxide and water. Ecolyte S (ketone modified polystyrene) has recently been developed for the manufacture of disposable packaging.[29]

Photopolymerisation of a monomer in the presence of a precipitant for the polymer, yields occluded radicals which may be used to initiate the block copolymerisation of a second monomer. Bamford et al[30-32] studied such occluded radicals of vinyl monomers, obtaining evidence for their existance by radical scavenger and electron paramagnetic resonance techniques. Hiemeleers and Smets[33] photopolymerised various monomers under conditions favouring the formation of trapped radicals, but attempts to prepare block copolymers by subsequent reaction with a second polymer resulted in poor yields.

A recent Russian paper[34] describes the two step formation of acrylic block copolymers in the presence of orthophosphoric acid. The monomer/acid mixture was irradiated with U.V. radiation to c.30% conversion, and then placed in the dark where the reaction proceeded to a high degree of conversion. A second monomer was added and copolymerisation continued via the long living macroradical formed in the first step. Homopolymer formation from the second monomer was reported to be absent.

(ii). <u>Radiation synthesis.</u>

Commonly used energy sources are ^{60}Co γ-rays, electron accelerators, nuclear reactors, etc. Radiation synthesis of copolymers is experimently accomplished by:-

a) the mutual irradiation in an inert atmosphere of a polymer swollen by, or dissolved in, another monomer.

b) the preirradiation of a polymer in air to yield peroxy-groups or trapped radicals on the backbone and subsequent contact with a different monomer in the absence of air, accompanied by heating.

c) the preirradiation of a polymer in vacuo to yield trapped radicals followed by heating in the presence of another monomer and in the absence of air.

The initial concentrations and formation of the free radicals produced within any irradiated system are dependant upon the type of radiation, the total energy absorbed, the rate of absorbtion and the radiation sensitivity of the materials. Subsequent reactions of these active species are chemical phenomena, dependant upon the usual variations in temperature, concentration, etc.

Occluded growing chains have been reported[35,36] as resulting from an irradiation induced polymerisation of monomer emulsions to less than 100% conversion; addition of a second monomer can lead to block copolymerisation. Comprehensive reviews are available on the topic of radiation synthesis of block copolymers.

(iii) Mechanochemical synthesis.

When stresses are applied to macromolecules, both local segmental motions and molecular flow occur. If a stress of sufficient magnitude is localised in one segment of a molecule, bond scission, usually of the carbon-carbon bonds, may take place which can lead to the formation of free radicals. Block copolymers can be prepared from these free radicals by subjecting polymer mixtures, or polymer-monomer mixtures, to bond breaking stresses. Various methods have been used and these include mastication of a polymer-monomer blend,[37,38] milling, ultrasonic irradiation of two polymers in solution,[39] extrusion, high frequency discharge, freezing and thawing,[42,43] and vapour phase swelling.

Beniska and Stander[45] subjected a polymer plasticised with a polymerisable vinyl monomer to mechanical degredation to give a block copolymer. Alternatively, by mechanically degrading a polymer in the presence of oxygen, they introduced peroxidic groups that were used to initiate block copolymerisation at a later stage.

Even shaking and stirring of some polymer-monomer systems have been claimed to give rise to the formation of block copolymers.[46,47]

Ultrasonic irradiation has been found to be a potential tool in the block copolymer formation. Recently, Japanese workers described a mechanochemical synthesis of copolymers of polystyrene and methyl methacrylate by such a method. They found that the effect of the polymer concentration on the mechanical degredation of the polymers was very small and that the degredation rate constant was $1.1 \times 10^{-7} sec^{-1}$. The methyl methacrylate chains in the block copolymer were more scissile than were the polystyrene chains.

Russian workers[48] discovered some interesting chemical conversions during ultrasonic welding of thermoplastics. Potentiometric titration and infrared spectroscopy showed that graft and block copolymers are formed in the seam during ultrasonic welding.

One Russian author[49] considered the energetics of the destruction of mechanically stressed chemical bonds in already mechanically stressed sections of macromolecules. He found that the activation energy of this decomposition and the activation energy of their restoration are nonlinear functions of the true stress, the character of the nonlinearity and the absolute values of the energy barriers depend upon the length of the stressed fragment of a macromolecule.

A recent review[50] on the mechanical synthesis of block and graft copolymers has been written.

(iv) Chain transfer reactions on polymer backbones.

Transfer constants for polymers can be obtained from data on low molecular weight compounds of similar structure, assuming identical reactivity towards the attacking radical.[51,52]

The validity of this assumption has been confirmed by transfer constant determinations in the presence of oligomers.[53,54]

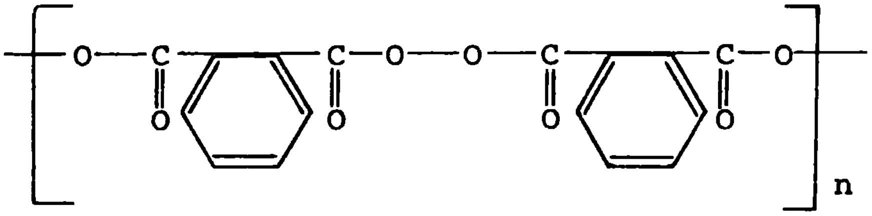
In this method, the problem is the incorporation of an appropriate chemical function terminating the chain on a macromolecular backbone, this can be achieved by two main methods. The first is to polymerise or copolymerise suitable monomers already containing the desired functions in their molecules.The second method involves performing one or more modification reactions on a suitable macromolecule, thus introducing the desired functions on a presynthesised polymer. The first method has limitations in as much as the function required may interfere with the polymerisation process, even if the monomers can be synthesised satisfactorily in the first place.When the second method, the introduction of reactive functions into conventional polymers, is attempted, difficulties such as partial degradation and crosslinked products have been reported,[55] as well as poor selectivity through side reactions and site of control, also chain scission may occur.

The process of functionalisation can also be achieved by chemical transformation of the polymerisation products of suitable monomeric precursors. This method has been widely used to synthesise multifunctional polymers designed for special applications. Its main advantages are that both the number of reactive functions introduced into the polymer and the absence of unwanted groups deriving from side reactions can be easily achieved, providing the precursor units have been properly chosen, so that they are able to react in the desired way.

The method of chain transfer reactions on polymer backbones is so well cited in the literature that it is impossible to describe in detail all the various methods of introducing reactive sites into a polymer, some of the techniques will now be described under the appropriate headings:-

a). Block copolymerisation initiated by terminal peroxy groups.

A method, developed at the University of Louvain,[56-58] makes use of polymeric phthaloyl peroxide[59] as initiator,



a prepolymer is formed at as low a temperature as possible which contains segments of the polymeric initiator. By dissolving the isolated polymer in the second monomer and polymerising at a higher temperature, block copolymers are synthesised. Some[60] patents recommend for this purpose use of polyfunctional hydroperoxides containing two or more hydroperoxide groups with different activities so as to reduce homopolymer formation to a minimum.

Smets et al[61] introduced peroxide end groups into polymers by polymerising the monomer with tertiary butyl hydroperoxide in the presence of a small amount of copper(11) octanoate. The reaction scheme involves two steps:-

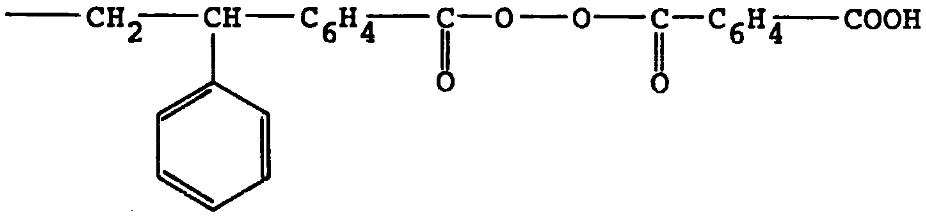
$$\mathrm{ROOH} + \mathrm{Cu(11)} \longrightarrow \mathrm{RO_2^{\bullet}} + \mathrm{H^+} + \mathrm{Cu(1)}$$

$$\mathrm{ROOH} + \mathrm{Cu(1)} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{OH^-} + \mathrm{Cu(11)}$$

$$\mathrm{2ROOH} \xrightarrow{\mathrm{Cu(11)}} \mathrm{RO_2^{\bullet}} + \mathrm{RO^{\bullet}} + \mathrm{H_2O}$$

If both $\mathrm{RO_2^{\bullet}}$ and $\mathrm{RO^{\bullet}}$ initiate equally the polymerisation of a monomer, on average, half the number of the end groups are present as terminal peroxybutyl groups and are able to initiate a second step polymerisation. Others[62-64] describe the use of p- and m-diisopropyl benzene dihydroperoxides in the presence of iron(11) ions. Molyneux[65] has studied the reaction leading to block copolymerisation of styrene with methyl methacrylate using a dihydroperoxide of m-diisopropylbenzene to give polystyrene with terminal hydroperoxide groups. Yields of around 10% were reported. This low yield was thought due to a relatively low number of terminal hydroperoxide groups on the polystyrene chains and also to chain transfer reactions giving homopolymeric methyl methacrylate. The chain transfer reaction can also be used to obtain a homopolymer block with a terminal hydroperoxide group. It has been reported[66] that polymers or random copolymers of alkenes containing terminal hydroperoxide groups are obtained by polymerising alkenes or their mixtures at $0-35^{o}$ in an aqueous emulsion containing monomer, in the presence of diisopropylphenyl dihydroperoxide as initiator and chain terminating reagent. The polymeric derivatives formed in this way are isolated and used as initiators for block copolymerisation with vinyl monomers.

Low molecular weight polyfunctional peroxy compounds may be used to initiate the polymerisation of vinyl monomers, which leads to polymers containing terminal peroxy groups, viz:



Such polymers may be used as macromolecular initiators in block copolymerisation reactions with a second monomer.[67]

In 1960, Ceresa[68] found that during the bulk polymerisation of methyl methacrylate in the presence of dissolved oxygen, peroxy linkages were introduced into the polymer backbone in sufficient numbers to allow the synthesis of block copolymers from poly(methyl methacrylate) by this process.

Recent papers use more complicated chain transfer agents, such as poly(dioxy(2-bromo-1,9-dioxo-1,9-nonanediyl)dioxy(1,9-dioxo-1,9-nonanediyl) in the preparation of poly(methyl methacrylate).[69]

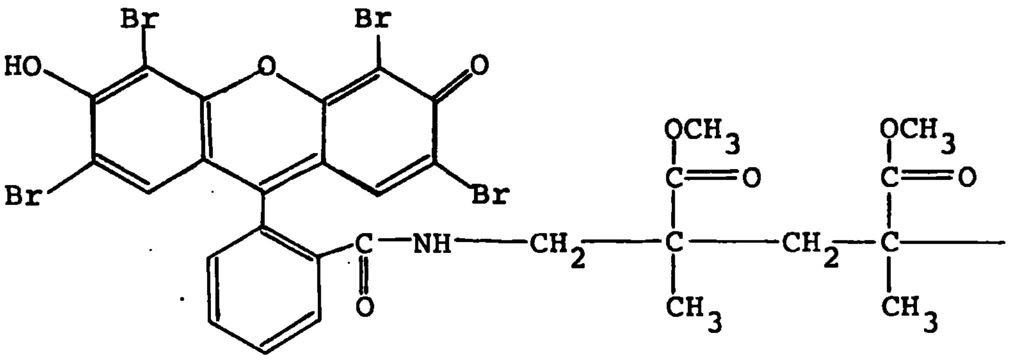
Bis(p-bromomethyl benzoyl) peroxide was used by Reiss[70] to terminate a living styrene polymer, giving a peroxy containing reagent, used to react with vinyl chloride to give a block copolymer.

b). Block copolymerisation initiated by terminal amino groups.

By using triethylamine as a transfer agent, Bamford[71-3] prepared poly(methyl methacrylate) with terminal amine groups. The polymerisation of acrylonitrile in the presence of this polymer gave a good yield of block copolymer. He reported little transfer along the poly(methyl methacrylate) backbone and only a small amount of polyacrylonitrile homopolymer was formed.

A polymer containing a terminal aromatic amine group is obtained by a polymerisation reaction initiated by a diazonium salt and an aromatic acid containing a free amino group or a group from which a free aromatic amino group can be prepared by subsequent reactions. This method was used to obtain an acrylonitrile polymer with a terminal amino group, and after diazotisation, this was used as a macromolecular initiator for block copolymerisation with 2-methyl-5-vinylpyridine.[74,75]

Smets et al[76] synthesised poly(methyl methacrylate) with an amino end group by polymerising the monomer in ammonia, then by subsequent reaction with eosin lactone, the end group was transformed into an eosin amide group. The final polymer contained about 1 eosin group per 48 methyl methacrylate units and had the formula:-



This functionalised polymer was used for photoinitiating the polymerisation of styrene and acrylamide, the blocks of the two orthodox polymers being separated by a leuco eosin group. No homopolymerised second monomer was reported as being present in the reaction products.

c).Block copolymerisation initiated by terminal halogen containing groups.

Homopolymeric blocks with terminal halogen atoms absorb light of a suitable wavelength(288-350nms.) whilst being raised to an excited state. Dissociation can occur to yield reactive polymeric free radicals which are used as macromolecular initiators in block copolymerisation.

Earlier workers[77-79] prepared the macromolecular bromides by thermal or photolytic polymerisation of monomers in the presence of CBr_4 or $CBrCl_3$ which terminate the chain by chain transfer. Subsequent irradiation with ultraviolet light cleaves the C-Br bonds which, in the presence of a second suitable monomer, can initiate secondary polymerisation with the formation of the block copolymer.

d).Others.

Although the main end groups used in this approach are peroxy, amino and halo, other less well tried and tested functionalising reagents are available. Sulphur containing end groups can be used in the photoinitiation polymerisation of a second monomer. Terminal SH groups, formed by chain transfer reactions are particularly effective, but other thermally activated groups derived from the use of simple organic disulphides and disulphides such as bis(diethylthiocarbamoyl) disulphide in the initiation of the polymerisation of the primary monomer have also been reported.[80]

Shimomura and Kudo[81] suggested that treatment of living polymers of styrene or dimethyl styrene with $\alpha\alpha'$ azobis-

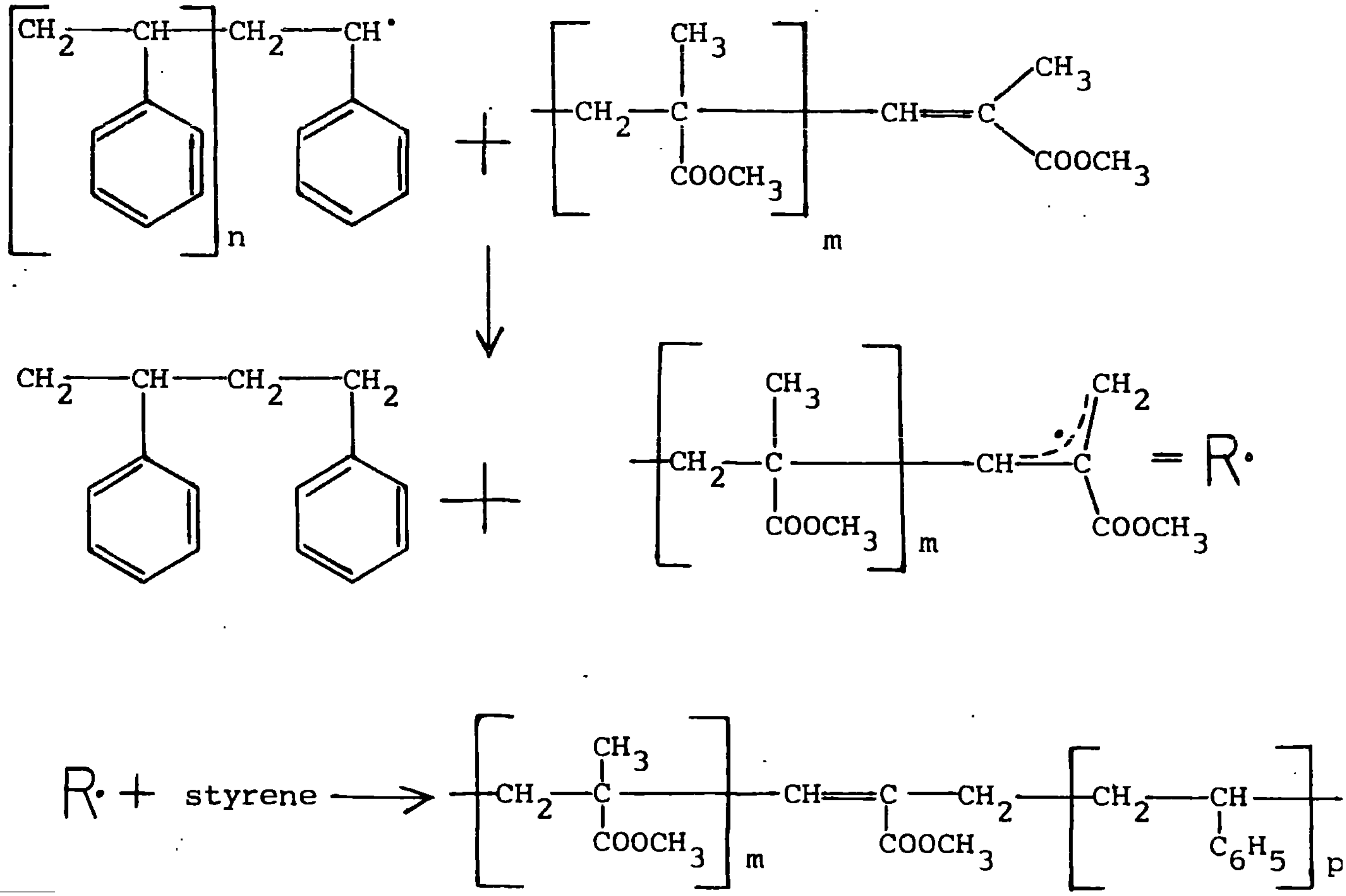
(isobutyronitrile) or oxygen would give polymers with reactive end azo or hydroxy groups respectively, which could subsequently act as a macromolecular radical initiator.

Phosphines have been used by several workers[82-84] as chain transfer agents. Both di- and tributyl phosphines have been used to prepare poly(styrene-b-acrylonitrile).

(v) Radical attack on unsaturated polymers.

