SYNTHESIS AND CHARACTERIZATION OF SOME POLYEPICHLOROHYDRIN GRAFT COPOLYMERS

by

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Dedicated
to the memory of my
late Father

ABSTRACT

Poly(epichlorohydrin-g-styrene) copolymers have been prepared in vacuo or under an inert atmosphere from polyepichlorohydrin by three different methods: firstly by coupling or deactivation of living polystyrene anions with chloromethyl groups in solution, usually at 20°C; secondly, by coupling the potassium salt of polystyryl carboxylic acid in N,N-dimethylformamide at 60°C; and thirdly, by coupling the potassium salt of polystyryl propylene sulphide in tetrahydrofuran at 40°C.

In the first method, when both polystyryl lithium and the polyepichlorohydrin were in benzene or toluene, grafting reactions were accompanied by cross-linking due to lithium-halogen interchange, colloidal phase separation and degradation of the backbone polymer. When the polystyryl lithium in either benzene or tetrahydrofuran was coupled with polyepichlorohydrin in tetrahydrofuran, cross-linking was eliminated and degradation was minimized. Some non-degradative termination reactions also occurred on coupling in tetrahydrofuran and tetrahydrofuran-benzene mixtures. The degradation of polyepichlorohydrin induced by n-butyl lithium was also studied. Graft copolymers were purified by fractional precipitation and their molecular weights and compositions were determined.

In the second method, the graft copolymers contained ester groups that could be hydrolysed by potassium hydroxide solution at room temperatures. At higher temperatures hydrolysis and main chain cleavage occurred.

In the third method, grafting occurred with formation of thioether linkages but cleavage of the backbone was also observed.

Poly(epichlorohydrin-g-styrene)s with limited grafting were also prepared by the mutual γ-irradiation technique. All samples of polyepichlorohydrin without added antioxidant underwent oxidative degradation particularly in the presence of sunlight.

The poly(epichlorohydrin-g-styrene)s were studied by solution viscometry, differential scanning calorimetry, dynamic mechanical testing and electron microscopy. The results suggested that incomplete microphase separation of the graft copolymers usually occurred.

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CONTENTS

Page

ABSTRACT 3

ACKNOWLEDGEMENTS 5

CONTENTS 6

CHAPTER 1 12

LITERATURE SURVEY AND GENERAL BACKGROUND 12

1.1. Properties and Importance of Blends, Block and Graft Copolymers 12

1.1.1. Introduction 12
1.1.2. Different Types of Copolymers 12
1.1.3. Physical Blends and Their Properties 13
1.1.4. Properties of Random and Alternating Copolymers 14
1.1.5. Properties and Applications of Block and Graft Copolymers 14
(a) General properties
(b) Some special features
(i) Colloidal behaviour
(ii) Morphological behaviour
(c) Some applications

1.2. Synthesis of Graft Copolymers by Ionic Mechanisms 21

1.2.1. Introduction 21
1.2.2. Grafting by the Anionic Mechanism 23
1.2.2A Grafting by Carbanionic Deactivation or Anionic Coupling Reactions 23
(i) Deactivation of living polymers with chloride functions
(ii) Side reactions and conditions affecting the coupling reactions of living polymers with halide functions
(iii) Deactivation of living polymers with ester functions
(iv) Some other multifunctional backbone polymers
1.2.2B Grafting by Carbanionic Initiation 30
(i) Synthesis of polymeric initiators by metal-halogen interchange reactions and grafting therefrom
(ii) Synthesis of polymeric initiators by replacement of a H-atom by a metal atom and grafting therefrom
(iii) Synthesis of polymeric initiators by the reaction of suitable unsaturated groups on the polymer with a metal or metallic compound
1.2.3. Grafting by Cationic Mechanism 34
1.2.3A Grafting by Cationic Deactivation 35
1.2.3B Grafting by Cationic Initiation 36

Page

1.3. Graft Copolymers of Epichlorohydrin Polymers 37
1.3.1. Introduction 37
1.3.2. Initiators/Catalysts used for Grafting by Free Radical Mechanism 39

1.4. Chemical Modification of Epichlorohydrin Polymers 40
1.4.1. Introduction 40
1.4.2. Modification Involving Substitution Reactions 41
1.4.3. Reaction with Mg and Grignard Reagents. 45

CHAPTER 2 47

SYNTHESIS OF POLYSTYRENE BY ANIONIC MECHANISM

2.1. Introduction 47
A. Anionic polymerization - general
B. Anionic polymerization of Styrene with organo-alkali metal initiators
2.2. Experimental Procedures 51
2.2.1. The Vacuum Line and the Argon Line 51
2.2.2. Purification of Materials 52
(a) n-Butyl lithium
(b) Dilution of stock n-BuLi solution
(c) n-Hexane
(d) Estimation of n-BuLi concentration
(e) Cumyl potassium
(f) Dilution, filtration and storage of cumyl potassium
(g) Estimation of cumyl potassium concentration
(h) Benzene
(i) Tetrahydrofuran
(j) Styrene
2.2.3. Polymerization Procedure and Isolation of Polymers 58
(a) Polymerization in benzene initiated by n-BuLi
(b) Polymerization in THF initiated by cumyl potassium
(c) Precipitation and Purification of the Polymers
2.2.4. Characterization of Polymers 60
2.3. Results and Discussion 60
Table 2.1 62
Figures 2.1 - 2.7 63

CHAPTER 3 68

SYNTHESIS, CHARACTERIZATION AND STABILITY STUDY OF POLYEPICHLOROHYDRIN

A. POLYMERIZATION OF EPICHLOROHYDRIN

3.1. Introduction 68
3.2. Polymerization with Triethyl Al-H_2O Catalyst: Experimental Procedure 71
3.2.1. Purification of Materials 71
(a) n-Heptane, (b) Diethyl ether
(c) Epichlorohydrin, (d) Triethyl-Al
3.2.2. Polymerization and Separation of the Polymer into Amorphous and Crystalline Fractions 72

Page

Chapter 3 (continued)

3.2.3. Characterization of the Polymers 73
(a) Infra-red spectra
(b) Proton nuclear magnetic resonance spectra
(c) Elemental microanalysis
(d) Thermal analysis
(e) GPC analysis
3.3. Results and Discussion 74

B. STABILITY STUDY OF AMORPHOUS POLYEPICHLOROHYDRIN FREE FROM ANTIOXIDANT

3.4. Introduction 74
3.5. Experimental 76
3.6. Results and Discussion 77
Table 3.1 81
Figures 3.1 - 3.5 82

CHAPTER 4 87

SYNTHESIS AND CHARACTERIZATION OF POLY(EPICHLOROHYDRIN-g-STYRENE) BY THE CARBANIONIC DEACTIVATION (ANIONIC COUPLING) TECHNIQUE AND CLEAVAGE OF POLYEPICHLOROHYDRIN BY n-BUTYL LITHIUM