Free radical transfer reactions with unsaturated polymers will most likely occur through the abstraction of allylic hydrogen atoms. The formation of such resonance stabilised macroradicals was studied by Schultz and co-workers.[85-87] They used poly(methyl methacrylate) containing terminal double bonds which resulted from termination by disproportion. The chain transfer constant for AIBN initiated polystyrene radicals with the allylic hydrogens at the chain ends is 11×10^{-2} and with hydrogen atoms along the backbone is 0.3×10^{-4}

Thus, if polystyrene is polymerised in the presence of such a polymer, the preferred reactivity at the chain ends leads to block copolymer formation, according to the equation:-



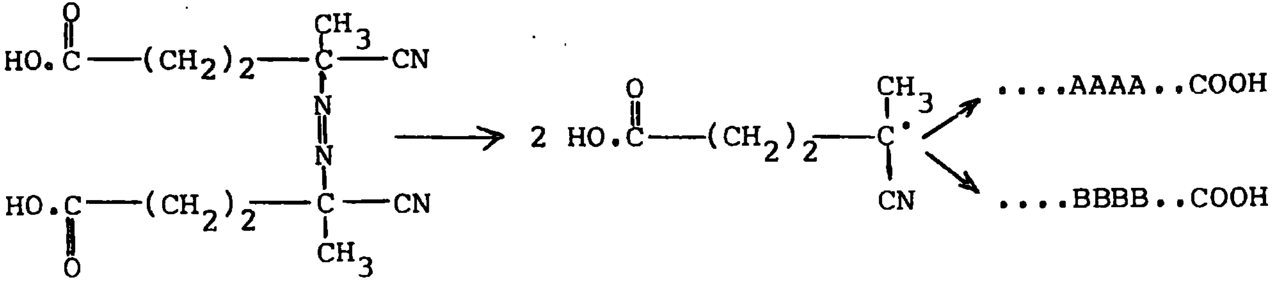
vi) Electrolytic synthesis.

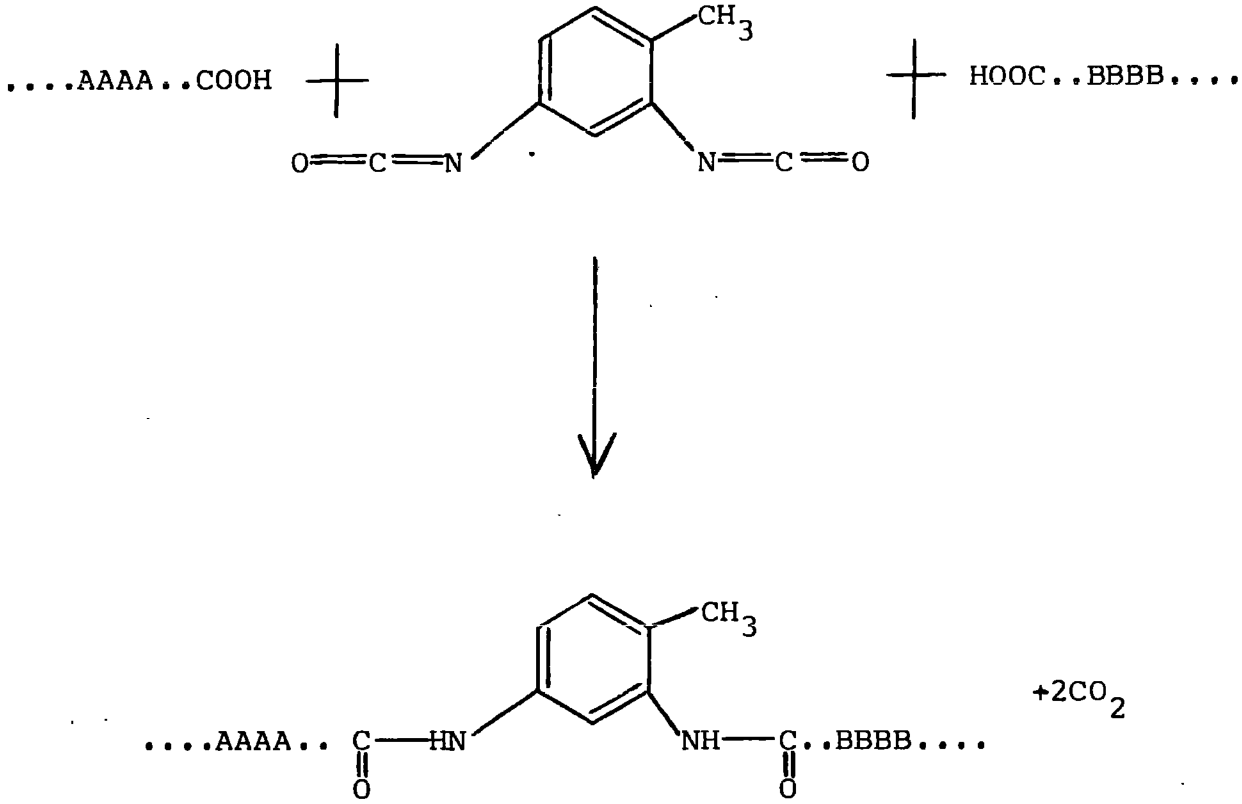
A Japanese patent[88] reported the synthesis of various copolymers by electrolytically decarboxylating solutions of poly(vinyl alcohol), polystyrene etc., containing carboxyl end groups in polar liquids such as DMSO and DMF in the presence of a radically polymerisable monomer, such as methyl methacrylate or styrene.

1.3b. Block copolymer synthesis via coupling reactions.

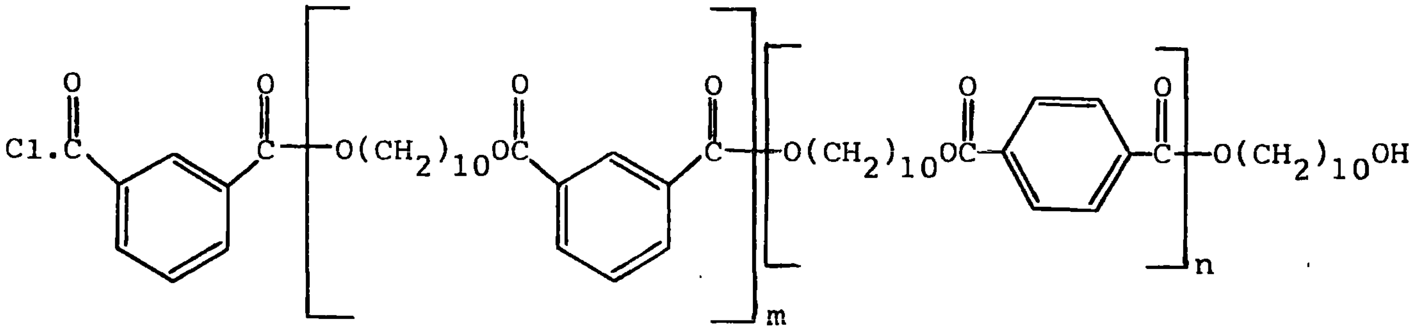
Condensation reactions can be used to couple together polymer molecules containing hydroxy, carboxyl, amine, thiol and certain ester groups to give block copolymers with an essentially linear structure. This method has been described by Coffey and Meyrick[89] and by Bayer,[90] Iwakura,[91] Cusano[92] and their respective co-workers for the coupling of polyesters and polyurethans. The same basic process is used for the industrial synthesis of certain polyester-amide rubbers, such as the Vulcollans (Bayer AG.) and the Vulcaprenes (ICI Ltd).

A difunctional initiator capable of both free radical initiation and of coupling reactions, such as 4,4'-azobis-(4-cyanovaleric acid) may be used to introduce terminal carboxyl groups into two chemically different vinyl polymers. These initial polymers may be either mono- or difunctional depending upon whether termination is via radical combination or disproportionation, and can be coupled with suitable reagents such as diisocyanates. In this way, Bamford and Jenkins prepared poly(styrene-b-methyl methacrylate), with a "sandwich" structure of segments of 100 styrene units between two segments of 120 methyl methacrylate units in the average molecule. In this way, dissimilar polymers can be coupled with diisocyanates to give linear block copolymers.

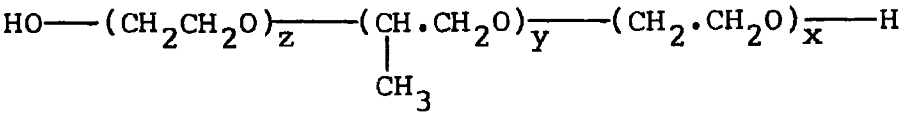




Polyesters with terminal hydroxyl groups are readily prepared by carrying out the condensations with reactant concentrations sufficient to give an overall slight excess of -OH groups. For example, poly(decamethylene terephthalate) with hydroxy end groups has been reacted with poly(decamethylene isophthalate) with acid chloride end groups to give a block copolymer with the structure shown overleaf.[93]



Alkylene oxides can be block copolymerised via a coupling reaction to yield industrially important products. For example, the polymerisation of ethylene oxide is initiated by hydroxyl containing compounds; thus, since poly(propylene oxide) has a terminal hydroxyl group, it can be used to initiate the block copolymerisation of of ethylene oxide to give the ABA block copolymer shown:-



$$HO—(CH_2CH_2O)_z—(\underset{CH_3}{CH}.CH_2O)_y—(CH_2.CH_2O)_x—H$$

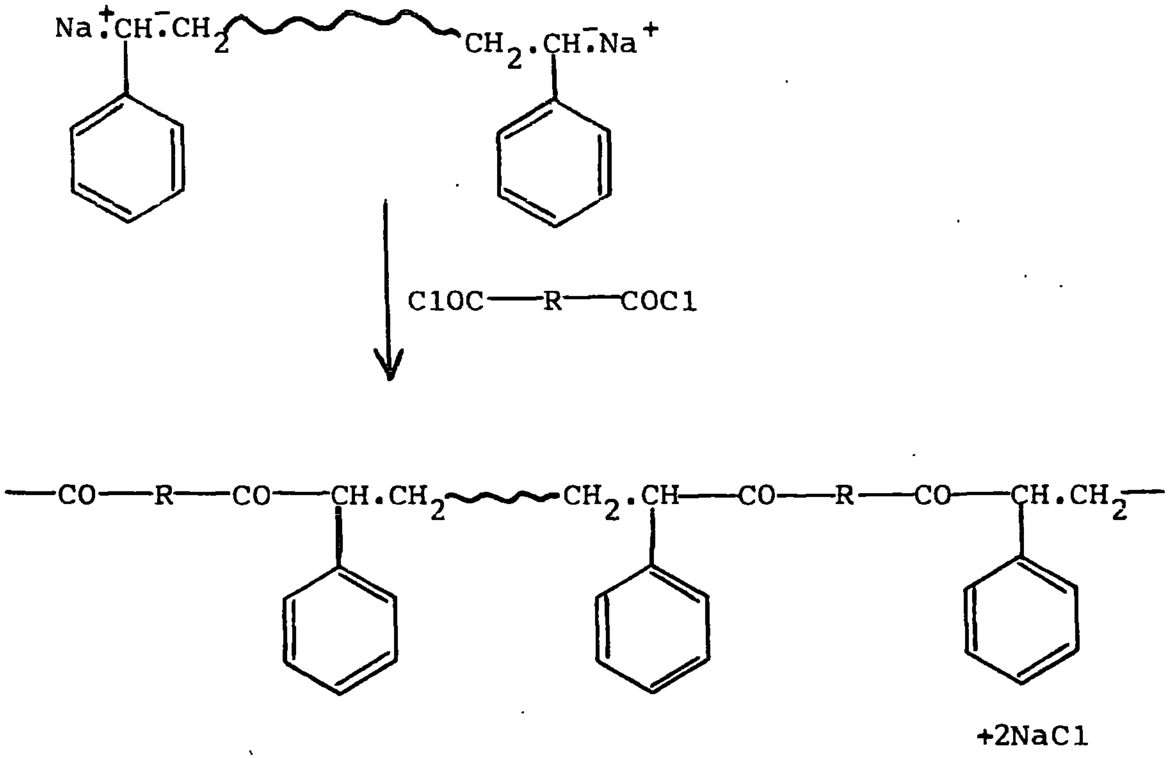
A variation in the lengths of the blocks can be achieved by controlling the reaction conditions at each stage of the polymerisation.[94] This was the basis of the first commercially successful range of block copolymers, the Pleuronics and Tetronics (Wyandotte Chemicals Corp.).

1.3c. Block copolymer synthesis via ionic polymerisations.

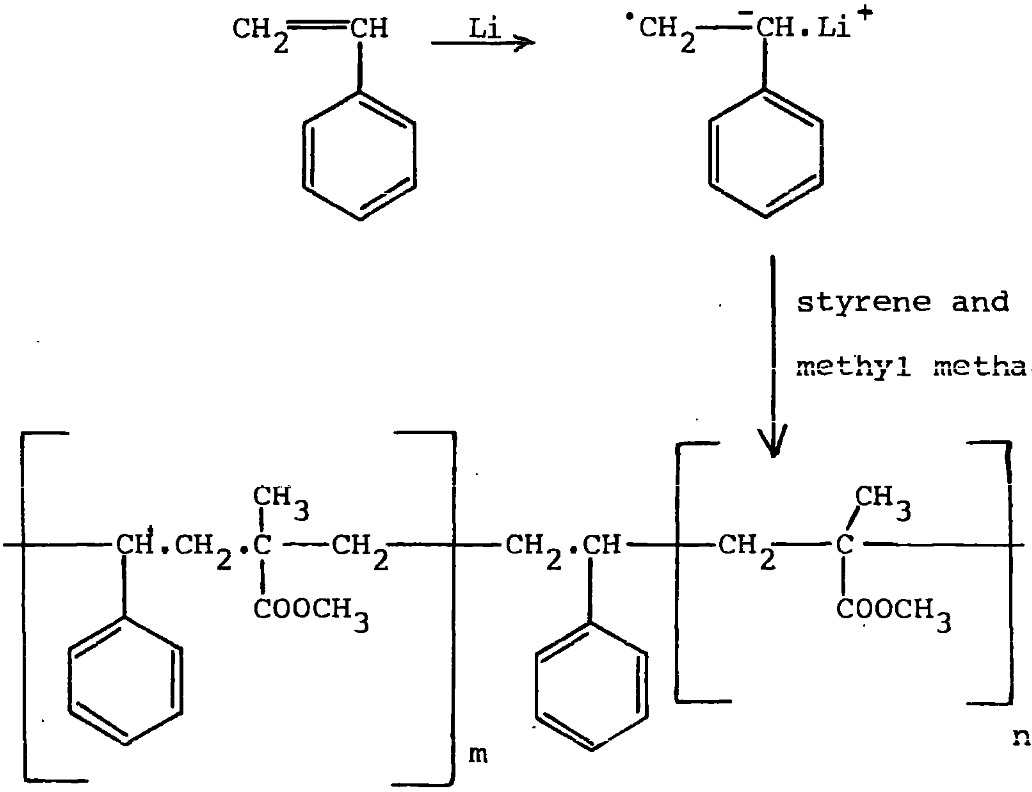
In recent years, especially since the pioneering work of Szwarc in the mid fifties, ionically initiated block copolymerisations have become more important.[95-8] In general, the termination step in ionic polymerisations is easier to control than in free radical processes, so that the possibilities of commercial production of block copolymers by ionic mechanisms are very real and the patent literature since the nineteen-sixties has been rich in examples of block copolymers formed ionically.For example, Scoggin[99] described a technique for preparing block copolymers by feeding batch prepolymers into a continuous reactor. Propylene was batch polymerised in the presence of a catalyst containing diethylaluminium chloride and titanium(IV)chloride, and the prepolymer was continually flushed into a second reactor by using an inert diluent, such as heptane or isoöctane, and continuously polymerising with ethylene. This cationic process was reported to give a uniform block copolymer. The field of commercialisation of ethylene-propylene block copolymers has been exploited by the Texas Eastman Company with the introduction of "polyallomers",[100,101] which are crystalline block copolymers, quite different from the ethylene-propylene rubber copolymers. More recent work on industrial applications of ionically initiated block copolymerisations includes Niemann's patent[102] claiming that an improvement could be obtained in such reactions involving polar monomers by modification of the normally used alkyllithium initiators with certain sulphur containing compounds.

In the anionic polymerisation of styrene, when all the monomer is consumed, the carbanion chain ends remain "living" since no termination occurs.These living polymers continue to grow if fresh monomer is added to the system, or undergo block copolymerisation if the second monomer is different from the first. Graham[103] prepared poly(methyl methacrylate-b-styrene) in this way. Copolymers containing two or three blocks have also been prepared by this method.[104-6] The order of monomer addition is an important factor in determining the formation of block copolymers by this technique. For example, Graham et al[107] found that methyl methacrylate can be polymerised by living polystyrene but not the other way around. They suggested that the poly(methyl methacrylate) anion was not basic enough to initiate the polymerisation of styrene. Likewise, living polystyrene will add to ethylene oxide to yield a linear block copolymer, but the alkoxide will not add to styrene.[108] Such reactivities have been related to Q-e values[109,110] and it has been suggested that the activity of a living polymer is quantitativly related to the e value of the monomer from which it is formed. The anion of a monomer with a low e value will initiate the polymerisation of a monomer with a higher e value, but not vice-versa.

Reactions of living polymers with multifunctional electrophiles have been studied by French workers.[111-3] They treated dicarbanionic living polystyrene with diacid chlorides, diesters or dihaloalkanes. A polycondensation reaction occurred, resulting in a large molecular weight increase.



An interesting case of block copolymer formation was observed by O'Driscoll and Tobolsky[114] in the lithium initiated copolymerisation of styrene and methyl methacrylate. The authors suggested that initiation occurred 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 at the radical end. The relative lengths of the blocks being determined by the relative rates of radical and anionic growth.



Work by Fetters[115] concerns itself with the homogeneous anionic polymerisation to produce block copolymers. Listed in the article are species that can generate stable chain ends and that can therefore be considered as being potentially useful in block copolymer formation. The paper also contains a comprehensive compilation of reviews on this subject. Other reviews on the topic of anionic polymerisations include those by Janes[116] and Morton.[117]

Of particular interest in the context of the work reported in this thesis are the examples quoted in the literature of the preparation of methyl methacrylate polymers blocked with a variety of alkyl acrylates and methacrylates. One paper[118] describes the synthesis and characterisation of block copolymers of methyl, hexyl, lauryl and octadecyl methacrylates, prepared in THF with diphenylmethylsodium or diphenylmethylpotassium as initiator. Ito,[119] using a variety of anionic catalysts in toluene or THF solvent at 0^o, reported the formation of poly(methyl methacrylate-b-benzyl methacrylate), whilst the poly(methyl methacrylate-b-cyclohexyl) system was studied by Bevington[120] using naphthalenesodium in dioxane.

If a given monomer can polymerise in two different modes, it is sometimes possible to prepare stereoblock copolymers, designated A--A'. For example, in diene polymerisation, the microstructure of the polymer is dependant upon the solvent environment. When dienes are polymerised in hydrocarbon solvent with organolithium initiators,the microstructure of the polymer is predominantly the result of 1,4 addition. Introduction of low levels of ethers, for example, results in a substantial increase in the proportion of 1,2 addition.[109] Thus, it is possible to introduce ethers at an intermediate stage in the polymerisation to form an A--A'block copolymer where the microstructure of A is largly 1,4 and A' largly 1,2.[110] Similarly, polystyrene having blocks of isotactic and atactic segments can be formed using butyllithium as the initiator. The polymerisation is conducted in hydrocarbon medium and the stereoregularity is altered by cycling the polymerisation temperature between -30 and -5^o.[121]

1.4.Purification and isolation of block copolymers.

The methods of synthesis described previously normally involve reactions of monomer with polymer. The reaction products from such a system often contains a mixture of polymeric species. Thus,the copolymer is contaminated by the homopolymer of the monomer used in the synthesis as well as the unreacted polymer. Isolation of the copolymer fraction is essential before any characterisation can be carried out. Normally, separations are carried out by a method based upon the differing solubilities of the chemically different polymeric species and several methods have been developed to accomplish the fractionation.[122] The ability of a liquid to act as a solvent for a block copolymer depends not only upon the molecular weight of the copolymer but also on the chemical nature of the segment species and the length, the number and the distribution of the homopolymeric or random copolymeric species, therefore, although generalisations cannot be made, there are several definite procedures which may be adopted singly or, if necessary, sequentially, to free a particular block copolymer from unwanted polymeric contaminants.

1.4.a. Fractional precipitation.

This method involves the stepwise addition of non-solvent to a solution of the polymer mixture.[123-5] The precipitated polymer fractions are then isolated and characterised. In applying this technique, it is useful to know the difference in the precipitation ranges of the polymers, that is, the ratio volume of precipitant: volume of solvent within which a particular polymer precipitates. As a general guide, the properties of random copolymers from two monomers usually pass through a maximum or minimum as composition is changed, whereas for block copolymers, the value of a given property (in this case, solubility) should be very close to the value computed for the hypothetical mix of two homopolymers, each having a molecular weight equal to the block copolymer as a whole.

In a solution of homopolymers mixed with a block copolymer, the progressive addition of a precipitant first collapses the molecular chains of the least soluble polymer species, causing it to precipitate (either as a gel, or in a granular form, or in a form intermediate between the two). Thus the nature of the precipitated block fraction, aside from precipitation range, will help to decide the solvent-precipitant system to be used.

As the precipitation proceeds, the solution develops a characteristic turbidity, due to the scattering of light by the particles. 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 aggregates does not differ greatly from that of the solution; thus, the absence of a stable turbidity does not preclude the presence of a block copolymer in the system. On the other hand, its presence is almost a certain indication of the presence of a block copolymer fraction.[126-130]

1.4.b. Selective precipitation.

This is a useful variation of fractional precipitation.[131,132] In this method, only one of the polymers is precipitated with a given non-solvent, yielding a very clean separation. It is not carried beyond the precipitation of the first component to be deposited from solution. Some limitations of the method are described in the literature.[133]

1.4.c. Separation by elution.

Here, the polymeric material is subjected to extraction at low or at elevated temperatures with successive mixtures of non-solvent and solvent containing increasing fractions of the solvent component for the polymer. This is the reverse of fractional precipitation, requiring smaller quantities of solvents and non-solvents and it is more easily applied to large scale separations. The differential solubility of molecular weight fractions of the components may also be achieved with a constant ratio of solvent : non-solvent by carrying out the extractions at increasingly higher temperatures. If this method is used, the eluting liquid may consist of one component only which is a good solvent for the species at an elevated temperature but becomes a poor solvent at lower temperatures.

When solvent pairs are available, so that each solvent dissolves only one of the polymer species (i.e. a non-solvent for the other), selective elution will often give a good separation of the fractions. If the block copolymer is particulaly rich in one of the homopolymers, then it may dissolve partially or wholly in the solvent for that polymer, and the copolymer can then be separated from the solution by a precipitation process.

Co-elution of the block copolymer invariably results in a non-precipitable turbidity which may disappear when the solution is heated, but reappears on cooling. This elution of the block copolymer may not be apparent if selective elution is carried out in a soxhlet extraction apparatus, unless the extracting solvent is cooled to room temperature.

1.4.d. Turbimetric titration.

This is a type of fractional precipitation. It is a rapid analytical method for showing the presence of block copolymers in a polymer mixture.[134,135] Using this technique, the amount of turbidity is measured, resulting from the addition of a precipitant to a dilute polymer solution. The turbidity is expressed as the ratio of the amount of absorbtion at complete precipitation. The titration curve is obtained by plotting the turbidity against the amount of precipitant added. The curve obtained from polymer mixtures shows distinct inflections, while a smooth curve is obtained from a single homogeneous polymer fraction. The technique has been the subject of a review.[136]

In practice, the separation and purification of block copolymers from the product mixtures obtained during their syntheses is an essentially empirical process, although where new systems are relatively closely related to those which have previously been separated, a separation may be fairly easily devised. The solution properties of copolymers have been reviewed by Molau.[137]

1.5. Characterisation of block copolymers.

a) Solution properties.

During the separation processes just described, considerable information will have been obtained as to the probable structure of the copolymeric species present. For example, the presence of homopolymeric fractions virtually eliminates the possibility of the copolymer fraction being a simple random copolymer and suggests a block or graft structure. Comparison of the precipitation range of the copolymer fraction in a given solvent-precipitant system with the determined precipitation ranges of the constituent polymeric species in the same solvent-precipitant system, analysis of successive fractions of the precipitated copolymer, confirmation of the presence or absence of a stable turbidity in specific solvent-precipitant systems and determination of the general behaviour with respect to swelling or solutions in different solvents may provide information relating to the structure of the copolymer.

Other methods of measurement on polymeric solutions can provide useful characterisation data, the typically used techniques are briefly listed below.

(i) Light scattering and refractive index measurements.

The study of optical properties of solutions of block copolymers, such as light diffusion, light scattering and flow birefringence has, in some cases, helped in the elucidation of copolymer structure.[138-142] If variations in the composition exist, there are fluctuations in the refractive index. As a result, the contribution of the individual block copolymer molecules to the scattered intensity is dependant upon molecular weight and composition. So, the variations of the apparent molecular weight with the solvent refractive index can lead to information regarding compositional fluctuations in, for example, block lengths. In solvents with a high refractive index, the measured weight average molecular weight will be very close to the true value. Hence, light scattering can lead to molecular weight averages, as well as indicating polydispersity and compositional variations.[140] Indeed, Urwin[143] has shown, using computer analysis of light scattering data for block copolymer solutions in several different solvents, that precise accounts of molecular weight and structure can be obtained.

(ii) Osmometry.

This technique has been applied to obtain a variety of thermodynamic parameters,[144,145] examples include second virial coefficients, heats of dilution, entropy of dilution and solvent-solute interaction parameters as well as providing a method for molecular weight determination.

(iii) Viscosity measurements.

The dilute solution viscosity technique will not always lead to valid molecular weights since the size and shape of the macromolecule is a function of molecular structure, composition and the distribution of segments along the chain. However, in regard to the linear poly(styrene-b-butadiene-b-styrene) and poly(styrene-b-butadiene) polymers, Utracki and others[146] have developed equations relating the intrinsic viscosity to molecular weight, the only prior information required was knowledge of composition.

(iv). Gel permeation chromatography.

GPC is relativly insensitive to compositional heterogeneities and is thus a potent tool in the characterisation of linear block copolymers. Since the product of intrinsic viscosity and molecular weight determines retention times,[147] a universal calibration can be established that is valid for linear homopolymers as well as random and block copolymers. It has been found that, in favourable cases, GPC can be used to characterise block copolymer polydispersity, estimate the percentage of the various polymer types and determine molecular weights.

b). Spectroscopic characterisation.

Electromagnetic irradiation from radio frequency through infrared and ultraviolet to X-rays has been used widely in the analysis of block copolymers. Nuclear magnetic resonance spectroscopy used in the study of the structures of copolymers has been reviewed by Nishioka,[148] while another Japanese worker[149] recently discussed the ^{19}F nmr analysis of fluorine containing polymers. Infrared analysis may be used to compare block lengths by using a calibration curve and comparing specific absorbtions for each component polymer. X-ray analysis is becoming more popular as an analytical procedure to investigate block copolymers, for example, Ailhaud[150] used small angle X-ray diffraction to determine the structure of gels formed by mixing alkyl methacrylate block copolymers with solvents selective for one of the blocks.

The surface sensitive techniques such as multiple internal reflectance infrared spectroscopy and E.S.C.A. can be used to investigate specific surface segregation in block copolymers.[151]

Mass spectroscopy has been used in the analysis of copolymers of methyl methacrylate and methyl acrylate in order to determine relative amounts of each monomer in the polymer.[152]

c). Thermal analysis.

(i) Differential thermal analysis.

This technique is widely used in polymer science to determine transition temperatures, in particular glass transition temperatures and melting points; both these parameters are useful in distinguishing between a block and a random copolymer, since the block sequence will generally display the transitions associated with the appropriate homopolymers whereas the random copolymer will display unique transitions.

(ii). Thermal degredation.

Thermogravimetric analysis is a process used to establish the temperature of catastrophic degredation of polymeric materials, and in some cases, to obtain kinetic parameters for decomposition reactions. Pyrolosis with subsequent gas-liquid chromatographic analysis can also be used to characterise block copolymers.[153] In this method the polymer is pyrolysed on a platinum wire in the inlet system of the glc apparatus. The chromatograms obtained from various polymers contain peaks that can be correlated with the appropriate decomposition products and hence structural assignments may be made.

d). Physical and mechanical properties.

(i). Mechanical properties.

Comparison of mechanical properties can be made between homopolymers of the block copolymers components, the corresponding random copolymers containing the same monomer ratios as the copolymers themselves. Observed differences can be used to differentiate between the polymer types. The difference in the mechanical properties of block and random copolymers has been attributed to phase separation and to stress concentrations at the phase boundaries.

(ii).Microscopy.

The details of block copolymer morphology are of particular interest, and microscopy, especially electron microscopy, is a powerful tool for studying this topic with ultrathin sections of polymer. Observations reveal that block copolymers show several different morphological configurations such as spheres, rods, stripes, networks and irregularly shaped "islands". Ailhaud[154] used this method to investigate the microstructures of block copolymers of different alkyl methacrylates. X-ray diffraction techniques (mentioned previously) can also be used to this end.[155,156]

(iii).Minimum film forming temperature.

The formation of films from emulsions of copolymers is a phenomenon of technological importance. Brown[157] developed a mechanism in which film formation is attributed to the capillary forces of the water within the interstices between the polymer spheres. As the water evaporates, the particles come closer together to form a continuous film by particle coalesence, if they can be deformed sufficiently. The lowest temperature at which coalesence occurs can be measured and is called the minimum film forming temperature (mft) and is related to the glass temperature, Tg. Since the evaporating phase is water, the mft must be located between 0 and 100^{o} to be measurable. As a rule, the value of the mft for a block copolymer lies between those of its two constituent homopolymers, its exact value depending in direct proportion to the percentage of each monomer incorporated in the blocks. Values of mft for a series of copolymers of ethyl acrylate (Tg,-22^{o}) and methyl methacrylate (Tg,105^{o}) were measured by Brown et al.[158] As expected, mft rose as the amount of methyl methacrylate was increased. Below the mft coalesence is prevented by the rigidity of the resin, and a powdery or spongy structure is obtained.

(iv). Inverse gas chromatography.

Recently, gas chromatography has been extensivly used to investigate properties of a polymer which is used as the stationary phase, and the retention data of a weakly interacting volatile solute are examined as a function of column temperature. This technique has been explored by Guillet[159-161] and was applied to block copolymers of poly(styrene-b-THF) by Ito and others[162] who concluded that the method of inverse gas chromatography gives useful information about bulk and surface properties of copolymers.

e). Chemical properties.

When monomer compositions differ, copolymer composition may be readily obtained by elemental analysis, which is the determination of a given element (usually C,H,N or halogen) as a mass percentage of the molecular mass of the compound.

Chemical degredation with subsequent glc analysis of the products has been reported by Haslam and coworkers.[163] They hydrolysed random copolymers of methyl methacrylate and ethyl methacrylate in the presence of HI to convert the alkoxy groups to methyl iodide and ethyl iodide, that could be determined by chromatographic analysis. Obviously, this type of analysis can also be gained by observation of possible chemical reactions between the repeating units. If the repeat unit exists as long segments of a single type, i.e. block copolymers, reaction may occur only at the boundaries between the segments. The behaviour in appropriate reactions may thus be used to distinguish between random and block copolymers and between alternating or uniform compounds and heterogeneous, non-uniform copolymers. An example of this distinguishing method was devised by Ceresa[164] who studied a styrene-methyl methacrylate resin. The random copolymer gave 79.6% cyclisation wheras the block copolymer did not cyclise.

1.6. Aims and objectives of the present work.

The work reported in this thesis is part of a programme designed to investigate methods of modifying the surface properties of polymers.

An attempt to synthesise poly(methyl methacrylate) containing fluoroalkyl acrylate and methacrylate blocks by an established method is described and their subsequent characterisation is reported. Interest is primarily aimed at their surface properties, particularly the anticipated surface segregation of the fluorinated blocks. Should the process occur, the characteristic low surface energies of the fluoropolymers would make themselves manifest, and the degree of segregation can be monitored by wetting tests on films prepared from these novel materials. Description of the preparation and analysis of the monomers, homopolymers and random and block copolymers is given in the following chapters.

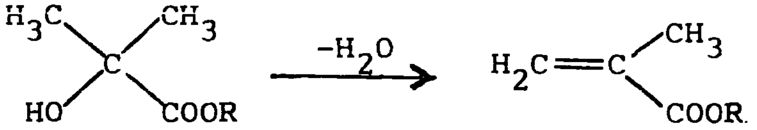
CHAPTER II

PREPARATION AND ANALYSIS OF THE MONOMERS.

2.1. Introduction.

It was Fittig[165] in 1879 who reported that methacrylic acid and some of its derivatives could easily be polymerised. An Imperial Chemical Industries worker[166] discovered that methacrylate ester polymers, especially poly(methyl methacrylate) were rigid, optically clear plastics, a fact that has lead to the commercial importance of such resins.

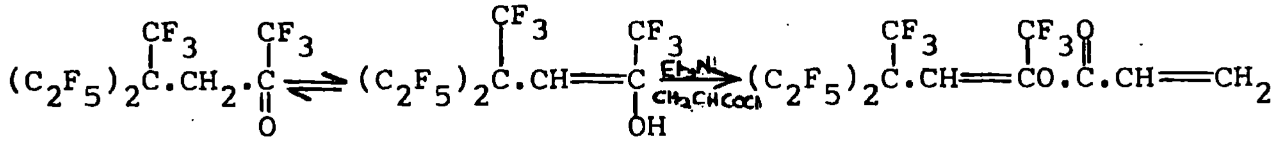
At first, methacrylic esters were prepared by the dehydration of α-hydroxyisobutyric acid esters.[167]



The removal of water has been achieved[168] with the use of excess phosphorous oxychloride in the presence of a small amount of sulphur or hydroquinone as a polymerisation inhibitor. The dehydration can also be carried out in the vapour phase over contact catalysts, such as phosphates, at 320°. Methyl methacrylate has been prepared directly from acetone cyanohydrin without the isolation of intermediates[169] and this method has been modified by later workers.[170-6]

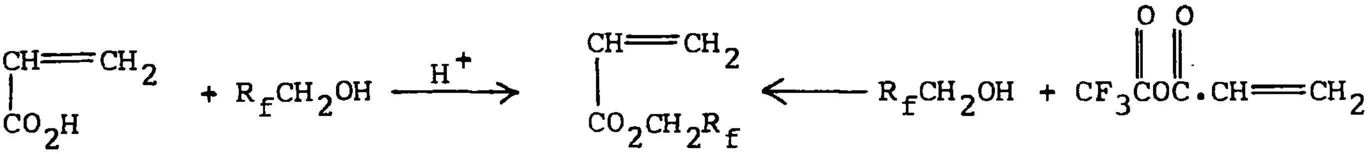
2.2. Fluorinated alkyl acrylates.