A. GRAFTING OF POLYSTYRENE ONTO POLYEPICHLOROHYDRIN

4.1. Introduction 87
4.2. Experimental Procedures 88
4.2.1. Purification of Materials 88
(a) Commercial PECH, 'Herchlor H'
(b) Topanol CA
(c) Benzene, (d) THF, (e) styrene
(f) n-BuLi and cumyl potassium
(g) Toluene
4.2.2. Grafting Procedure 90
(a) Preparation of living polystyrene
(b) Preparation of polyepichlorohydrin solutions for coupling reactions
(c) Coupling reactions
4.2.3. Purification of Polymers from the Coupling Experiments 92
(a) Isolation of the total polymer
(b) Purification of the graft copolymers by extraction and fractional precipitation procedure
(c) Turbidimetric titration
4.2.4. Characterization of the Graft Copolymers 98
(a) Molecular weights and molecular weight distributions by GPC
(b) Infra-red spectra
(c) Overall composition
(i) UV spectroscopy
(ii) Elemental microanalysis and percentage of PS (w/w) content

Page

Chapter 4 (continued)

4.2.4. (c)
(iii) Expected $\bar{M}_n$
(iv) Grafting efficiency of PS
(v) Degradation factor, f
(vi) Ratio R

4.3. Results and Discussion 104
4.3.1. Molecular Weights and Molecular Weight Distribution of Starting Polyepichlorohydrin and Polystyrene Samples 104
4.3.2. Molecular Weights and Composition of Graft Copolymers and Side Reactions in Grafting Experiments 105
(a) Coupling reaction in pure hydrocarbon solvents
(b) Heterogeneous nature of grafting and degradation reactions in pure hydrocarbon solvents
(c) Coupling reactions in benzene with a small amount of THF in the coupler solution
(d) Coupling reaction in THF using potassium counter-ion
(e) Coupling reactions in THF/C_6H_6 using Li-counter ion.
(f) Grafting efficiencies of PS^- in C_6H_6 and THF/C_6HT mixtures (67:33 v/v)
(g) Chemical nature of side reactions
(h) Molecular weights, $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ ratios of the graft copolymers

B. BUTYL LITHIUM CLEAVAGE OF POLYEPICHLOROHYDRIN

4.4 Introduction 113
4.5. Experimentals 114
4.5.1. Purification of Materials 114
(a) PECH (b) Benzene (c) n-BuLi
4.5.2. The cleavage Reaction and the Recovery of the products 114
4.5.3. Characterization of Degraded Polymers 115
(a) Molecular weights
(b) Limiting viscosity numbers
(c) Percentage of chlorine loss
(d) I.R. spectra
(e) The relative amounts of different groups formed
(f) Unsaturation in the degraded polymers
4.6. Results and Discussion 118
4.7. Mechanism of Polyepichlorohydrin Cleavage by n-Butyl lithium and Polystyryl lithium 119
4.7.1. Cleavage by n-BuLi 119
4.7.2. Cleavage by PS^-Li^+ 122
Tables 4.1 - 4.8 124
Figures 4.1 - 4.16 134

Page

CHAPTER 5 149

CHEMICAL MODIFICATION OF POLYEPICHLOROHYDRIN AND SYNTHESIS OF POLY(EPICHLOROHYDRIN-g-STYRENE) USING POLYSTYRENE WITH A FUNCTIONAL END GROUP

5.1. Introduction 149
5.2. Purification of Materials 150
(a) Benzene, THF, Styrene
(b) n-BuLi, Cumyl-K
(c) DMF (d) Thiophenol
(e) Sodium thiophenoxide
(f) Phenyl acetic acid
(g) Propylene sulphide
(h) Polyepichlorohydrin
5.3. Chemical Modifications of Polyepichlorohydrin 151
5.3.1. Experiments and Results 151
(a) Substitution of Cl atoms with thiophenoxide groups
(b) Substitution of Cl atoms with phenyl acetate groups
5.3.2. Discussion 153
5.4. Synthesis of Polystyrene with -COOH End-group (PS COOH) 154
5.4.1. Polymerization and Purification of Polymers 154
5.4.2. Characterization: Determination of Number Average Molecular weights 155
(a) The end-group titration method
(b) Vapour pressure osmometry
(c) Gel permeation chromatography
5.4.3. Results and Discussion 157
5.5. Synthesis of Poly(epichlorohydrin-g-styrene) by Coupling the K-salt of PS COOH with PECH 158
5.5.1. Coupling Reaction and Purification of Graft Copolymers 158
(a) Coupling reaction
(b) Purification of graft copolymers
(c) Recovery of unreacted polystyrene
(d) Purification of graft copolymers for composition determination
5.5.2. Characterization 161
(a) Overall composition
(i) UV analysis
(ii) Elemental microanalysis
(b) Molecular weights
(c) Limiting viscosity numbers
(d) I.R. spectra
(e) Calculations on the composition
5.5.3. Study of the Effect KOH on the Graft Copolymers and PECH 163
5.5.4. Results and Discussion 164
(a) Grafting through ester linkage and stability
(b) The grafting efficiency of PS COO^- onto PECH as a function of time, temperature and molar ratio R

Page

Chapter 5 (continued)

5.5.4.
(c) Effect of excess alkali on the molecular weights of graft copolymers and grafting efficiency of PS COO⁻
(d) Molecular weights (GPC values) and limiting viscosity numbers (in toluene at 30°C) of the graft copolymers

5.6. Synthesis of Poly(epichlorohydrin-g-styrene) by Coupling Polystyrene containing Propylene Sulphide End-group with PECH 169
5.6.1. Experimental: Coupling reaction and Isolation of Graft Copolymers 169
5.6.2. Characterization 170
5.6.3. Results and Discussion 170
5.7. Appendix to Section 5.5 171
Synthesis of Poly(epichlorohydrin-g-styrene) and Poly[(epichlorohydrin-co-ethylene oxide)-g-styrene] using PS COOH of long chain length
5.8. Attempted Grafting of Polystyrene onto PECH Induced by γ-Irradiation 172
5.8.1. Experiments and Results 172
(a) Mutual irradiation method
(b) Peroxide method
5.8.2. Discussion 175
Tables 5.1 - 5.7 177
Figures 5.1 - 5.10 185

CHAPTER 6 193

SOLUTION AND BULK PROPERTIES OF POLY(EPICHLOROHYDRIN-g-STYRENE) COPOLYMERS

6.1. Introduction (General) 193
6.2. Solution Properties 193
6.2.1. Experimental 193
6.2.2. Results and Discussion 194
6.3. Thermal Analysis 198
6.3.1. Experimental 198
6.3.2. Results and Discussion 199
6.4. Dynamic Mechanical Testing 202
6.4.1. Introduction 202
6.4.2. Experimental 204
6.4.3. Results and Discussion 205
6.5. Transmission Electron Microscopy 207
6.5.1. Introduction 207
6.5.2. Experimental 208
6.5.3. Results and Discussion 210
Tables 6.1 - 6.5 212
Figures 6.1 - 6.12 216

CHAPTER 7 227

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

REFERENCES 233

CHAPTER I

LITERATURE SURVEY AND GENERAL BACKGROUND

1.1. Properties and Importance of Blends, Block and Craft Polymers (1-8)

1.1.1. Introduction

During the last two decades, various sophisticated applications of polymeric substances have been developed. These applications demanded a combination of properties not attainable with simple homopolymers. So far, the combination of properties has been achieved to some extent by physical blending of the polymers and to a greater extent by copolymerization. Many copolymers, specially the block and graft copolymers, in addition to combining the properties of the component homopolymers, show some extra unique properties, not shown by any of the component homopolymers. This discussion is mainly concerned with the properties and importance of multicomponent polymer systems, that is, of physical blends and block and graft copolymers. For comparison, some of the properties of random and alternating copolymers have been mentioned.