Ahlbrecht reported the preparation of 2,2,3,3,4,4,4-heptafluorobutyl acrylate using a mixture of acrylic acid and perfluoroacetic anhydride with the fluoroalcohol.[177] The reaction can be used to prepare a variety of fluorinated alkyl acrylates by using the appropriate alcohol; totally fluorinated alcohols cannot be used, however, due to their low stability, decomposing to the perfluoroacyl fluoride and hydrogen fluoride.[178] Fluorinated acrylates can also be prepared from fluorinated ketones, containing an α C-H bond, in the presence of base;



$$(C_2F_5)_2\overset{CF_3}{C}.CH_2.\underset{O}{\overset{CF_3}{C}} \rightleftharpoons (C_2F_5)_2\overset{CF_3}{C}.CH{=}\underset{OH}{\overset{CF_3}{C}} \xrightarrow[CH_2CHCOCl]{Et_3N} (C_2F_5)_2\overset{CF_3}{C}.CH{=}\overset{CF_3}{C}O.\overset{O}{C}.CH{=}CH_2$$

or, alternativly obtained from commercially available alcohols of general formula $CH_3(CF_2)_xCH_2OH$ or $H(CF_2)_yCH_2OH$ in the conventional manner, either directly[179] or via the mixed anhydride.[180]

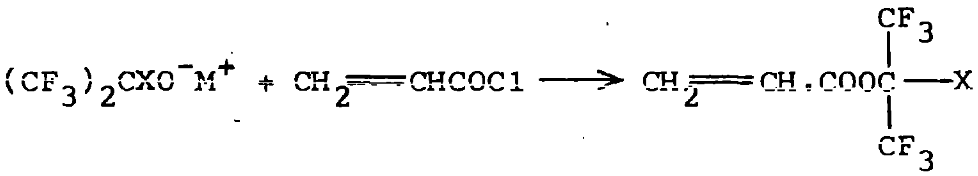


$$\underset{\mathrm{CO_2H}}{\mathrm{CH{=}CH_2}} + \mathrm{R_fCH_2OH} \xrightarrow{\mathrm{H^+}} \underset{\mathrm{CO_2CH_2R_f}}{\mathrm{CH{=}CH_2}} \longleftarrow \mathrm{R_fCH_2OH} + \mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{.CH{=}CH_2}$$

Fluorinated ketones react with a variety of nucleophilic reagents such as alkoxides, nitriles and fluorides and the intermediate addition products can often be converted to acrylates and methacrylates.[181]

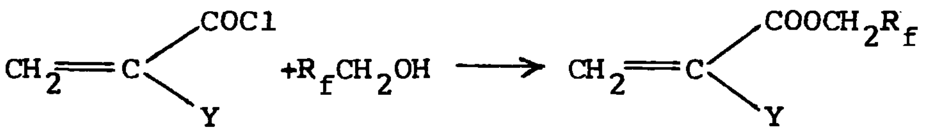
$$(CF_3)_2C{=}O + MX \longrightarrow (CF_3)_2CXO^-M^+$$

where M= alkali metal and X= CN^-,F^-,OCH_3^-,CH_3^-,Ph^-.



$$\mathrm{(CF_3)_2CXO^-M^+} + \mathrm{CH_2{=}CHCOCl} \longrightarrow \mathrm{CH_2{=}CH.COO}\overset{\mathrm{CF_3}}{\underset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{{-}X}$$

Due to the low reactivity of the fluorinated alcohols, direct esterification using acrylic acid in the presence of strong acids has been found to be inefficient, for example, using sulphuric acid as the catalyst and benzene as the entrainer, a yield of only 14% of the fluorinated butyl acrylate was obtained in 30 hours.[182] A more useful reaction described in the same paper, and adopted in this work, is the interaction of fluorinated alcohols with acrylyl and methacrylyl chlorides to prepare the required acrylates and methacrylates respectivly.



where Y is $-CH_3$ in the methacrylate case and $-H$ for the acrylates.

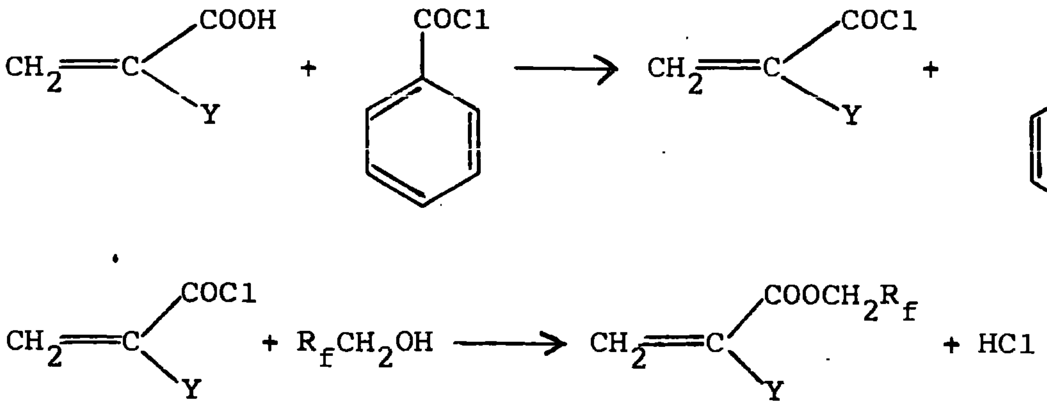
2.3.Experimental.

a). Materials.

Acrylic acid stablised with 0.05% p-methoxyphenol and benzoyl chloride(B.D.H. laboratory reagents); methacrylic acid inhibited with 1000p.p.m. hydroquinone and 250p.p.m. hydroquinone monomethyl ether (Aldrich chemicals); 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol (Bristol Organics Limited); and 2,2,3,3,4,4,5,5-octafluoropentanol (E.I.Du Pont de Nemours and Co.(Inc.)), were obtained from the manufactures and used without further purification.

2.3b).Synthesis.

The routes to the required monomers are summarised for the general case below:



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 on 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 (1l.;2 necked) was fitted with a nitrogen inlet and a fractionating column (20 cms.long; 1cm. internal diameter, containing glass helices). This was connected to the second flask

(1l.;3 necked) via the column by a still head and condenser. The remaining necks of the flask were fitted with a reflux condenser through which a nitrogen bleed was passed, terminating about 1 cm. from the bottom of the flask, and a pressure equilibrated dropping funnel, connected to a dry nitrogen supply. The entire apparatus was oven dried at 120° for two hours and then assembled hot whilst purging with dry nitrogen, thus removing any traces of moisture. Acrylic acid (216g.;3moles) and benzoyl chloride (630g.; 4.5moles) were introduced into the two necked flask. A small quantity of hydroquinone (about 2.5gms) 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° using an electric mantle before 2,2,2-trifluoroethanol (300g;3moles) was added rapidly. The formation of unwanted 2,2,2-trifluoro -chloropropanate is avoided by this technique.[182] The mixture was refluxed for 15½ hours at 75°, 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 6x200cm^3 aliquots of deionised water. The acrylate was dried ($MgSO_4$) and distilled (Spaltrohr concentric tube fractionating column, HMS500 with 75 theoretical plates). The fraction at 44-46° at 120mms of mercury was collected at a reflux ratio of 5:1 and examined by glc (column A at 100°), infrared and mass spectroscopy.

Acid	Benzoyl chloride	Alcohol	Product	Yield	b.pts^{o}c/mms Hg.
Acrylic acid (216g;3 moles)	630g;4.5 moles	2,2,2-trifluoroethanol. (300g;3 moles)	2,2,2-trifluoroethyl acrylate. (290g;2.04moles)	68%	50^{o}/125mms
Methacrylic acid (258g;3 moles)	630g;4.5 moles	2,2,2-trifluoroethanol (300g;3 moles)	2,2,2-trifluoroethyl methacrylate. (297g;1.90mole)	63.3%	44^{o}/100mms
Acrylic acid (216g;3 moles)	630g;4.5 moles	1,1,13,3,3-hexafluoropropan-2-ol (504g;3 moles)	1,1,1,3,3,3-hexafluoroisopropyl acrylate (402g;1.91mole)	63.7%	32^{o}/100mms
Methacrylic acid (258g;3 moles)	630g;4.5 moles	1,1,1,3,3,3-hexafluoropropan-2-ol (504g;3 moles)	1,1,1,3,3,3-hexafluoroisopropyl methacrylate (448g; 2mole)	66.7%	44^{o}/100mms
Acrylic acid (72g;1 mole)	120g;1.5 moles	2,2,3,3,4,4,5,5-octafluoropentanol (232g;1 mole)	1,2,3,3,4,4,5,5-octafluoropentyl acrylate (220g;0.80mole)	80.0%	50.5^{o}/100mms

Table 2.1.

The ultrapure monomers thus formed were stored at -25^{o} over hydroquinone inhibitor.

2.3c). Analysis.

i). Infrared.

The spectra were run as thin films between sodium chloride plates. All monomers gave the expected spectrum, demonstrating the characteristic frequencies and confirming the presence of the anticipated groups in the esters. The spectra are considered in more detail later in the thesis and are reproduced in the appendix.

ii). Elemental analysis.

All monomers were analysed by standard techniques (see appendix). The results are recorded in table 2.2

iii). Mass spectroscopy.

The mass spectra of the five monomers were recorded and are tabulated in the appendix of this thesis. All showed prominent molecular ion peaks and the expected fragmentation pattern, confirming the anticipated structure.

iv). Gas-liquid chromatography.

All compounds gave only one peak when injected to estimate the retention time (0.5 μl injection) and to detect minor impurities (7 μl injection). The analytical technique used would have detected impurities present in greater than 0.1% concentration, providing their retention times were not coincident with that of the monomer. Table 2.3 lists retention times of the monomers.

The combined evidence from the four analytical methods used confirmed the structure and purity of the fluorinated acrylates and methacrylates used in this work. The monomers were estimated to have a purity better than 99.9%.

Table 2.2

Monomer	Element	Calculated	Found
1). 2,2,2-trifluoroethyl acrylate	Carbon	38.97	38.85
	Hydrogen	3.27	3.44
	Oxygen	20.77	20.89
	Fluorine	36.99	36.82
2). 2,2,2-trifluoroethyl methacrylate.	Carbon	42.87	43.02
	Hydrogen	4.20	3.98
	Oxygen	19.03	18.88
	Fluorine	33.90	34.12
3). 1,1,1,3,3,3-hexafluoro isopropyl acrylate	Carbon	32.45	32.24
	Hydrogen	1.82	1.98
	Oxygen	14.41	14.16
	Fluorine	51.33	51.62
4). 1,1,1,3,3,3-hexafluoroisopropyl methacrylate	Carbon	35.61	35.48
	Hydrogen	2.56	2.40
	Oxygen	13.55	14.01
	Fluorine	48.28	48.11
5). 2,2,3,3,4,4,5,5-octafluoropentyl acrylate	Carbon	33.58	33.49
	Hydrogen	2.11	2.00
	Oxygen	11.18	11.20
	Fluorine	53.12	53.31

Table 2.3

Monomer	Retention time (minutes)[a]
2,2,2-trifluoroethyl acrylate	4.0
2,2,2-trifluoroethyl methacrylate	6.5
1,1,1,3,3,3-hexafluoroisopropyl acrylate	2.2
1,1,1,3,3,3-hexafluoroisopropyl methacrylate	3.0
2,2,3,3,4,4,5,5-octafluoropentyl acrylate	13.9

[a] Carried out at 100° using column A. (see appendix).

CHAPTER III

PREPARATION OF THE POLYMERS.

3.1. Introduction.

Homopolymers of fluoroalkyl acrylates and methacrylates are well known and their surface properties, notably their oleophobic characteristics have been thoroughly investigated.[181-5] Some have properties that make them useful as solvent resistant rubbers that have flexibility at low temperatures,[186] and so these resins are well known commercially. Random copolymer properties have also been investigated.[187,191-3]

Homopolymerisation and random copolymerisation of the monomers can be carried out in bulk or solution but the most convenient method is an emulsion technique; complete reaction taking only about half an hour, unless oxygen is present in the system, when considerable induction periods can occur.

Several methods of preparation of block copolymers have been discussed previously in chapter I. The method adopted in this work was that initially suggested by Szwarc[95] via the "living" methyl methacrylate macroradical. The fluoroblock is incorporated simply by adding the monomer to the living system. The reaction must be carried out in the absence of chain transfer agents, including oxygen and water, as they would kill (to continue Szwarc's metaphor) the macroradicals prior to second stage reaction. Alternative procedures are, in principle, possible, for example, a French paper[188] describes the synthesis of methacrylate block copolymers by an anionic route. Seymour and Stahl[189] prepared block copolymers by precipitating the first stage living macroradical from viscous poor solvents such as silicone oils. The same workers also described a method in which the radically initiated reaction was stopped as the macroradicals precipitated out of poor solvents such as propanol or hexane.[190] The presence of species with unpaired electrons in the precipitated polymers has been confirmed by esr techniques.[195] Using the precipitating macroradical procedure, a variety of poly(methyl methacrylate-b-alkyl acrylates) have been prepared. However, certain criteria must be met before this method can be successfully used.

Firstly, it has been found that methyl methacrylate macroradicals are stable in solvents which have solubility parameters (δ) below 7.4 or above 11.0 hildebrand units;[194] hexane has a δ value of 7.3H. Since the macroradicals precipitate when the molecular weight exceeds the solubility limit, initiator concentration has little effect on the molecular weight of the macroradicals.[190]

Secondly, it has been shown that the difference in the solubility parameter values of the monomer and macroradical must not be greater than 3.1 units.[196] The solubility parameter of poly(methyl methacrylate) is 9.1, so the solubility parameters of the fluoroalkyl monomers must have δ values lying between 6 and 12.2H. Solubility parameters may be calculated from a number of physical constants; Small[197] suggested a method to determine values from a knowledge of the structural formula of the compound and its density. A parameter G, the molar attraction constant, is assumed to be additive over the formula and is related to the solubility parameter by the equation:

$$\delta = \frac{d\sum G}{\text{m.wt.}}$$

where d is the density and $\sum G$ is the sum of the molar attraction for all the atoms and groupings in the molecule.

More recently, Hoy[198] devised a new concept of molar attraction constant, consistent with data derived from measurements of vapour pressure. Compilations of both types of G values are available, and in general, computed values of δ agree to within a few tenths of a hildebrand unit.

Table 3.1.

Monomer	Density	ΣG value	Mol.wt.	δ
2,2,2-trifluoroethyl acrylate	1.22g.cm^{-3}	1018	146	8.51
2,2,2-trifluoroethyl methacrylate	1.17g.cm^{-3}	1140	160	8.34
1,1,1,3,3,3-hexafluoroisopropyl acrylate	1.36g.cm^{-3}	1187	222	7.27
1,1,1,3,3,3-hexafluoroisopropyl methacrylate	1.28g.cm^{-3}	1309	236	7.10
2,2,3,3,4,4,5,5-octafluoropentyl acrylate	1.45g.cm^{-3}	1434	286	7.27

Densities of the monomers were determined by weighing a known volume of liquid (50μl) in a syringe, repeating several times and averaging. Their values are given in table 3.1. The values of δ for the monomers used in this work were determined by the method of Small, the values obtained all fell within 3.1 units of the value for poly(methyl methacrylate); thus, the solubility parameter requirements were fulfilled.

The final practical constraint is that of temperature. At the theta temperature for the polymer-solvent system, by definition,[199] the polymer should exist as a statistical coil, and it has been found that the yield of insoluble methyl methacrylate macroradical fell off as the polymerisation temperature approached the theta temperature.[200] A further important parameter is the glass tranision temperature (Tg) of the initially formed polymer. As Tg is approached, chain motion becomes more facile and is accompanied by a greater probability of premature termination. For poly(methyl methacrylate), the value of Tg is 105°. The second block formation stage is diffusion controlled and therefore temperature dependant; the rate is most rapid when the macroradical is highly swollen by the solvent and when a relatively high temperature is maintained. Minoura[201] developed this further and produced block copolymers in good yields by the addition of good solvents to a suspension of macroradical, vinyl monomer and poor solvent.

In summary, macroradicals are unstable in the presence of oxygen, moisture or good solvents, at temperatures above Tg and/or the theta temperature, so that block copolymerisations carried out using this technique must be done under strictly controlled conditions.

3.2. Experimental.

a). Homopolymer production.

i). Materials.

Methyl methacrylate monomer, stablised with p-hydroxyphenol, was obtained from Hopkin and Williams; sodium lauryl sulphate and potassium persulphate from B.D.H. Chemicals Ltd. The fluoroalkyl acrylate and methacrylate monomers, stablised with hydroquinone, were prepared as described in the previous chapter.

Before use, the monomers were freed from their inhibitors by washing with two alliquots of sodium hydroxide solution (10%, 100cm^3), followed by shaking vigorously with deionised water in order to remove residual alkali from the washings, as demonstrated by indicator paper; the monomers were then dried ($MgSO_4$) and finally distilled at reduced pressure. Other chemicals were used without further purification.

ii). Synthesis.

The polymerisation of 2,2,2-trifluoroethyl acrylate will be described, the amounts of chemicals used and techniques employed were the same for all the other homopolymer preparations.

The freshly distilled monomer (2.5g) was pipetted into a clean, necked pyrex tube (ca. 20cm. x 1cm. dia.) fitted with an S19 ball joint. A solution of potassium persulphate initiator (.0125g) and sodium lauryl sulphate emulsifier (.075g) in deionised water (4.5g) was pipetted into the reaction tube which was then attached to a conventional vacuum line. The mixture was degassed by several freeze-thaw cycles and the tube sealed under vacuum(10^{-3}mm.Hg) The tube was placed in a water bath maintained at 50° for 30 minutes, and shaken occasionally to ensure complete emulsification throughout the reaction. The homopolymers of poly(2,2,2-trifluoroethyl methacrylate), poly(1,1,1,3,3,3-hexafluoroisopropyl acrylate and methacrylate), poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate) and poly(methyl methacrylate) were prepared in a similar way.

iii). Polymer recovery.

The crude polymer was a white, rubbery solid. The aqueous solution was decanted from the polymer which was then broken up mechanically and washed with several aliquots of deionised water. The excess water was drained off and the product dissolved in the least quantity of acetone. The resulting viscous solution was added dropwise to a large excess of rapidly stirred, ice cold methanol. The supernatant liquid was decanted from the precipitated polymer which was then dried under reduced pressure (.1mm.Hg for at least 48 hours) to remove residual methanol. The acrylates tended to be more soluble in methanol than the corresponding methacrylates, as reflected in the percentage recoveries (table 3.2.). This fact was used later to fractionate the acrylate block copolymers.

3.2b). Random copolymer production.

i). Materials.

The materials were as described in 3.2a(i) with the addition of disodium tetraborate (borax), obtained from B.D.H. Chemicals Ltd. and used without further purification.

ii).Synthesis.

The copolymerisation of methyl methacrylate with 2,2,2-trifluoroethyl acrylate will be described. The amounts of chemicals used and the techniques employed were the same for the other copolymers subsequently prepared.

The freshly distilled monomers (1.25g each) were pipetted into a clean, necked pyrex tube (20cm x 1cm dia.), fitted with an S19 ball joint. A solution of potassium persulphate (.025g), borax (.05g) and sodium lauryl sulphate (.075g) in deionised water (5g) was pipetted into the tube which was then attached to a vacuum line. The mixture was degassed by several freeze-thaw cycles and the tube sealed under vacuum (10^{-3}mm.Hg). The tube was placed in a water bath maintained at 50^{o} for 30 minutes and shaken occasionally to ensure complete emulsification throughout the reaction. The copolymers of methyl methacrylate with 2,2,2-trifluoroethyl methacrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate and methacrylate and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate were prepared in a similar way.

iii). Copolymer recovery.

The procedure was as described for the homopolymers (3.2a(iii). The yields of recovered polymers are given in table 3.2.

3.2c). Block copolymer production.

i). Materials.