1.1.2. Different Types of Copolymers

Based on their structures, copolymers are classified as follows:

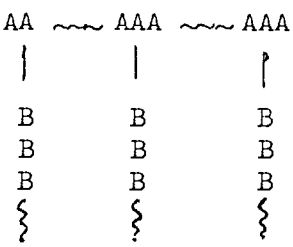
1. Random Copolymers of Structure ~~ ABBAAABA ~~ when the comonomer repeat units A and B are randomly distributed along the chain.
2. Alternating Copolymers of Structure ~~ ABABAB ~~ when the comonomer repeat units are linked in an alternating fashion.
3. Block Copolymers Here the copolymer contains a long sequence or block of one monomeric repeat unit joined by chemical bonds to a long sequence of a second monomeric repeat unit. The sequential arrangement of a diblock copolymer is as follows:

AAAA ~~~ AABBB ~~~ BB

or $\{A\}\ \{B\}$

where $\{A\}$, $\{B\}$ are the polymeric blocks from monomeric repeat units A and B, respectively.

4. Graft Copolymers A graft copolymer is also a sequential polymer where a long sequence of one polymer commonly called backbone is attached by chemical bonds to a number of sequences of a second polymer, commonly called grafts or branches. A simple representation of a typical graft copolymer is as follows:



1.1.3. Physical Blends and Their Properties

Polymers, because of very small entropies of mixing due to their high molecular weights usually give a positive free-energy of mixing. This is why the great majority of the physical polymer blends are highly incompatible. This incompatibility often leads to complete phase separation, poor interphase adhesion and hence relatively poor mechanical properties. These incompatible polymer blends have two distinct glass transition temperatures, (T_g), and physical and chemical properties mostly characteristic of the component homopolymers.

There are very few polymer pairs which are completely compatible. The reason for the compatibility in some polymer pairs is in the interactions between the polar substituents in the polymer chains as with the blend of poly(vinylchloride) and butadiene-acrylonitrile copolymer (9). Essentially identical solubility parameters and also intermolecular interactions are believed to be the reasons for the compatibility of

polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (10). These compatible blends are characterized by a single phase morphology. They have physical properties such as the glass transition temperature, rheology and permeability intermediate to those of the components.

There are a good number of polymer pairs which show partial compatibility. A well-known example of such a polymer blend of commercial importance is that of butadiene-acrylonitrile copolymer and styrene-acrylonitrile copolymer (11), which is one form of ABS resin. The compatibility of such a polymer pair depends on the closely matched composition of the random copolymer pairs (12). The partially compatible blends, like the incompatible blends, also show a two-phase morphology and two glass transition temperatures. Because of greater interphase ahdesion, they possess improved mechanical properties.

1.1.4. Properties of Random and Alternating Copolymers

Because of the requirements for pairs of monomers to have specific copolymerization reactivity ratios and often also special reaction conditions, alternating copolymers are relatively rare (13). Random copolymers are the most common of all types of copolymers.

Both alternating and random copolymers present homogeneous systems with a single phase morphology. Microphase separation does not occur because of short sequences in these polymers. They have physical and chemical properties such as glass transition temperatures, mechanical properties, permeability and chemical resistances which can be represented by weighted averages of those of the corresponding homopolymers (14).

1.1.5. Properties and Applications of Block and Graft Copolymers

(a) General properties Block and graft copolymers may be regarded as systems consisting of homopolymers joined by chemical bonds.

Because of their fundamentally similar structural composition, both block and graft copolymers often display very similar properties.

Block and graft copolymers combine some of the features of incompatible physical blends and homogeneous random copolymers. Especially when the sequences in the block copolymer are short, and when the grafted sequences in the graft copolymer are short and numerous, they tend to behave like random copolymers, whereas when the sequences are long, they resemble in some respects physical blends. These copolymers have many properties found neither in their parent homopolymers nor in random copolymers.

Both block and graft copolymers exhibit a two phase morphology (1-6,15-19), but because of intersegment linkages, phase separation occurs on a micro-scale. However, macro-scale phase separation occurs in incompatible physical blends. Although two-phase morphology is the usual phenomenon, single-phase morphology is also possible, especially when the segments are short and the component homopolymers have similar solubility parameters (1). Single-phase morphology is more common with graft copolymers than with block copolymers. With respect to properties, graft copolymers lie between block and random copolymers, although most resembling block copolymers. This relation will, of course, depend upon the structure of the graft copolymers, that is the graft frequencies, graft lengths and other factors.

The micro-phase separation in block and graft copolymers leads to small domain size. The small domain size and good interphase adhesion produce a higher degree of optical clarity and a good balance of mechanical properties in these copolymers. Thus optical clarity and balance of mechanical properties is also characteristic of random copolymers and not of physical blends.

The thermal properties of block and graft copolymers are similar to those of the physical blends. They show multiple glass transition points and also multiple melting points in crystalline polymers. In contrast, the random copolymers display a single composition-dependent glass transition. When one of the components is crystalline, the crystallinity is retained in block and graft copolymers, but it is reduced or eliminated completely in random copolymers due to disruption of chain regularity (14).

(b) Some Special Features Block and graft copolymers display some interesting properties which are not observed in any of the random copolymers or polymer blends. These are (i) colloidal and interfacial properties in solution, and (ii) complex morphology in the solid state.

(i) Colloidal behaviour (2,20) The colloidal properties of block and graft copolymers arise principally from two factors:

(1) repulsive interactions of chemically different sequences in the solid state as well as in solution, and

(2) non-identical interactions of the sequences with the environment, such as solvent when in solution (20).

Repulsive interactions of chemically different sequences in a block or graft copplymer lead to intra-molecular micro-phase separation and expansion of the molecules, especially in a good solvent. The micro-phase separation may lead to the occupation of different domains by sub-chains of similar chemical nature even in a non-selective solvent. The molecules ultimately form a core-shell micellar structure with sub-chains of one kind forming the core and with the sub-chains of the other kind forming the surrounding shell. Formation of micelles was observed in the electron microscopic investigation of the fixed polymer samples when styrene was polymerized in the presence of styrene-butadiene block

copolymer (21). Styrene was a non-selective solvent for both of the polymer sequences. This is indirect evidence of the colloidal nature of a block or graft copolymer in a non-selective solvent.

Direct evidence of the colloidal properties of block and graft copolymers in non-selective solvents is the emulsifying effect of these copolymers in polymeric "oil-in-oil emulsions" (22). Thus when a block or a graft copolymer and the corresponding homopolymers are dissolved in a mutual solvent, the two chemically different homopolymers, because of their incompatibility, form two phases or immiscible solutions, while the block or graft copolymer by accumulating at the interface of the two phases, forms a stable emulsion. Based on the emulsifying properties, the copolymers can be expected to be efficient homogenizing agents and to be useful in blending incompatible polymer solutions and solid polymers. They have considerable commercial importance in certain rubber-modified polymers (22). The emulsifying behaviour is also sometimes responsible for the optical clarity of a film prepared from a blend containing a considerable amount of the corresponding block or graft copolymer (6).