The monomers were freed from inhibitor as described previously; 2,2'-azobis-2-methylproprionitrile (AIBN), was obtained from B.D.H. Chemicals Ltd. and was recrystallised from hot methanol; hexane from B.D.H. Chemicals Ltd. was distilled (20cm x 1cm dia., glass helices, b.pt. 68^{o} at 760mm Hg) before use.

ii). Synthesis.

The block copolymerisation of methyl methacrylate with 2,2,2-trifluoroethyl acrylate will be described. The apparatus used consisted of a flask (250cm^{3}; 2 necked) connected to a conventional vacuum line via a condenser. The flask was fitted with a magnetic stirrer. The glassware was oven dried at 120^{o} for several hours, assembled hot and attached to the vacuum system while hot and allowed to cool under vacuum; it was then let down to an atmosphere of dry nitrogen. Freshly distilled hexane (50g) was introduced into the flask against a countercurrent of dry nitrogen. AIBN (.075g; 1.5%) and freshly distilled methyl methacrylate (5g)were also added in this manner. The system was degassed by several freeze-thaw cycles to remove any traces of dissolved oxygen. The apparatus was maintained under an atmosphere of dry nitrogen and the reaction mixture was heated by an oil bath at 50^{o}, whilst being stirred slowly. The reaction was assumed to be complete after 48 hours. At this stage, 2,2,2-trifluoroethyl acrylate (2.5g) was vacuum transferred into the reaction flask, and the second phase reaction continued at 45^{o} for a further 72 hours under an atmosphere of dry nitrogen. Other block copolymerisations were carried out in the same way.

iii). Copolymer recovery.

The polymeric material formed was recovered by filtration, washed with hexane, dissolved in the minimum amount of acetone, reprecipitated from ice cold methanol and dried on a vacuum line (.1mm Hg for at least 48 hours). Yields of precipitated products are recorded in table 3.2.

Table 3.2.

monomer.	% recovery		
	Homo	Random	Block
methyl methacrylate	97%	-	-
trifluoroethyl acrylate	57%	84%	72%
trifluoroethyl methacrylate	94%	86%	85%
hexafluoroisopropyl acrylate	62%	77%	69%
hexafluoroisopropyl methacrylate	89%	82%	-
octafluoropentyl acrylate	47%	79%	62%

iv). Fractionation of the block copolymers.

Due to the low solubility of the fluoroalkyl acrylates in ice cold methanol, and their enhanced solubility in hot methanol, it was decided to attempt to separate the block copolymer from any homopoly(methyl methacrylate) formed in the reaction by soxhlet extraction using methanol as the solvent. This technique led to a successful fractionation of methanol soluble (high fluoroalkyl ratio) and methanol insoluble (low fluoroalkyl ratio) constituents, as revealed by infrared analysis of the fractions (see appendix C). In the case of poly(methyl methacrylate-b-octafluoropentyl acrylate), the separation of the block copolymer from homopoly(methyl methacrylate was achieved more or less completely after 96 hours, due to the relativly high solubility of poly(octafluoropentyl acrylate) in methanol. Less well defined separations were obtained for the other copolymers; fluorinated components being present, but to differing proportions, in the methanol soluble and insoluble fractions.

A sample of poly(methyl methacrylate) was prepared by quenching the macroradicals, whose method of production was described previously, in acetone. In this way a low molecular weight polymer was prepared with an average chain length equal to the hydrocarbon chain length in the block copolymers prepared, and also a molecular weight equal to any homopoly(methyl methacrylate) byproduct formed during the block copolymerisations. This material was not extracted under the conditions used to fractionate the block copolymers, and therefore it was assumed that the product extracted from the crude copolymers contained no homopoly(methyl methacrylate). However, infrared analysis of the methanol soluble fractions of the block copolymers, showed the presence of methyl methacrylate in the samples. This could not be homopolymer as this was shown previously not to extract, therefore the methyl methacrylate present in the fractions must be chemically combined with the fluoromonomer in the polymers. Since the methyl methacrylate macroradicals were formed prior to the introduction of fluoroalkyl monomer, then the arrangement of the monomers in the polymer chain can only be in the form of blocks.

CHAPTER IV

POLYMER CHARACTERISATION.

4.1. Introduction.

The polymers, prepared as described in the previous chapter, were characterised by a variety of techniques. Dilute solution viscosity measurements and gel permeation chromatography were used to establish molecular weights. Analysis of the infrared spectra of the materials established the mode of polymerisation as addition (loss of vinylic C═C stretching, all other absorbtion frequencies remaining intact), and for the homopolymers, this was confirmed by elemental analysis. Nmr spectroscopy was used in two respects; proton magnetic resonance allowing the relative amounts of methyl methacrylate and fluoroalkyl acrylate and methacrylate monomers incorporated into the copolymers to be established (elemental analysis was also used for this purpose); ^{19}F nmr proved useful in distinguishing between block and random copolymers by a comparison of chemical shifts. The surface free energies of polymer films were determined by contact angle measurements.

The results of the individual characterisation techniques are recorded in this chapter, their implications and conclusions drawn will be mentioned in the last chapter, together with suggestions for further work.

4.2. Molecular weight determination.

i). By viscosity.

Intrinsic viscosities were determined for the homopolymers in solution (chloroform for poly(methyl methacrylate) and α,α,α-trifluorotoluene for the fluoropolymers) using a Ubbelohde dilution viscometer with a solvent efflux time greater than 100 seconds. All measurements were taken at $25.00^{\circ} \pm .01^{\circ}$. The results are presented in table 4.1.

iii). Gel permeation chromatography.

This recently developed technique, in which polymers are eluted from a chromatography column as a function of their molecular weight, depends for its application on prior calibration with standard samples characterised previously by absolute techniques. In favourable cases, it provides detailed information on molecular weight and molecular weight distribution; however, for novel materials, reliable results will only be obtained where the solution behaviour of the test polymer closely resembles that of the calibrating polymer. Chang[210] obtained good results when he used gpc to analyse a block copolymer of styrene and butadiene; however,for the fluoroalkyl polymers discussed here, difficulties were met. In several cases, little or no response was obtained from the refractive index detection system used. This, allied to the fact that the column is calibrated with respect to the behaviour of polystyrene, suggests that the results must be treated with caution. The results obtained for the homopolymers are given in table 4.1, those for the block copolymers in table 4.5.

Table 4.1.

Polymer	Intrinsic viscosity[a]	Molecular weight	
		viscosity[b]	G.p.c.
1) poly(methyl methacrylate)[c]	11.14	$1.61x10^4$	$1.2x10^4$
2) poly(2,2,2-trifluoroethyl acrylate)	1.14	$16.6x10^6$	
3) poly(2,2,2-trifluoroethyl methacrylate)	1.84	$25.7x10^6$	$0.59x10^5$
4) poly(1,1,1,3,3,3-hexafluoroisopropyl acrylate)	0.94	$2.94x10^6$	
5) poly(1,1,1,3,3,3-hexafluoromethacrylate)	0.64	$3.91x10^6$	
6) poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate)	1.17	$10.58x10^6$	$0.69x10^5$
7) poly(methyl methacrylate)[d]	1.45	$1.25x10^3$	

[a] The intrinsic viscosity is determined by plotting $\left(\frac{\text{specific viscosity}}{\text{concentration}}\right)$ and $\left(\frac{\text{inherent viscosity}}{\text{concentration}}\right)$ versus concentration and extrapolating both curves back to infinite dilution. The common intercept at zero concentration is the value of the intrinsic viscosity, $[\eta]$

[b] The molecular weight is determined from a knowledge of the intrinsic viscosity by the use of the Mark-Houwink equation:

$$[\eta] = K.\ M^{\alpha}$$

where K and α are constants for the given system.

For poly(methyl methacrylate) in chloroform, $K = 4.8 \times 10^{-3}$ and $\alpha = 0.8$. For the fluorocarbon polymers in α,α,α-trifluorotoluene, $K = 1.3 \times 10^{-4}$ and $\alpha = 0.56$.[182]

[c] The data refer to emulsion polymerised methyl methacrylate.

[d] The data refer to quenched poly(methyl methacrylate).

4.3. Spectroscopic data.

i). Infrared analysis.

Polymer solutions in acetone (about 1% w/v) were slowly evaporated in turn from a sodium chloride plate. The residual polymer film was gently warmed with a hot air blower to remove any traces of solvent, and spectra were recorded on the thin film thus formed. The spectra obtained are reproduced in the appendix. The main functional group absorbance frequencies namely the carbon-hydrogen stretching frequencies, the carbonyl and the vinylic C═C stretch and the carbon-fluorine absorbtions are listed in table 4.2. The differences in the carbonyl stretching frequencies of the monomers can be explained in terms of the electronic effects of the neighbouring groups. The fluoroalkyl moiety has a strong electron withdrawing effect on the carbonyl; while, the introduction of a +I methyl group on

Compound		C—H stretch	C=O stretch	C=C stretch	C—F
1). methyl methacrylate	monomer	3000,2960,2940cm^{-1}	1730cm^{-1}	1640cm^{-1}	-
	polymer	3000,2960cm^{-1}	1735cm^{-1}	-	-
2). 2,2,2-trifluoroethyl acrylate	monomer	2990cm^{-1}	1750cm^{-1}	1640cm^{-1}	1170cm^{-1}
	polymer	2990cm^{-1}	1760cm^{-1}	-	1170cm^{-1}
3). 2,2,2-trifluoroethyl methacrylate	monomer	2980,2940cm^{-1}	1740cm^{-1}	1640cm^{-1}	1160cm^{-1}
	polymer	3000,2980,2940cm^{-1}	1755cm^{-1}	-	1170cm^{-1}
4). 1,1,1,3,3,3-hexafluoroisopropyl acrylate	monomer	2980cm^{-1}	1770cm^{-1}	1640cm^{-1}	1220,1120cm^{-1}
	polymer	2980cm^{-1}	1775cm^{-1}	-	1235,1110cm^{-1}
5). 1,1,1,3,3,3-hexafluoroisopropyl methacrylate	monomer	2980,2940cm^{-1}	1760cm^{-1}	1640cm^{-1}	1235,1130cm^{-1}
	polymer	2980,2940cm^{-1}	1780cm^{-1}	-	1240,1110cm^{-1}
6). 2,2,3,3,4,4,5,5-octafluoropentyl acrylate	monomer	3030,2990cm^{-1}	1750cm^{-1}	1640cm^{-1}	1300-1100cm^{-1}
	polymer	2990,2960cm^{-1}	1760cm^{-1}	-	1300-1110cm^{-1}

Table 4.2.

going from acrylate to methacrylate, increases the electron density associated with the adjacent carbonyl. Therefore, the increased carbonyl stretching frequency, on going from methyl methacrylate to the fluoroalkyl methacrylates, and from the methacrylate to the corresponding acrylate is as expected. Another point of interest is the upfield carbonyl absorbtion shift following polymerisation of the monomers. This observation is in line with expectation and is due to the loss of conjugation in the polymer as the vinylic C═C, formerly allowing electronic delocalisation, is consumed in the polymerisation reaction. The saturation of the C═C during polymerisation is also demonstrated by the loss of the stretching frequency at 1640 cm^{-1} on going from monomer to polymer.

ii). Nmr analysis.

Nmr has been used in two ways in the characterisation of these materials.

For the case of methyl methacrylate and hexafluoroisopropyl acrylate, differences in the ^{19}F chemical shifts were used to distinguish between random and block copolymers. Both copolymer samples had a monomer ratio of 1;that is, equal amounts of fluorinated and non-fluorinated monomers. The centre of the broad signal observed for the block copolymer (14.39 ppm downfield from $CFCl_3$) was almost coincident with that for the homopolymer of hexafluoroisopropyl acrylate (14.33 ppm) since the $-CF_3$ groups in the block and homopolymer are in chemically similar environments. The signal from the random copolymer, however, was shifted downfield (14.89ppm) with respect to the block and homopolymer, confirming the different environment that the $-CF_3$ groups in the random copolymer are experiencing.

Monomer incorporation could also be determined from ^1H nmr data of the copolymers. Because of the highly electronegative character of the perfluoroalkyl groups, and the deshielding effect associated with this, it was anticipated, and found, that the protons of the fluoromonomers incorporated within the copolymers generally absorbed downfield from those of the methyl methacrylate units. Then, integrating sufficiently well resolved signals from each constituent, with regard to the number of protons in resonance, an estimation of the monomer incorporation ratio for the copolymer may be made. Results of this analysis, and a comparison with the results obtained by elemental analysis, is given in table 4.3.

Table 4.3.

Polymer[a]	Mole % fluoromonomer incorporation.	
	Elemental analysis	Nmr analysis
poly(tfea-b-mma)	88.8%	83.7%
poly(tfem-b-mma)	69.6%	70.8%
poly(hfpa-b-mma)	52.0%	50.2%
poly(ofpa-b-mma)	68.3%	71.8%

[a] A guide to abbreviations is given at the front of this thesis.

The differences in the results obtained by using the two methods are probably due to the inherent difficulties of integrating broadened peaks that are characteristic of polymeric materials.

4.4. Elemental analysis.

Results for the homopolymers are given in table 4.4a and confirm that the materials were addition polymers.

By determining the %F in the copolymers, an estimation of the methyl methacrylate : fluoroalkyl ester incorporation in the copolymers may be made. Results of such analysis are given in table 4.4b.

Table 4.4a.

Polymer	Element	Calculated	Found
1). poly(methyl methacrylate)	Carbon	59.98	59.79
	Hydrogen	8.05	7.71
	Oxygen	31.96	32.50
2). poly(2,2,2-trifluoroethyl acrylate)	Carbon	38.97	39.21
	Hydrogen	3.27	2.97
	Oxygen	20.77	20.42
	Fluorine	36.99	37.40
3). poly(2,2,2-trifluoroethyl methacrylate)	Carbon	42.87	42.81
	Hydrogen	4.20	4.33
	Oxygen	19.03	18.62
	Fluorine	33.90	34.24
4). poly(1,1,1,3,3,3-hexafluoroisopropyl acrylate)	Carbon	32.45	32.21
	Hydrogen	1.82	1.84
	Oxygen	14.41	14.48
	Fluorine	51.33	51.47
5). poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)	Carbon	35.61	35.84
	Hydrogen	2.56	2.39
	Oxygen	13.55	13.31
	Fluorine	48.28	48.26
6). poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate)	Carbon	33.58	33.44
	Hydrogen	2.11	2.23
	Oxygen	11.18	11.37
	Fluorine	53.12	52.96

Table 4.4b.

	Block copolymer		Random copolymer	
Polymers[a]	%F;	%fluoropolym	%F;	%fluoropolym
poly(mma) and poly(tfea)	32.85%;	88.80%	19.73%;	53.33%
poly(mma) and poly(tfem)	23.58%;	69.66%	20.31%;	59.90%
poly(mma) and poly(hfpa)	26.68%;	51.98%	26.45%;	51.53%
poly(mma) and poly(hfpm)	-	-	24.02%;	49.72%
poly(mma) and poly(ofpa)	36.29%;	68.32%	25.59%;	48.17%

[a] A guide to abbreviations is given at the front of this thesis.

For the block copolymers, the molecular weight of the methyl methacrylate block is known from a study of the quenched macroradicals, which terminate mainly by disproportionation; therefore, knowing the mole percentage incorporation of fluoromonomer, the molecular weight of the block copolymer may be calculated. Results are given in table 4.5 together with those obtained by gpc analysis.

Table 4.5.

Polymer[a]	Calculated m.wt.	M.wt. by gpc
poly(mma-b-tfea)	16.69×10^3	28.5×10^3
poly(mma-b-tfem)	5.84×10^3	
poly(mma-b-hfpa)	4.25×10^3	
poly(mma-b-ofpa)	8.96×10^3	8.93×10^3

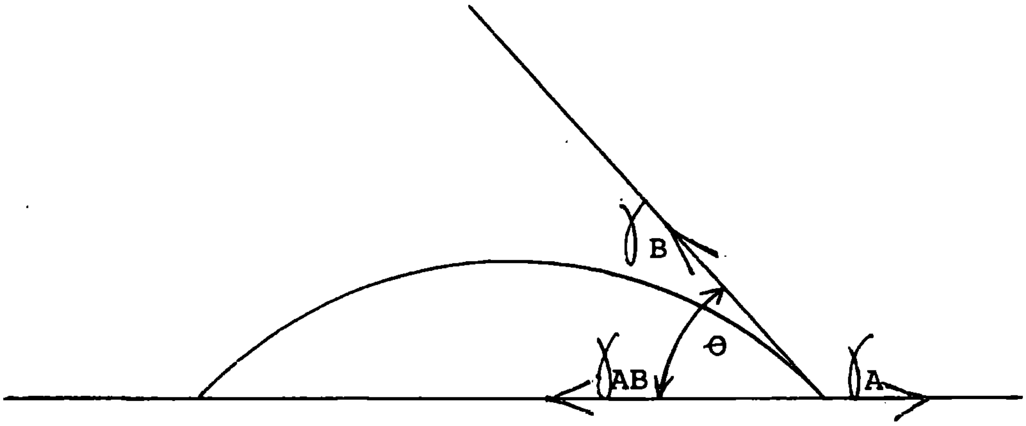
[a] A guide to abbreviations is given at the front of this thesis.

4.5. Surface characterisation.

i). Introduction.

From the viewpoint of this work, the surface properties of the polymers are of great interest in the characterisation studies. The fluoroalkyl ester polymers have low surface energies, thought to be due to very low Van der Waals forces, common to highly fluorinated substances; in fact, surfaces comprised of $-CF_3$ groups have the lowest wettability observed for any substances.[181]

Direct determination of surface free energy is not easy, and it is common practice to use an extrapolation technique. A drop of a non-wetting liquid on a horizontal surface is represented in the diagram over the page.



Since the system is at equilibrium, the forces acting parallel to the surface can be equated, hence:

$$\gamma_A = \gamma_{AB} + \gamma_B \cos \theta$$

where γ are surface tensions and θ is the contact angle.

For an homologous series of liquids, γ_B can be obtained from tables, and θ can be measured. At the point where the liquid just wets the solid, γ_A is equal to γ_B ; consequently, extrapolation of a series of measurements to $\theta = 0$ i.e. $\cos \theta = 1$ gives a value of the surface tension of the solid. This approach, introduced by Zisman[202] gives a value of the "critical surface tension" which has been widely used as an approximation of the surface free energies of solids. Wu[210] confirmed this by comparing surface tensions of solid polymers obtained by contact angle measurement with those determined by direct measurements on molten polymers.