Block and graft copolymers with sequences showing the dual solubilities of the parent homopolymers in some solvents and solvent mixtures, also exhibit colloidal behaviour (23,24). When the solvent behaves as a good solvent for one type of sequence of the copolymer and a poor solvent for the other type, the copolymer is held in a stable colloidal suspension in the medium in the form of micelles similar to soap micelles in water. The collapsed sequence having poor solubility forms the core and the other sequence having greater solubility forms the surrounding shell. By analogy with soap micelles, these polymeric micelles are aggregates of a number of block and graft copolymer molecules.

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Any added homopolymer molecules, corresponding to the collapsed portion of the copolymer, will be occluded in the micelles just like the solubilization of oils in soap micelles in water. The copolymer thus behaves as a solubilizer or emulsifier. Well-known examples of this type of emulsifying agent are the ethylene oxide-propylene oxide copolymers marketed under the trade names 'Pluronics' and 'Tetronics' 25).

(ii) Morphological behaviour (1-6,15-19) These systems are comprised of two normally incompatible polymers forced to co-exist together by means of chemical links. Repulsive interactions due to incompatibility tend to pull away the sequences of one kind from those of the other. This leads to phase separation and aggregation of one particular kind of sequence into well-defined regions or morphological domains in the solid polymer. Due to intersegment linkages, phase separation takes place on a micro-scale and the domain sizes are of colloidal dimensions.

The extent of micro-phase separation to form morphological domains depends on factors such as compositional dissimilarity, the length and the crystallizability of the sequences. Single-phase morphology results when the sequences are of similar chemical nature and of short chain length and two phase morphology is produced when the segments are long or of dissimilar chemical nature. Crystallinity in one or both segments helps phase separation (26).

Morphological studies are usually made with films of the polymer cast from solution. The type of morphology usually depends on the volume fractions of the two components and the specimen fabrication. The major component usually exists in the continuous phase with the minor component as discrete domains assuming spherical, rod-like or alternating lamellar structures depending on the relative composition(20,27). In compositions containing nearly equal concentrations of both the

components, the phase continuity can be altered by varying the specimen fabrication conditions such as the type of casting solvent (20,27,28).

Morphological variations exert a great influence on the properties such as chemical resistance, modulus, rheology and permeability. These properties depend to a great extent on the nature of the continuous phase.

The polymers mostly used so far for morphological studies are block copolymers. Progress on the morphological study of graft copolymers has been rather limited. However, because of their fundamentally similar structure, both types of copolymer are expected to give similar morphological behaviour. In some cases, where investigation has been possible, the morphological pattern in graft copolymers has been found to follow the same basic rule as that in block copolymers (19,29).

A remarkably important feature of some block copolymers, arising out of micro-phase separation, is their behaviour as thermoplastic elastomers. Block copolymers of the types A-B-A or $(A\text{-}B)_n$ where A, a hard block (T_g or T_m above room temperature) comprises a minor fraction of the copolymer and B, a soft block comprises the major fraction, behave as thermoplastic elastomers. The hard blocks associate to form small morphological domains that serve as cross-linking or reinforcement sites imbedded in a matrix of the soft block. These copolymers have similar behaviour to that of cross-linked rubbers and also have the processibility of conventional thermoplastic polymers.

In principle, graft copolymers with appropriate compositions should show similar elastomeric behaviour to that of the block copolymers. But the success in achieving elastomeric properties in graft copolymers so far is limited. This may be due to the difficulties in the synthesis of graft copolymers with requisite structural control.

(c) Some Applications (29-31) Because of the comparatively greater success in the preparation of well-defined block copolymers, they have more commercial applications than graft copolymers. The principal applications are as elastomers, toughened thermoplastic resins and surfactants (30).

The different block copolymers, commercially exploited as thermoplastic elastomers are styrene-diene-styrene triblock copolymers, urethane-ester, ester-ether, urea-urethane multiblock copolymers marketed under different trade names. For example, the styrene-butadiene-styrene block copolymer is marketed as 'Kraton' and 'Thermoplastics' by the Shell Oil Company. The thermoplastic elastomeric behaviour of these copolymers is based on the micro-phase separation and formation of physical cross-linking sites. These elastomers are superior to the chemically cross-linked thermoset rubbers in their ease of fabrication and reprocessibility.

An example of the use of a block copolymer as a toughened resin is the radial styrene-butadiene block copolymer having a relatively high weight per cent of polystyrene ($\sim$ 75%). Emulsifying behaviour of block and graft copolymers has already been discussed. An example of a block copolymer emulsifier having a hydrophobic segment and a hydrophilic segment for oil-in-water type emulsion is propylene oxide-ethylene oxide, commercially known as 'Pluronics' and 'Tetronics'.

The few graft copolymers of commercial importance are rubber-styrene graft copolymers used in impact resistant polystyrene (32) and acrylonitrile-butadiene-styrene copolymer (polystyrene grafted onto acrylonitrile-butadiene backbone).

Graft copolymers of several natural products such as starch, natural rubber, wool with suitable monomers are also used for specific

purposes (31). Grafting onto natural products is sometimes done to impart special characteristics to the product. For example, shrink proofing of wool was achieved through interfacial graft copolymerization and formation of a thin film of polyurea on the fibre surface (33).

One significant application area of graft copolymers based on surface active properties is the use of some graft copolymers in paints and adhesives (34). Another important application of graft copolymers is based on the blending or homogenizing of the corresponding homopolymers.

In spite of limited known applications, controlled graft copolymerization is the technique by which certain properties such as compatibility, adhesive properties, dyeability and permeability can be significantly changed without altering markedly the mechanical properties (6).

1.2. Synthesis of Graft Copolymers by Ionic Mechanisms (5,8,35-39)

1.2.1. Introduction

Graft copolymerization is the technique by which the synthesis of sequential polymers, composed of two (or more) monomeric repeat units, covering a wide range of composition and properties should be possible. This can be done by a change of parameters such as the length of the backbone, length and frequencies of the branches or grafts.

The following are the different methods used for the synthesis of graft copolymers.

1. Free-radical mechanisms
    (a) Chemical methods
    (b) Photolytic methods
    (c) High energy irradiation methods
    (d) Mechanochemical methods

2. Ionic mechanisms

(a) Anionic mechanism

(b) Cationic mechanism

3. Coordination mechanism

4. Ring opening and condensation coupling reactions.

In this chapter, discussion will be restricted only to the ionic methods of grafting.

Synthesis of a well-defined graft copolymer with proper architectural control is posed with the problems: (i) contamination with homopolymer (ii) uncertainty in the number of grafts per molecule (iii) uncertainty in the spacing of the graft sites (iv) polydispersity of the grafted segments as well as that of the backbone. So far these problems have not been completely solved. However, since the discovery of living polymers (40,41), the anionic method has been found to be the most suitable method for the preparation of graft copolymers of well-defined structures. The development of the synthesis of essentially pure graft copolymers free from adverse side reactions by cationic mechanisms is very recent. A short review of the graft copolymers prepared by anionic and cationic mechanisms is presented in the following sections.

There are in principle two ways of grafting:

(A) Living polymer chains, each with a reactive functional group at the end, react with suitable functional groups on a preformed polymer backbone and are thereby attached or grafted to it. This way of grafting is referred to as 'grafting by deactivation' or 'grafting onto' (35).

(B) Reactive initiation sites are introduced into a preformed polymer used as a backbone. The polyfunctional initiator then initiates polymerization of a suitable second monomer. This way of grafting is called the 'grafting from' reaction (35).

In the absence of any side reactions, grafting by deactivation can yield well-defined graft copolymers, as the backbone and the grafts can be characterized independently.

1.2.2. Grafting by the Anionic Mechanism

The method is the most suitable one for the preparation of block and graft copolymers of precisely well-defined structures, especially by the carbanionic deactivation technique. However, some serious limitations of the method are:

(i) the small number of monomers which can be polymerized anionically,

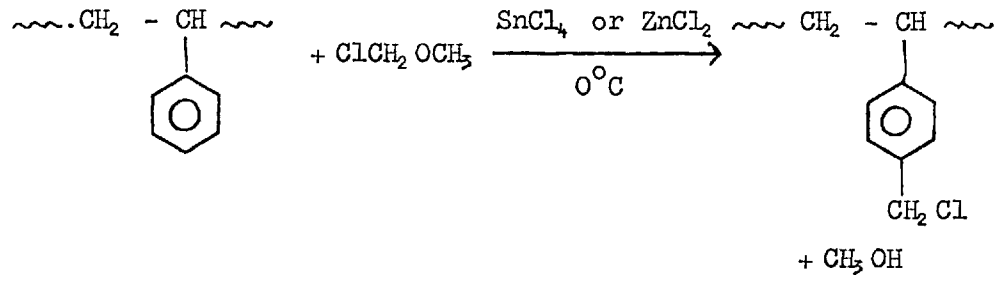
(ii) the requirements of the rigorous purification of the materials in the polymerization system, as the carbanions are very much prone to deactivation by impurities.

1.2.2. A. Grafting by Carbanionic Deactivation or Anionic Coupling Reactions. In order to act as a deactivator for the carbanion ends of the living polymer, the backbone polymer should contain electrophilic functional groups. Such groups are usually ester and halides.

(i) Deactivation of living polymer with chloride functions. A chloromethyl group of benzylic type is the most widely used group containing a chloride function for the coupling reaction with living polymers. Well-defined star-shaped, comb-shaped polymers and some graft copolymers have been prepared by such a coupling reaction.

For the synthesis of star-shaped polymers (42-45), smaller molecules polyfunctional in $-CH_2Cl$, for example, tetra(chloromethyl)benzene, have been used whereas for comb-shaped polymers (43,46-51) and graft copolymers (52,53) chloromethylated polystyrene has been used. Graft copolymers have also been prepared using poly(chloromethyl styrene) (54).

Chloromethyl groups can be introduced into polystyrene by a Freidel Crafts reaction (55) with chloromethyl methyl ether.



(1.1)

The reaction should be carried out under mild conditions in order to avoid cross-linking in such reactions (43).

Polystyryl lithium, $PS^- Li^+$ and polystyryl potassium, $PS^- K^+$ have been mostly used as living polymers for such coupling reactions to prepare star-shaped and comb-shaped polystyrenes. Very well-defined branched polystyrenes (star-shaped, comb-shaped and long-branched), termed 'model macromolecules' have been reported (44,47,49). Side reactions, such as cross-linking have also been noticed by some workers in coupling reactions of highly chloromethylated polystyrene (43,46,48) especially with $PS^- Li^+$(43,48).

Using polyisoprenyl-Li and living poly(2-vinyl pyridine) containing Li-counter ions, poly(styrene-g-isoprene) (52) and poly(styrene-g-2-vinyl pyridine) (53) have been prepared. In order to avoid possible cross-linking from Li-halogen interchange reactions, small amounts of a polar solvent such as TMEDA or THF have to be added to the living polymer.

Apart from chloromethylated polystyrene, poly(chloromethyl styrene) has been used for coupling with living $PS^- Li^+$, and $PS^- K^+$(54). Surprisingly, no cross-linking was observed even in the coupling reaction carried out in pure C_6H_6 using $PS^- Li^+$, though the number of chloromethyl groups in the backbone polymer was very high (one per repeat unit). A very high extent of coupling (> 80%) of $PS^- Li^+$ was achieved in C_6H_6 and THF/C_6H_6 misture (44/56 vol. %). Some side reactions were found to occur especially at high concentrations of living polymer used.

Poly(vinyl chloride) has also been used for coupling reactions with living PS^-K^+ (56) and PS^-Li^+ (57,58) in pure THF. Side reactions were found to occur affecting the grafting efficiency and the K-counter-ion (56) appeared preferable. The nature of the side reactions were not properly investigated.

Minoura et al. (59) studied the coupling reactivity of different chlorine containing polymers under various conditions. The chlorine containing polymers used were ethylene-propylene terpolymer, poly(chloroprene), chlorinated butyl rubber, poly(vinyl chloride), polyepichlorohydrin and epichlorohydrin-ethylene oxide copolymer. The living polymer was polystyrene prepared with Na-naphthalene complex initiator and also with n-BuLi. The coupling reaction was carried out in a pure THF medium. Gel formation was observed due to cross-linking by the bifunctional living polymer prepared with the Na-naphthalene complex initiator. Slight cross-linking was also due to metal-halogen interchange which was observed in coupling reactions with polystyryl lithium.

The authors also used living polyisoprene (PIS) for coupling reactions. No coupling was observed with living PIS prepared with Na-naphthalene in THF, but significant grafting was achieved with the living polymer prepared with n-BuLi in C_6H_6. Living PIS prepared with n-BuLi in C_6H_6 consists of 1,4 microstructure in the carbanionic end groups and living PIS prepared with Na-naphthalene in THF consists of 1,2 and 3,4 microstructures. It was concluded that the carbanions with 1,4 microstructures in PIS were more reactive than those with 1,2 or 3,4 microstructures.

Several brominated rubbers (60) were also used for coupling with polystyryl lithium but the success in preparing graft copolymers was limited, due to side reactions.

(ii) Side reactions and conditions affecting the coupling reactions of living polymers with halide functions. Altares et al. observed (43) that the coupling reaction of tetra(chloromethyl) benzene and chloromethylated polystyrene with PS^-Li^+ was favoured in C_6H_6/THF mixtures rather than in C_6H_6. A higher temperature was also favourable for the reaction. Under such conditions, PS^-Li^+ is unstable and a number of side reactions occurred (43,61). Cross-linking was also observed. They explained cross-linking as due to lithium-halogen interchange reactions between the living polymer and the chlorinated compound.

Pannell (48) observed cross-linking when the coupling reaction was carried out with PS^-Li^+ of lower $\bar{M}_n$ (< 5,000) in pure C_6H_6. He observed less cross-linking when the living polymer contained a small amount of THF used for the complete consumption of the initiator. Thus, according to the kinetic studies of the system C_6H_6/n-BuLi/styrene (62), there is the possibility of some unreacted initiator left if the following ratio of initial monomer concentration, M_o to the initiator concentration, a_o is not maintained:

$$M_o^{6/5}/a_o \geq 45 \text{ mol}^{1/5} \text{ cm}^{-3/5} \text{ at } 288^\circ K \qquad (1.2)$$

According to the author, the lithium compound responsible for the metal-halogen interchange reaction and hence cross-linking was either unreacted BuLi in the PS^-Li^+, when prepared in pure C_6H_6 or some lithium compounds formed from the cleavage of THF with BuLi when PS^-Li^+ was prepared in presence of a small amount of THF. Cleavage of THF with BuLi is known to occur above $238^\circ K$ (63).