Attempts to correlate surface behaviour with bulk properties have been made,[203-7] but quantitative reliability to date is low; however, these theoretical studies, as well as empirical work, indicate that the energy of a surface depends upon the number and types of chemical groups comprising it. Pittman et al[181] examined wetting properties of fluoroalkyl acrylates and methacrylates and found that, generally, modifications in the pendant fluoroalkyl group affected the critical surface tension, γ_C. Infact, γ_C was increased:

a) by substituting F with Cl or H,

b) as the fluorocarbon group is removed from the proximity of the polymer backbone by intervening methylene groups,

c) on going from iso- to n-propyl perfluoropolyacrylates

and d) by decreasing the fluorocarbon chain length.

Refinements and modifications of methods of determining surface free energies appear in the literature,[208,209] however, the simple approach outlined above was adequate for the requirements of this work.

ii). Materials.

Two series of liquids were used, the C_7 to C_{10} and C_{16} n-alkanes and the C_5 to C_8 and C_{10} straight chain 1^o alcohols. All were obtained from B.D.H. Laboratory reagents and all were used without further purification.

iii). Experimental.

Polymer surfaces were prepared by immersing scrupulously clean microscope slides (washed with nitric acid and detergent, followed each time with rinsing with deionised water) in about 1% solutions of the polymers in acetone. The slide was removed vertically and the solvent was allowed to evaporate slowly. Complete removal of solvent was achieved by drying the slides for several hours under reduced pressure (0.1 mm. Hg; ambient temperature).

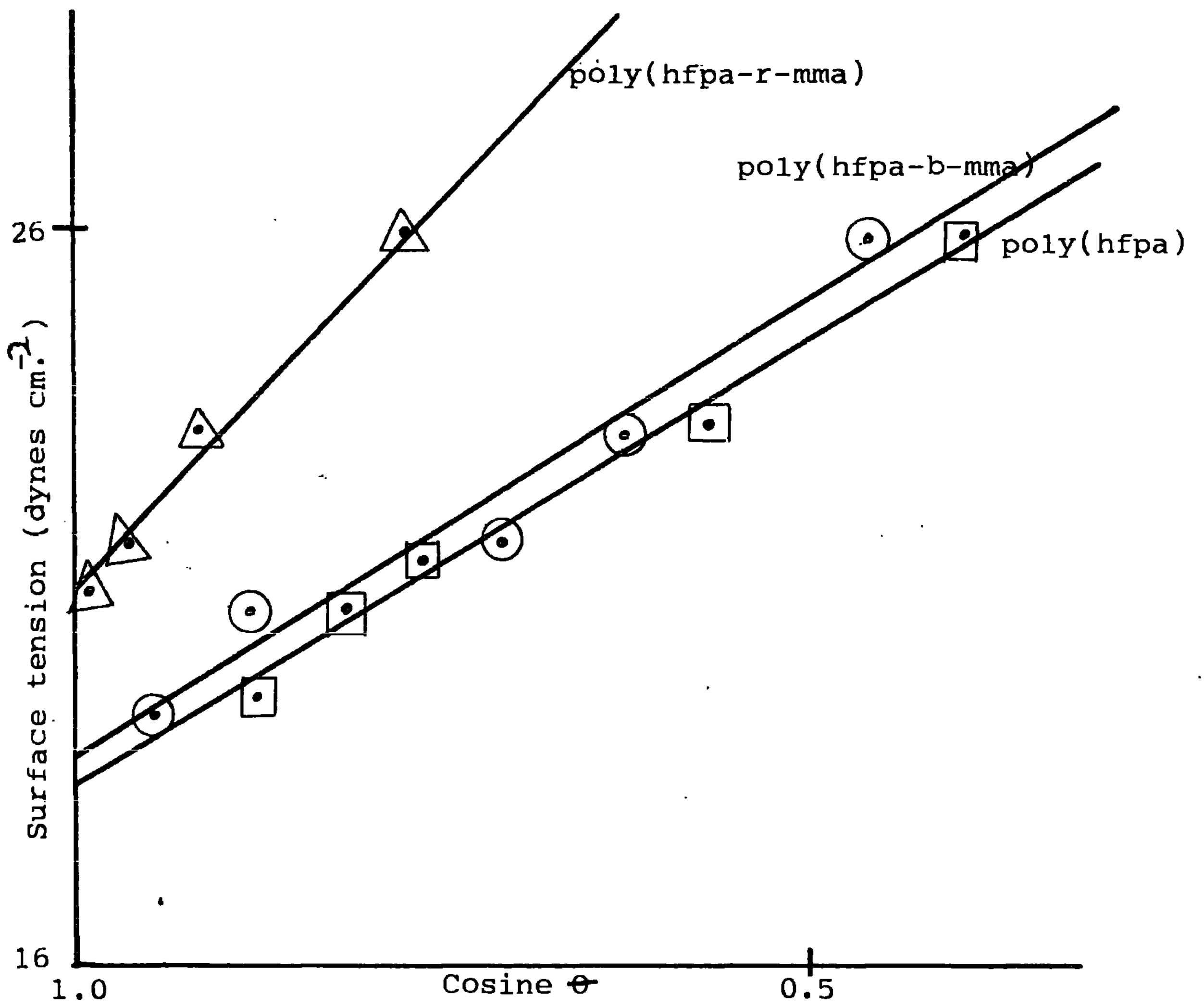
Contact angles were measured with a travelling microscope, after calibrating with polar graph paper. The rotating eye piece was set to align the cross-hairs horizontally and its position marked, then, by rotating through 10^{o} at a time, and marking off the linear scale attached to the instrument, the microscope was calibrated to read to the nearest degree. The test liquid was dropped onto the horizontal polymer surface, allowed to equilibrate for 2 minutes and the contact angle measured on both sides of the drop. The reading was averaged for three drops; the process being repeated for each liquid and each surface.

iv). Results.

A typical graph obtained by plotting cosine of the contact angle versus the surface tension of the test liquids (in this case the n-alkanes) is given in figure 4.1 for poly(hexafluoroisopropyl acrylate) and its copolymers (ca. 50:50) with methyl methacrylate. Results for all the polymers are given in table 4.6. The first figure in each column is the value obtained for the critical surface tension when using the n-alkanes as the testing liquids, the figure in brackets is that obtained from the straight chain primary alcohols.

A further test was devised to examine how the surface free energy of poly(trifluoroethyl acrylate) and its block and random copolymers with methyl methacrylate varied on "dilution" with poly(methyl methacrylate). Mixtures of the fluoropolymers and poly(methyl methacrylate) were dissolved in acetone and thin films, prepared as described previously, were examined and their surface free energies determined. Results are given in tables 4.7a, 4.7b, and 4.7c. The first column of figures in the surface energy group are the results obtained by using n-alkanes as the test liquids, those in brackets are the results from the tests using 1^{o} alcohols.

Figure 4.1



Intercepts:

poly(hexafluoroisopropyl acrylate)	18.5d.cm^{-1}
poly(hexafluoroisopropyl acrylate-b-methyl methacrylate)	18.8d.cm^{-1}
poly(hexafluoroisopropyl acrylate-r-methyl methacrylate)	21.1d.cm^{-1}

	Homopolymer	Block copolymer	Random copolymer
1). Poly(trifluoroethyl acrylate)	19.4 (22.4)	19.3 (23.5)	20.3 (24.5)
2). Poly(trifluoroethyl methacrylate)	20.6 (23.1)	20.6 (22.8)	23.1 (26.0)
3). Poly(hexafluoroisopropyl acrylate)	18.4 (18.2)	18.8 (17.9)	21.1 (25.2)
4). Poly(hexafluoroisopropyl methacrylate)	17.0 (19.0)	17.1 (19.3)	20.5 (24.0)
5). Poly(octafluoropentyl acrylate)	20.5 (24.2)	20.8 (24.8)	20.9 (25.6)

Table 4.6.

Table 4.7a.

a). Dilution of homopoly(trifluoroethyl acrylate).

Slide	% tfea.	Surface energy (dynes cm^{-2})
1	91.4%	20.9 (24.2)
2	81.9%	21.5 (24.1)
3	37.1%	22.0 (24.6)
4	27.2%	22.1 (24.8)
5	14.3%	22.3 (24.5)
6	9.0%	22.2 ((23.9)

Table 4.7b.

b). Dilution of poly(trifluoroethyl acrylate-b-methyl methacrylate).

Slide	% tfea.	Surface energy (dynes cm^{-2})
1	70.9%	21.1 (25.6)
2	24.4%	22.0 (26.2)
3	17.4%	22.2 (26.2)
4	7.6%	22.9 (27.4)
5	4.4%	22.2 (26.2)
6	1.6%	22.3 (26.4)

Table 4.7c.

c). Dilution of poly(trifluoroethyl acrylate-r-methyl methacrylate).

Slide	% tfea.	Surface energy (dynes cm^{-2})
1	46.5%	22.1 (25.8)
2	24.5%	25.1 (27.4)
3	13.3%	25.2 (27.7)
4	1.8%	26.0 (28.8)

CHAPTER V

DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

The work reported in this thesis was carried out in an attempt to answer two questions :-

i). Is it possible to prepare block copolymers of methyl methacrylate and fluoroalkyl acrylate and methacrylate using the living macroradical technique?

ii). Assuming such materials can be made, what will their surface properties be, and what factors will control the anticipated surface segregation of the fluorinated blocks?

The time available for the work inevitably makes this only a preliminary survey of these questions, however, the results reported in chapters III and IV demonstrate unambiguously that the answer to the first question is yes. Considerable work remains to be done to improve control over molecular weight and block length of the copolymers synthesised, in order that suitable materials may be prepared to investigate the second question in more detail; never-the-less, it has clearly been established that the living macroradical technique for preparing block copolymers is applicable to the systems investigated here.

In the synthetic procedure used, the methyl methacrylate block length was predetermined, since the macroradical precipitated from the poor solvent, hexane, in a restricted molecular weight range. Choice of alternative poor solvents would allow different block lengths to be obtained and this would merit attention in any extension of the work. Variation of the fluoroalkyl acrylate block length, not investigated in this study, could presumably be achieved by varying the proportion of monomer added to the system in the second stage.

Some aspects of the characterisation of the materials could be improved, or made more experimentally convenient. The determinations of monomer incorporation described earlier appear satisfactory, although future workers on the project may find pyrolysis-gas liquid chromatography an effective technique for routine analysis. Separation of the product into homopolymer and block copolymer fractions is another area where further consideration is needed, if a detailed understanding of the formation of a block copolymer is to be achieved; although, from the viewpoint of obtaining the required surface effect, it is probably not necessary to separate the various products (see later). Precipitation techniques may well prove more effective than the soxhlet extraction used in this work. Improvement of the fractionation techniques is a matter of time and patience and presents few experimental difficulties.

As expected, the homopolymers all had low surface free energies, ranging from 17.0 dynes $cm.^{-2}$ for poly(hexafluoroisopropyl methacrylate), containing two terminal trifluoromethyl groups per monomer unit, through poly(trifluoroethyl acrylate), containing one terminal trifluoromethyl group per unit, to poly(octafluoropentyl acrylate) which had the highest free energy at 20.5 dynes $cm.^{-2}$, and containing a terminal $-CF_2H$ group with three difluoromethylene groups in the fluoroalkyl side chain. These results are qualitatively in good agreement with those reported by Pittman and co-workers.[181]

The critical surface energies for the block copolymers, prepared and fractionated as described in chapter III, show a remarkable similarity to the homopolymers, indicating that the expected segregation of fluoroalkyl groups at the surface occurs. Poly(methyl methacrylate) has a surface energy of 39 dynes $cm.^{-2}$ and would be readily detected since all the test liquids used would spread on it.[210]

The random copolymers, on the other hand, have higher surface energies than either the corresponding block copolymer or homopolymer. Here, the fluoroalkyl ester units are dispersed randomly throughout the polymer molecule and consequently surface segregation is not so readily possible, as a result, the surface composition will be a mixture of fluoroalkyl and alkyl groups, and this is reflected in the higher values of the surface energies measured. Differences between surface energies for homo, random and block copolymers of octafluoropentyl acrylate are not observed, (see table 4.6). This may be due to a less random distribution through the supposed random copolymer structure; any blocks of monomer in the random copolymer would allow surface segregation, which would account for this observation. Alternatively, the fluorine surface migration may be more easily facilitated because of the relatively long fluoroalkyl side chains. Migration of these chains, even randomly dispersed through the matrix, may give a surface rich in fluorinated groups, thus endowing it with a low surface free energy. The ambiguity could be resolved by determining reactivity ratios for the fluoromonomer in relation to methyl methacrylate in order to determine the likely length of any block sequence in the random copolymers.[211]

The surface energies measured for films of homopoly(trifluoroethyl acrylate) and the block and random copolymers of trifluoroethyl acrylate with methyl methacrylate progressively diluted with poly(methyl methacrylate), (see tables 4.7a,b and c) merit further discussion. As would be expected, casting films from solutions containing mixtures of poly(trifluoroethyl acrylate) and poly(methyl methacrylate) results in complete segregation of the fluorinated material at the surface (table 4.7a). Similarly, it was found that the block copolymer presented an essentially fluorinated surface, even when diluted to the point where there was only 1.6 mole % of the fluorinated monomer left. The random copolymer, however, shows a marked increase in critical surface energy as the proportion of poly(methyl methacrylate), added as a diluent, increases. This reflects the inability of the randomly dispersed fluoroalkyl groups to surface segregate effectively, even at concentrations as high as 25 mole %.

On this evidence, surface segregation of the fluorinated blocks, even at low concentrations, occurs, and can be monitored by relatively unsophisticated techniques. This provides the beginning of an answer to the second question asked in the opening paragraph of the chapter. A more detailed examination of this question would, in the first place, require the synthesis of more copolymers, as outlined earlier.

In this work it has been demonstrated that the materials initially sought can be prepared by a relatively straightforward method and the surface properties anticipated for such materials have been demonstrated.

Erratum, p.69

Infrared spectra

were recorded on a Perkin-Elmer 197 Spectrophotometer as liquid films (monomers) or thin films cast from solution (polymers).

Nuclear magnetic resonance spectra

APPENDIX A

APPARATUS AND INSTRUMENTS.

Vacuum system.

Air sensitive substances were handled and polymers dried in a conventional vacuum system incorporating a rotary oil pump.

Mass spectra

were measured with an A.E.I. MS9 spectrometer at an ionising beam energy of 70 eV.

Infrared spectra

were run on a Bruker Spectrospin HX90E high resolution nmr spectrometer (operating at 84.64 MHz. for ^{19}F and 90.0MHz. for ^{1}H spectra).

Gas-liquid chromatography.

An analytical Pye Unicam GCD gas chromatograph, using nitrogen as carrier gas and a flame ionisation detector was used. Column A is 2.0 m x 5 mm. with a stationary phase of di-n-decylphthalate/Celite, 1:2.

Elemental analysis.

Carbon and hydrogen estimation was carried out with a Perkin-Elmer 240 CHN analyser, fluorine percentages were obtained by potassium fusion with subsequent titration and oxygen was calculated by difference.

Gel permeation chromatography.

Analysis was carried out at the Rubber and Plastics Research Association at Shrewsbury. Molecular weights quoted are number averages and are computed as 'polystyrene equivilent' materials. The system uses THF as solvent and uses a refractive index detector.

APPENDIX B

MASS SPECTRA.

The mass spectra of the monomers are tabulated below. Ions are written in the form:

50(50%, $C_xH_yF_z$, P-$C_aH_bF_cO_d$)

and describes an ion of mass number 50, and intensity 50% of that of the base peak of the spectrum. It has been assigned the formula $C_xH_yF_z^+$ (the positive charge being understood) and its origin has been interpretated as loss of $C_aH_bF_cO_d$ from the parent ion (P). The base peak is labelled B.

1). <u>2,2,2-trifluoroethyl acrylate.</u>

154(3.2% , $C_5H_5O_2F_3$, Parent)
83(12.9%, $C_2H_2F_3$, P-$C_3H_3O_2$)
69(3.6% , CF_3, P-$C_4H_5O_2$)
56(7.1% , C_2O_2, P-$C_3H_5F_3$)
B.55(100% , C_3H_3O, P-$C_2H_2OF_3$)
28(12.9%, CO, P-$C_4H_5OF_3$)

2). <u>2,2,2-trifluoroethyl methacrylate.</u>

168(23.6%, $C_6H_7O_2F_3$, Parent)
83(15.7%, $C_2H_2F_3$, P-$C_4H_5O_2$)
69(74.3%, CF_3/C_4H_5O, P-$C_5H_7O_2$ / P-$C_2H_2OF_3$)
B.41(100%, C_3H_5, P-$C_3H_2O_2F_3$)
39(44.3%, C_3H_3, P-$C_3H_4O_2F_3$)
28(32.9%, CO, P-$C_5H_7OF_3$)

3). 1,1,1,3,3,3-hexafluoroisopropyl acrylate.

222(8.9%,	$C_6H_4O_2F_6$,	Parent)
151(6.1%,	C_3HF_6,	P-$C_3H_3O_2$)
69(34.1%,	CF_3,	P-$C_4H_4O_2$)
B.55(100%,	C_3H_3O,	P-C_3HOF_6)
39(8.2%,	C_3H_3,	P-$C_3HO_2F_6$)
27(34.2%,	C_2H_3,	P-$C_4HO_2F_6$)

4). 1,1,1,3,3,3-hexafluoroisopropyl methacrylate.

236(22.2%,	$C_7H_6O_2F_6$,	Parent)
151(14.0%,	C_3HF_6,	P-$C_4H_5O_2$)
85(22.9%,	$C_4H_5O_2$,	P-C_3HF_6)
B.69(100%,	CF_3/C_4H_5O,	P-$C_5H_6O_2$/P-C_3HOF_6)
41(45.6%,	C_3H_5,	P-$C_4HO_2F_6$)
39(30.7%,	C_3H_3,	P-$C_4H_3O_2F_6$)

5). 2,2,3,3,4,4,5,5-octafluoropentyl acrylate.