Takaki et al. (54) did not observe any cross-linking in their coupling reaction of poly(chloromethyl styrene) with PS^-Li^+ of $\bar{M}_n \gg 5,000$

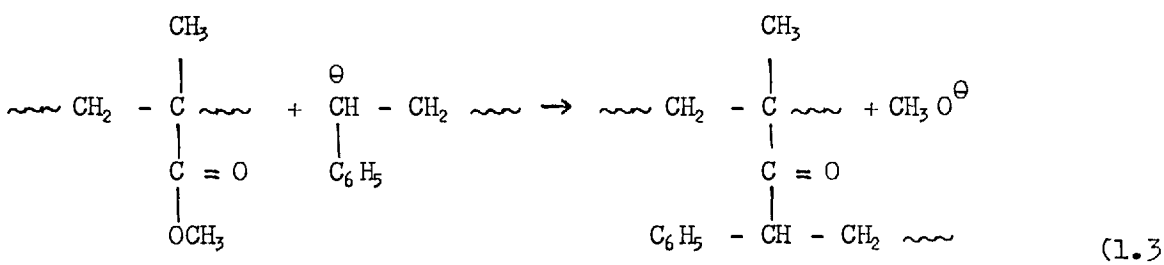
carried out in pure C_6H_6. There was very little possibility of BuLi remaining unreached in that case. The absence of cross-linking may be ascribed to the absence of any free lithium compound other than PS^-Li^+. Metal-halogen interchange reactions (64) responsible for cross-linking depend on the covalent character of the organo-lithium compound. PS^-Li^+ and polyisoprenyl lithium probably have greater ionic character than alkyl lithium compounds because of the resonance stabilization of the carbanions.

Yen (44) from his experiments on the synthesis of star-shaped polystyrene from tetra(chloromethyl)benzene claimed that potassium was a much better counter-ion than lithium for coupling. Thus, although slight cross-linking was observed by Fujimoto et al. (46) in their synthesis of comb-shaped polystyrene using highly chloromethylated polystyrene, no such cross-linking was reported by other workers in similar systems. It appears therefore, that the K-counter-ion, because of its greater metallic character, increases the nucleophilicity of the carbanion and favours coupling reactions. However, Takaki et al. (54) had somewhat different findings. In a THF/C_6H_6 solvent mixture, (44/56 vol. %), the extent of coupling of the Li-counter-ion was greater than that of the K-counter-ion. The higher extent of coupling reactivity with PS^-Li^+ than PS^-K^+ was related to the greater solvation of Li^+ with THF than that of K^+ (54).

As regards the dependence of the coupling reactivity on temperature, Candau and Franata's data (47) suggest that lower temperatures suppress the side reactions and thereby increase the extent of coupling. Takaki et al. (54) made similar observations but Wenger and Yen (42) presented different findings.

The order of addition of the prepolymer solutions was also found to affect the extent of coupling. It was reported by some workers (43) that the dropwise addition of the halogenated backbone polymer solution to the living polymer solution resulted in a higher extent of coupling. This was based on the assumption that the presence of an excess of living polymer in the reaction medium would minimize the metal-halogen interchange reaction and hence favour the coupling reaction. However, other workers (47,54) made different findings in this connection. They found a low degree of coupling when the backbone polymer solution was added to the living polymer solution while a high degree of coupling resulted in the reverse case. It was opined (54) that living polymer, if present in excess would induce side reactions.

(iii) Deactivation of living polymer with ester functions. The ester functions of polymethyl methacrylate have also been used for coupling with living polystyrene (56,65-67).

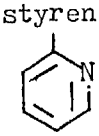
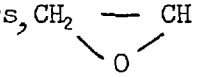


(1.3)

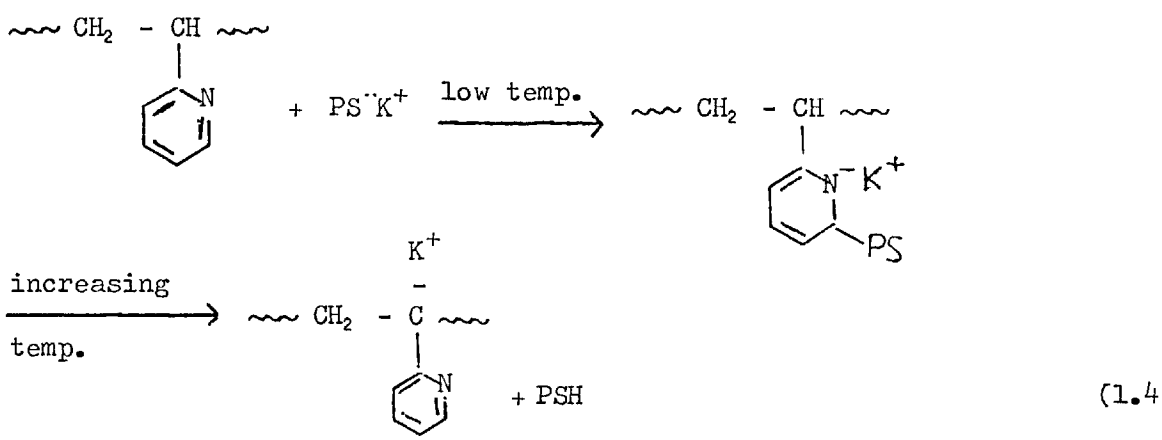
Gallot and co-workers (56,65) used polystyryl potassium in THF as the living polymer. They found that only 10% of the ester functions had undergone coupling reactions but no backbone molecule was left ungrafted. It was suggested that the backbone molecule had collapsed after some grafting had occurred and the free ester groups thus became inaccessible to the uncoupled living polymers (56).

Andreeva and Merkureva (66) observed that the degree of grafting of PMMA and the distribution of side chains in the graft copolymer

prepared by coupling PMMA with polystyryl lithium depended on molecular weight, molecular weight distribution of the backbone polymer and the solvent. A higher degree of grafting and a higher rate of grafting was observed in toluene rather than in THF.

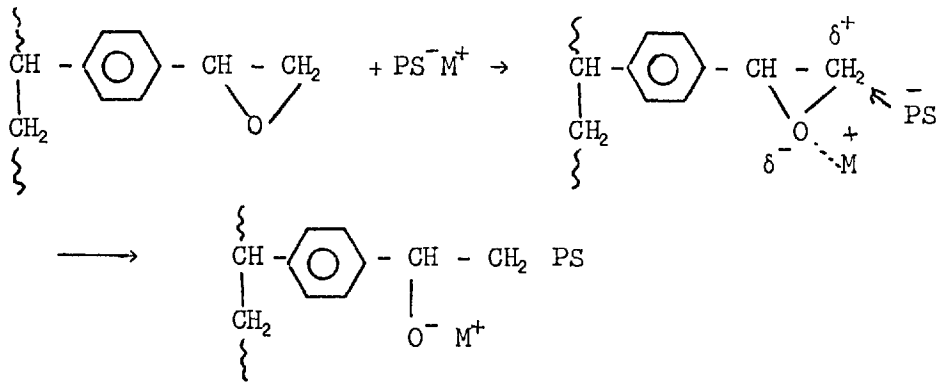
(iv) Some other multifunctional backbone polymers used for the preparation of graft copolymers by anionic coupling reactions with living polymers were poly(2-vinyl pyridine) (68,69), poly(p-vinyl styrene oxide) and poly(p-vinyl styrene oxide-co-styrene) (70). The electrophilic functional group in the former polymer is  and in the other polymers, 

Coupling was suggested to take place at the sixth carbon position of the poly(2-vinyl pyridine). When polystyryl potassium was used in the reaction, it was necessary to carry out the coupling at low temperature since at room temperature a rearrangement liberating free polystyrene occurred (69).