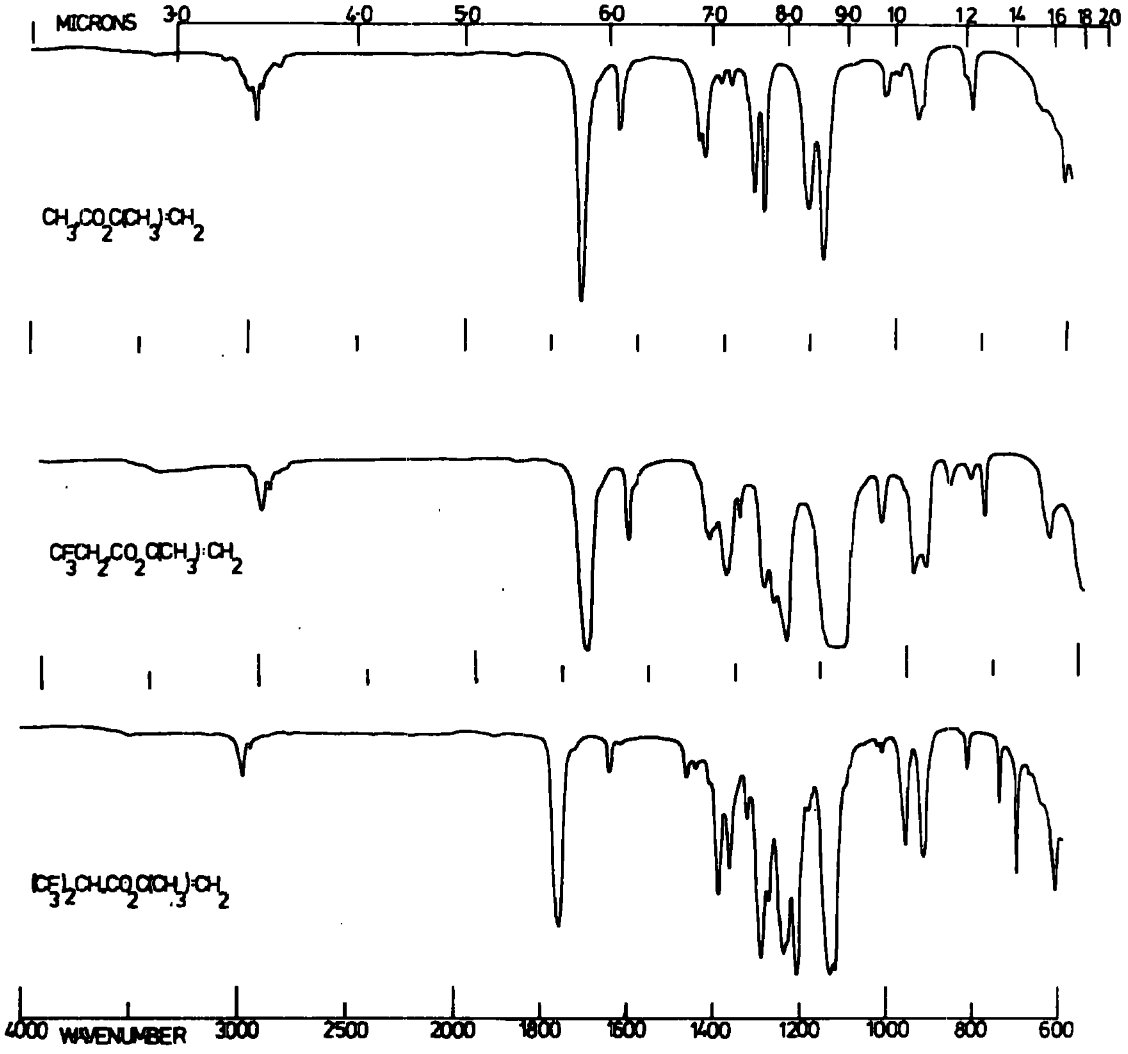
286(10.5%,	$C_8H_6O_2F_8$,	Parent)
201(38.9%,	C_4HF_8,	P-$C_4H_5O_2$)
84(17.4%,	$C_4H_4O_2$,	P-$C_4H_2F_8$)
B.69(100%,	C_4H_5O,	P-C_4HOF_8)
55(83.1%,	C_3H_3O,	P-$C_5H_3OF_8$)
27(23.0%,	C_2H_3,	P-$C_6H_3O_2F_8$)

APPENDIX C

INFRARED SPECTRA.

Infrared index.

Block copolymers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4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
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$CF_3CH_2CO_2C(CH_3){:}CH_2$
$(CF_3)_2CHCO_2C(CH_3){:}CH_2$
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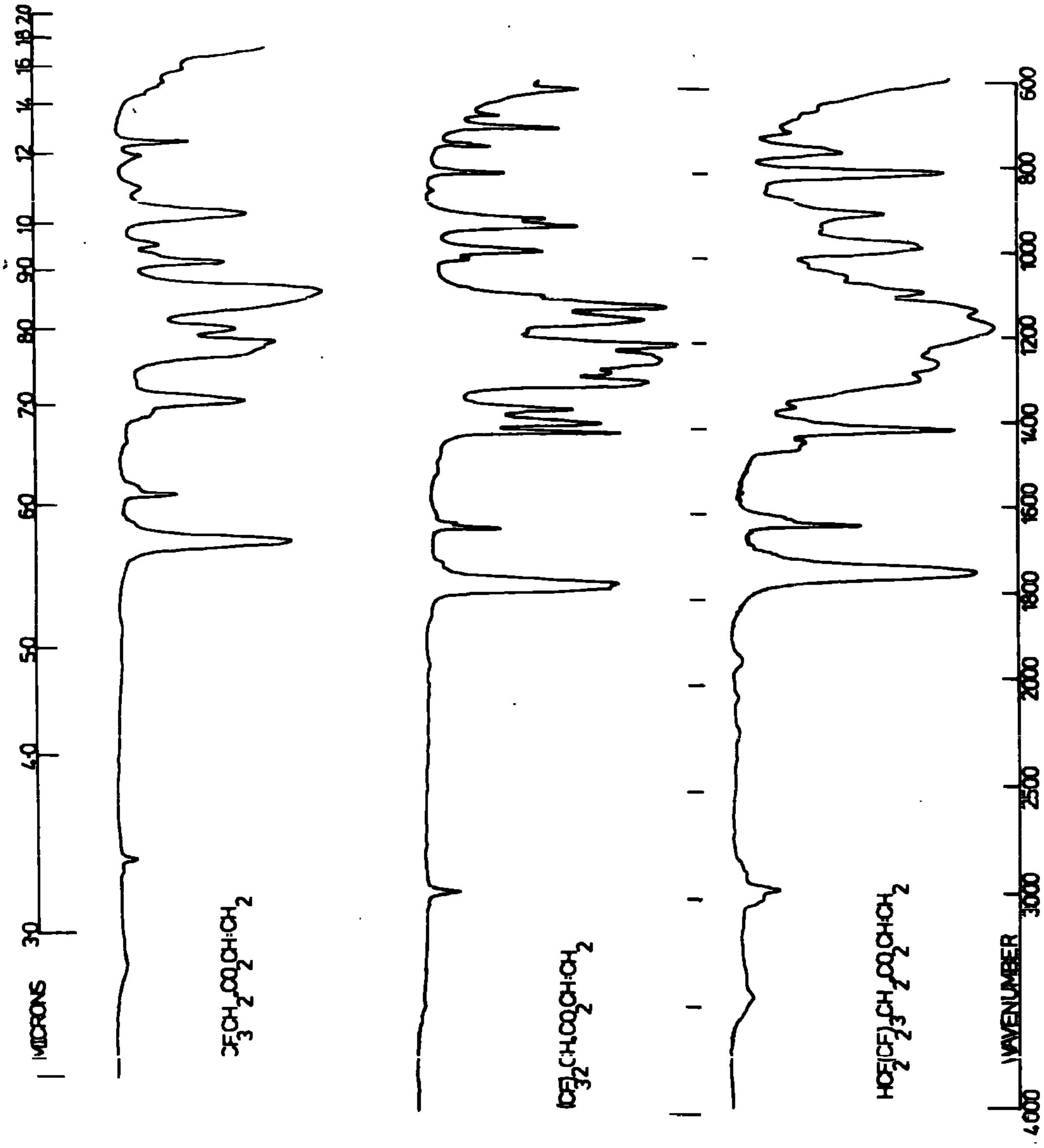
WAVENUMBER
3000
2500
2000
1800
1600
1400
1200
1000
800
600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5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
CF3CH2CO2CH:CH2
(CF3)2C:H.CO2CH:CH2
HCF2(CF2)3CH2CO2CH:CH2
WAVENUMBER
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3000
2500
2000
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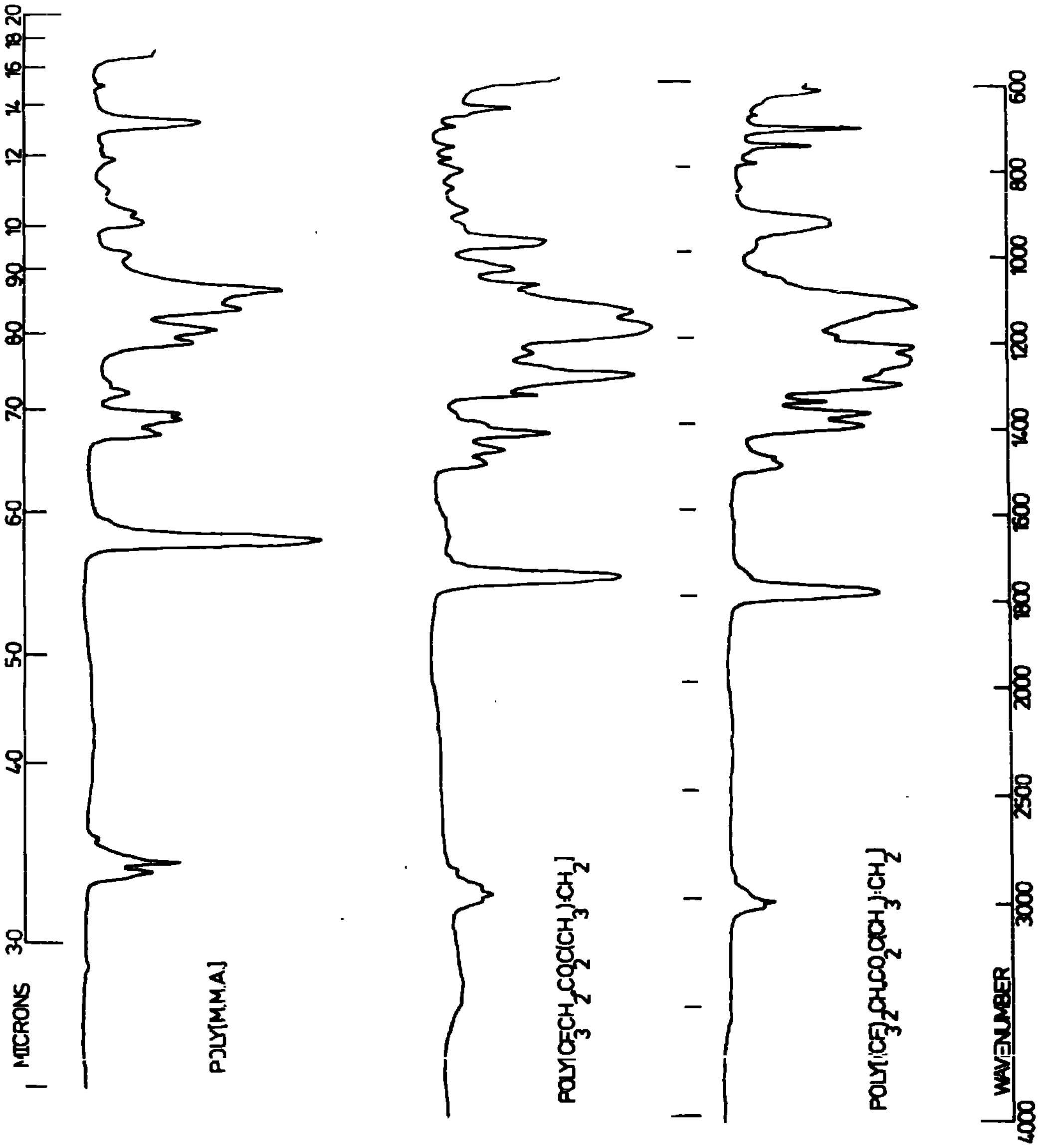
1600
1400
1200
1000
800
600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5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
POLY(M.M.A.)
POLY($CF_3CH_2CO_2C(CH_3):CH_2$]
POLY($(CF_3)_2CHCO_2C(CH_3):CH_2$]
WAVENUMBER
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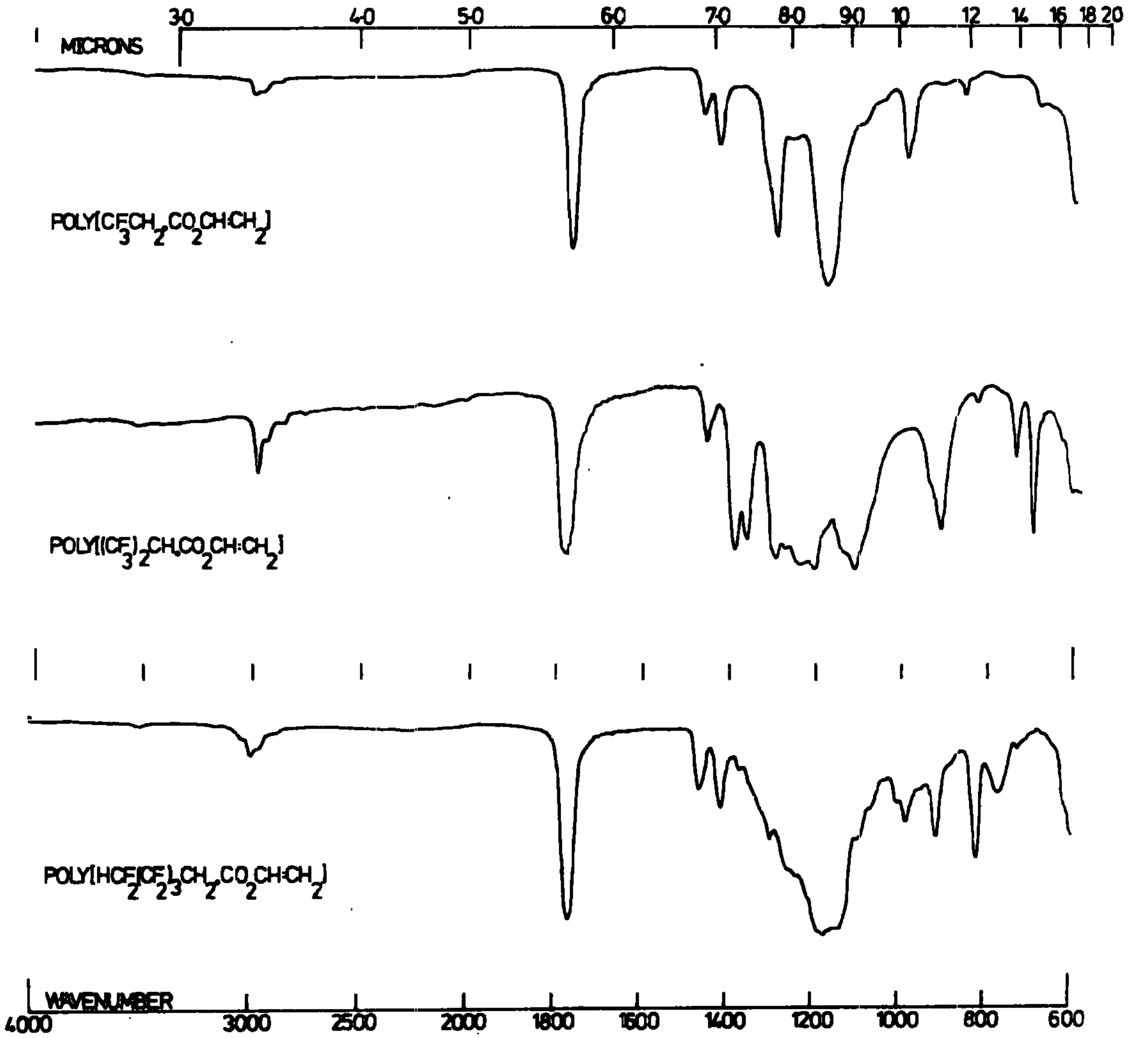
3000
2500
2000
1800
1600
1400
1200
1000
800
600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5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
POLY[$CF_3CH_2CO_2CH{:}CH_2$]
POLY[$(CF_3)_2CH.CO_2CH{:}CH_2$]
POLY[$HCF_2(CF_2)_3CH_2CO_2CH{:}CH_2$]
WAVENUMBER
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1800
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1200
1000
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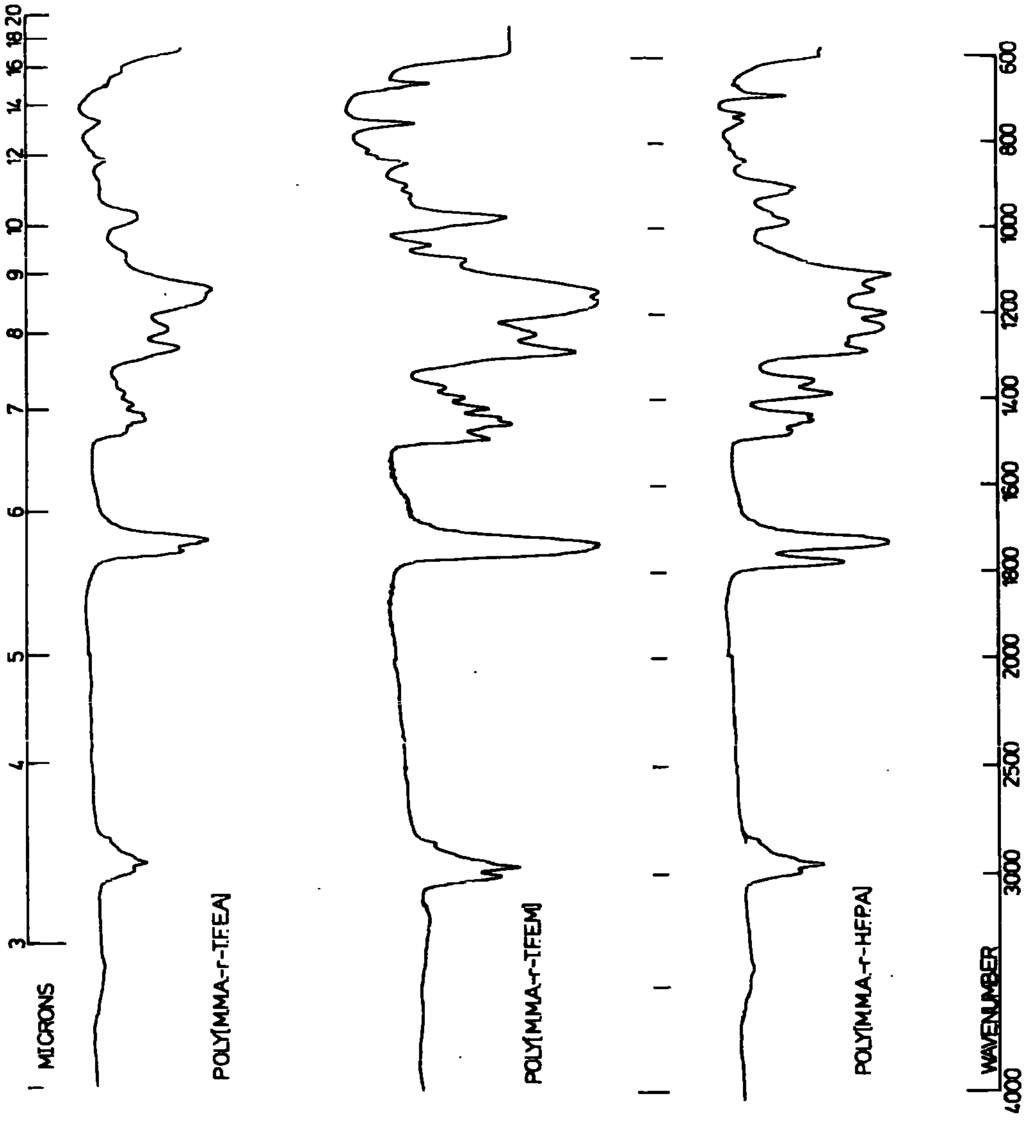
600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12
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16
18
20
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POLY[M.M.A.-r-T.F.E.M]
POLY[M.M.A.-r-H.F.P.A]
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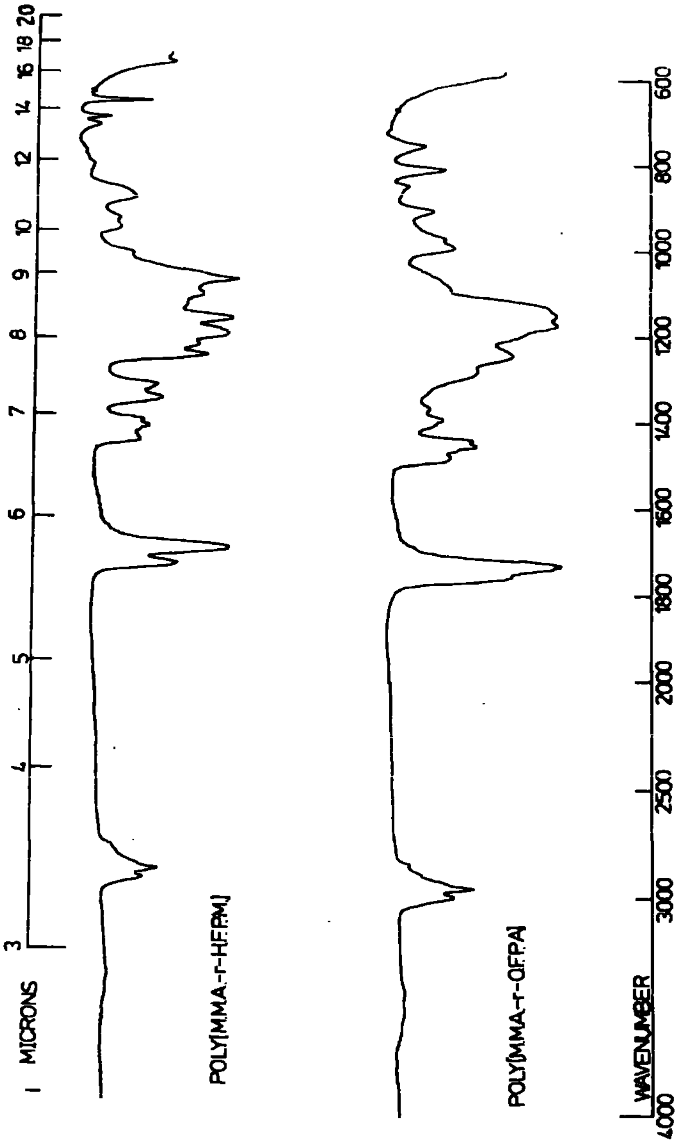
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POLY(M.M.A.-r-O.F.P.A.)
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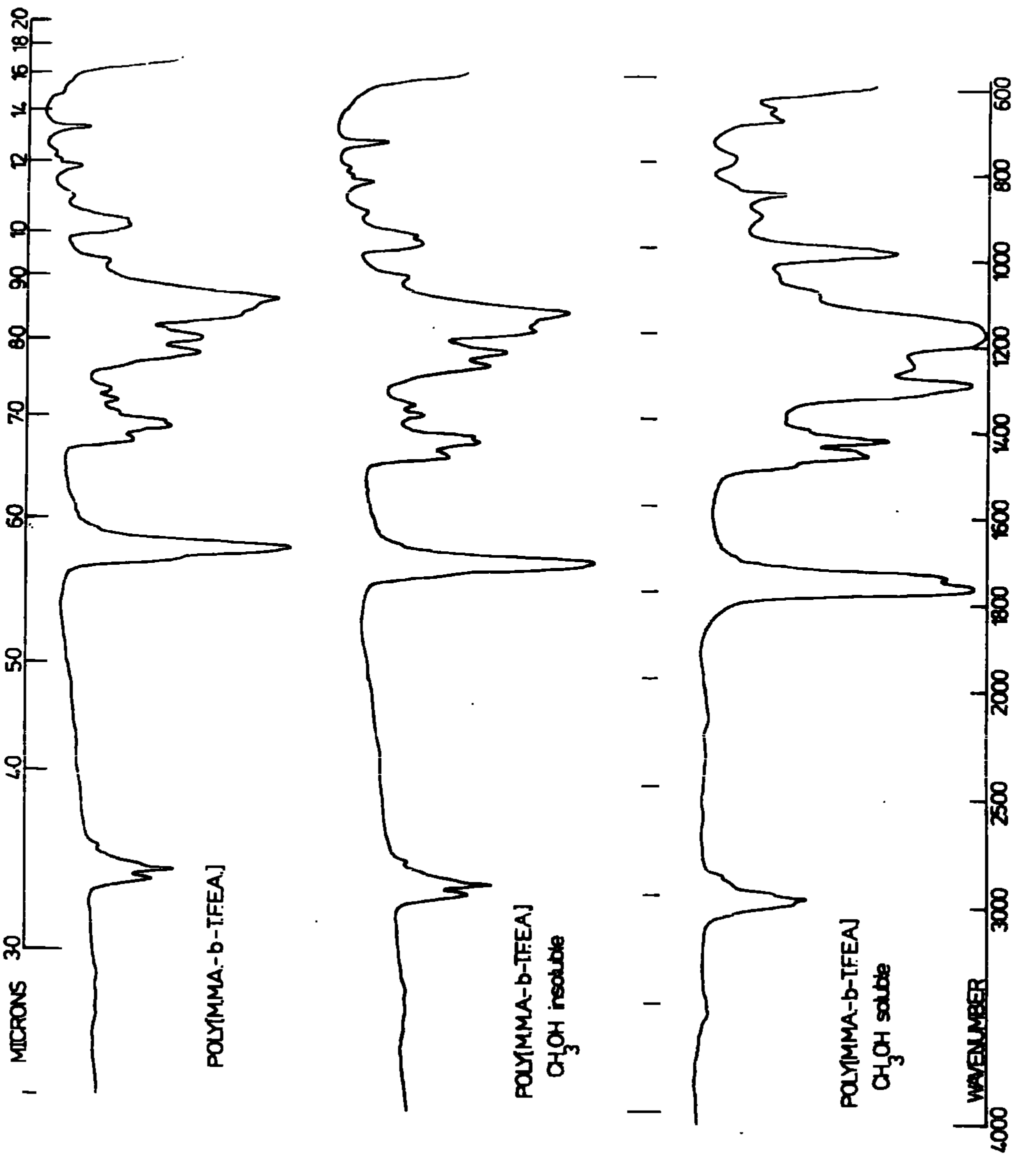
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6.0
7.0
8.0
9.0
10
12
14
16
18
20
POLY[M.M.A.-b-T.F.E.A.]
POLY[M.M.A.-b-T.F.E.A.]
CH_3OH insoluble
POLY[M.M.A.-b-T.F.E.A.]
CH_3OH soluble
WAVENUMBER
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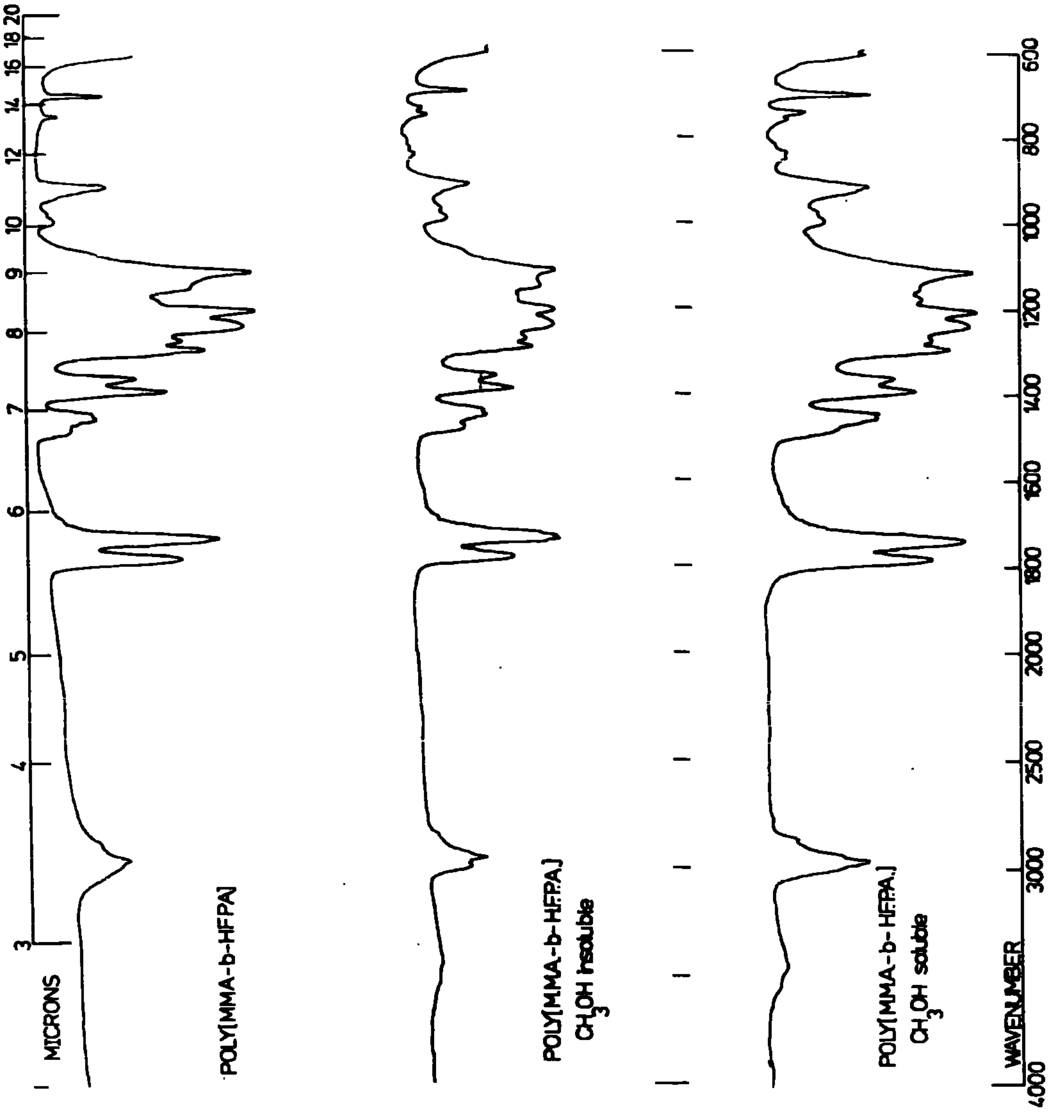
2500
2000
1800
1600
1400
1200
1000
800
600