(1.4)

With poly(p-vinyl styrene oxide) and p-vinyl styrene oxide-styrene copolymer, the coupling was suggested to take place at the epoxide ring through a coordination mechanism.



(1.5)

This suggestion was in agreement with the accepted idea that the coordination of a metal atom to the ring oxygen is the first step in the ring-opening polymerization of epoxides with organometallic compounds (71).

1.2.2. B. Grafting by Carbanionic Initiation. According to this method, carbanionic sites are first introduced into a pre-formed polymer by suitable chemical reactions and suitable monomers are graft copolymerized anionically from these reactive sites.

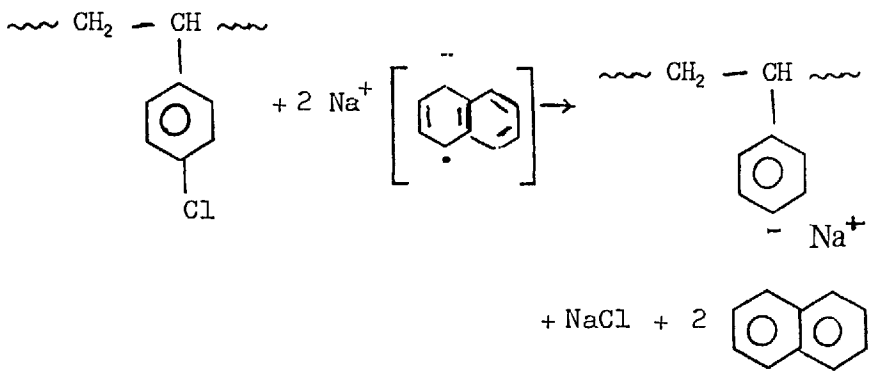
The introduction of anionic sites is achieved by (i) replacing a halogen atom by a metal atom (metal-halogen interchange reaction), (ii) replacing a hydrogen atom by a metal atom, (iii) reaction of a suitable unsaturated group on the polymer with a metal or suitable metallic compound (generation of radical anions).

(i) Synthesis of polymeric initators by metal-halogen interchange reactions and grafting therefom. Metalation of halogenated compounds by alkyl-alkali metal compounds is a known reaction. Alkyl-lithium compounds are the most efficient reagents for such reactions (64).

Halogen substituted polystyrene can be readily lithiated by n-BuLi. Para-bromo and para-iodo substituted polystyrenes were found to be particularly suitable for the preparation of lithiated polystyrenes. Thus iodinated polystyrene (72) was lithiated by n-BuLi and acrylonitrile was graft copolymerized anionically. In this type of metalation, it is

necessary to add the polymer solution to a large excess of the metalating agent in order to avoid Wurtz-Fittig cross-linking reactions. The graft copolymer prepared by this method is therefore contaminated with large quantities of homopolymers resulting from homopolymerization of monomers by unreacted metalating agent.

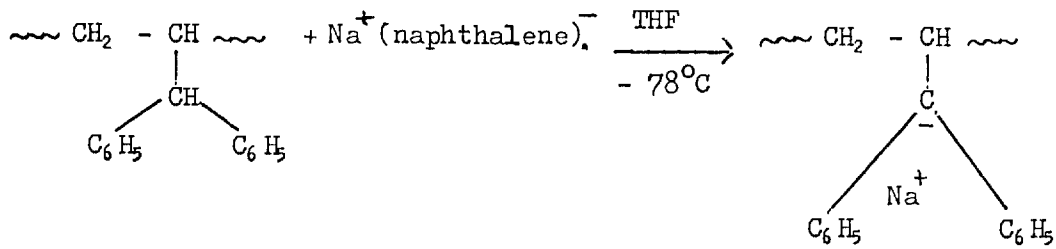
Na-naphthalene complex in THF was also used for metalation of para-bromo, para-iodo (73) and para-chloro (74,75) substituted polystyrenes. Different monomers such as styrene, MMA and 2- and 4-vinyl pyridine (74,75) were polymerized from the metalated sites.



(1.6)

Partially chlorinated polypropylene and polyethylene and brominated polyethylene (76) have been metalated by n-BuLi and phenyl lithium but except for chlorinated polyethylene, dehydrohalogenation occurred. This type of dehydrohalogenation was also noticed when poly(vinyl chloride) was metalated by n-BuLi (77).

(ii) Synthesis of polymeric initiators by replacement of a H-atom by a metal atom and grafting therefrom. As with simple organic compounds, metalation of polymers containing acidic hydrogen occurs readily. For example, poly(3,3-diphenyl prop-1-ene) has been metalated by Na-naphthalene in THF (78).



(1.7)

Metalation was found to be quantitative and graft copolymers with styrene were prepared (78).

One of the most widely used reagents for metalation is a BuLi complex of N,N,N',N'-tetramethylethylenediamine (TMEDA). This is a stronger metalating agent than BuLi or Na-naphthalene/THF and has been used for metalation of polymers not containing acidic hydrogen such as polystyrene and polydienes. TMEDA forms a (1:1) complex with many organo-lithium compounds. The increased reactivity of the complex in comparison to alkyl lithium compounds is attributed to the increased ionic character of the alkyl lithium bond in the complex and the possibility that the alkyl lithium becomes monomeric (79).

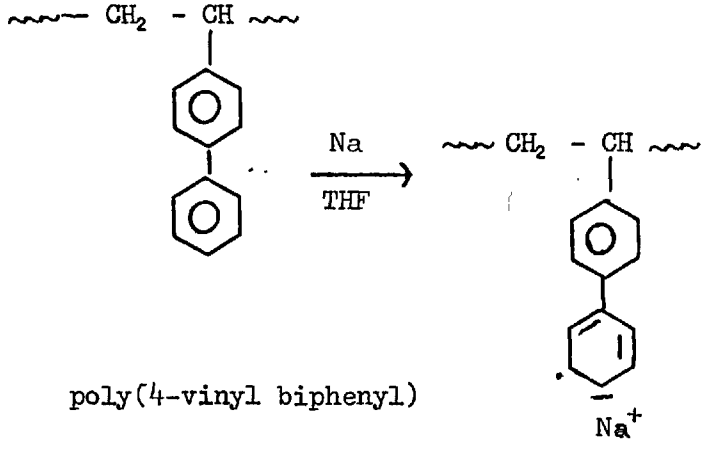
Sec-BuLi/TMEDA has been found to be a more effective metalating agent than n-BuLi/TMEDA, but a disadvantage in using sec-BuLi is that it is less stable than n-BuLi and needs to be purified immediately before use (80).