MICRONS
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4
5
6
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8
9
10
12
14
16
18
20
POLY[MMA-b-HFPA]
POLY[MMA-b-HFPA]
CH3OH insoluble
POLY[MMA-b-HFPA]
CH3OH soluble
WAVENUMBER
4000
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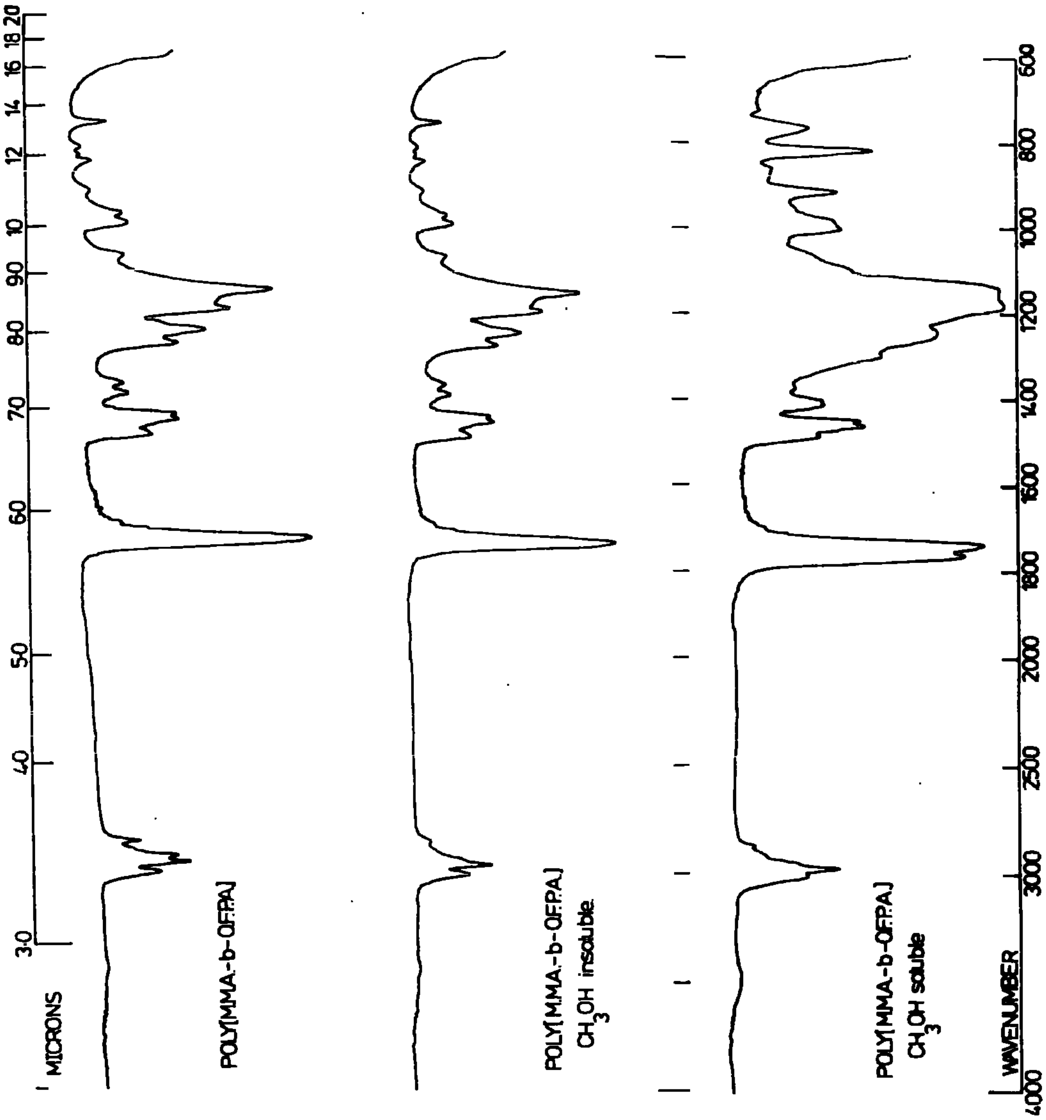
2500
2000
1800
1600
1400
1200
1000
800
600


MICRONS
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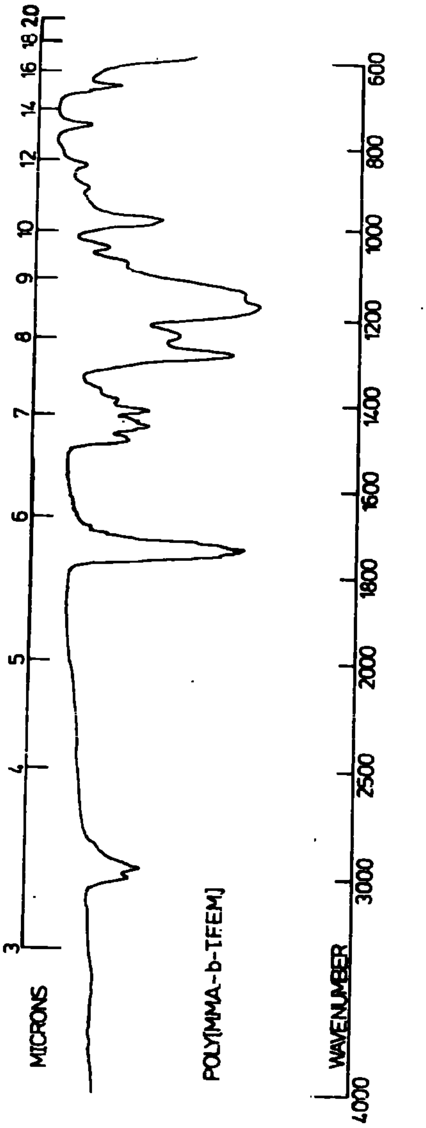
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
POLY[MMA-b-Q.F.P.A.]
POLY[M.M.A.-b-Q.F.P.A.]
CH$_3$OH insoluble
POLY[MMA-b-Q.F.P.A.]
CH$_3$OH soluble
WAVENUMBER
4000
3000
2500
2000
1800
1600
1400
1200
1000
800
600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6
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10
12
14
16
18
20
POLY[MMA-b-T.F.E.M.]
WAVENUMBER
4000
3000
2500
2000
1800
1600
1400
1200
1000
800
600

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