The literature contains numerous examples of metalation of polystyrene and polydienes using n-BuLi/TMEDA and sec-BuLi/TMEDA and graft copolymerization with suitable monomers from the metalated sites. Thus, for example, Folk et al. (81) metalated different polydienes by sec-BuLi/TMEDA and graft copolymerized styrene, α-methyl styrene with a high grafting efficiency of the monomers and low contaminations of homopolymers. Metalation reactions (82) of squalene, a model compound

for polydienes, reveals that the metalation with polydienes takes place at the allylic position.

Direct metalation of polyamides by replacing hydrogen atoms linked to the N-atoms of the polymer with Na/NH_3 has been achieved in this laboratory. Graft copolymers of polyamides with ethylene oxide were also prepared by this type of metalation (83). However, the metalation reaction was heterogeneous which limited its usefulness.

(iii) Synthesis of polymeric initiators by the reaction of suitable unsaturated groups on the polymer with a metal or metallic compound (generation of radical anions) One way of metalation involves electron transfer reactions between a vinyl aromatic compound and an alkali metal. Thus poly(4-vinyl biphenyl) was metalated in the presence of sodium or caesium metal in THF solution by electron transfer to the aromatic system of the pendant biphenyl groups (84,85). Graft copolymers of the metalated polymers with ethylene oxide were also prepared (85).



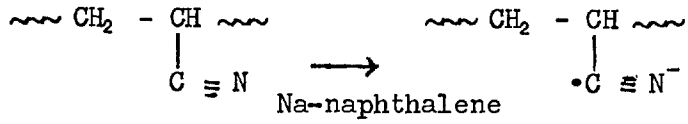
(1.8)

poly(4-vinyl biphenyl)

These polyradical anions are capable of initiating homopolymerization of vinyl monomers by electron transfer in a way similar to that of mono-radical anion but cannot initiate graft polymerization of the vinyl monomers.

Acrylonitrile-styrene copolymers have been metalated at the nitrile groups by electron transfer from sodium metal, sodium naphthalene and

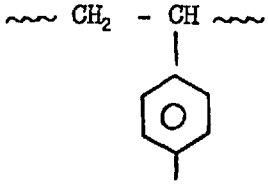
sodium biphenyl (86), with the formation of a radical anion.



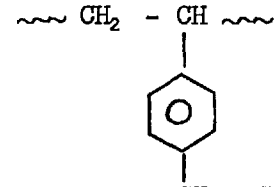
(1.9)

Although some cross-linking occurred due to radical combination, graft copolymerization of acrylonitrile and 2- and 4-vinyl pyridine was accomplished.

Under similar conditions, copolymers of styrene with p-allyl styrene and p-divinyl benzene produced dianions and graft copolymers with acrylonitrile were prepared

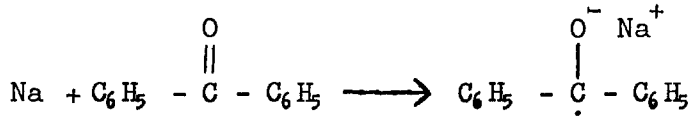


poly(p-allyl styrene)



poly(di-vinyl benzene)

Another type of radical ion initiator is the metal ketyl obtained by the reaction of a non-enolizing ketone with an alkali metal in a polar solvent. For example,



(1.10)

Thus, the radical anion produced on metalation of poly(vinyl benzophenone) initiated the polymerization of acrylonitrile, methylmethacrylate and vinyl pyridine and the dianion produced on prolonged metalation by the same reaction also initiated the polymerization of styrene and butadiene (87).

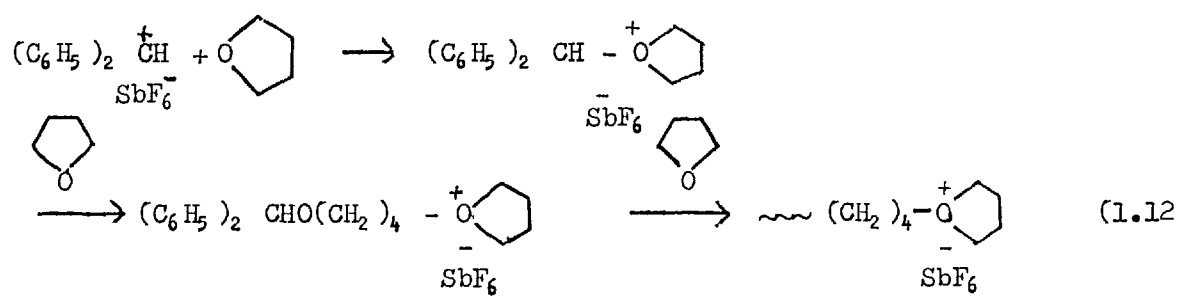
1.2.3. Grafting by Cationic Mechanism

Despite the fact that there are potentially a large number of monomers which can be polymerized cationically, the development of the synthesis of graft copolymers free from adverse side reactions by cationic mechanisms is very recent. Cationic routes to graft copolymer synthesis by the 'grafting from' technique are usually

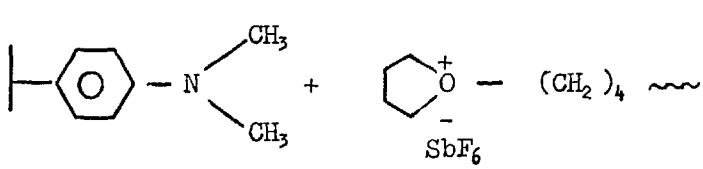
difficult to control and transfer to monomer leads to the formation of homopolymers. However, the synthesis of essentially pure graft copolymers by cationic initiation was first reported by Kennedy (88). Very recently there has been a report (89) on the synthesis of a graft copolymer by cationic deactivation or coupling reactions.

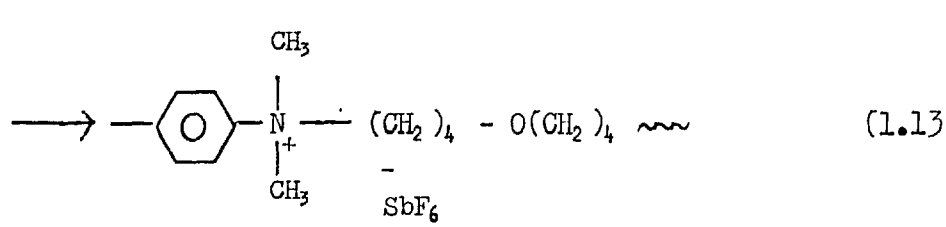
1.2.3. A. Grafting by Cationic Deactivation. There are only a few polymeric carbenium ions, so far prepared, free from termination and transfer processes. The cationic ring-opening polymerization of heterocyclic monomers such as THF offer living polymeric carbenium ions (90) under well-defined conditions. Living polymeric oxocarbenium salt, prepared by polymerization of THF, has been coupled with amino groups pendant to a backbone polymer such as poly(p-dimethyl amino styrene). Well-defined graft copolymers (89) by cationic deactivation have thus been prepared. The initiator, diphenyl methyl hexafluoro-antimonate, has been prepared, in situ, by an exchange reaction between diphenyl chloromethane and silver hexafluoroantimonate in THF.

$$(C_6H_5)_2CHCl + AgSbF_6 \xrightarrow{THF} (C_6H_5)_2\overset{+}{C}H\,SbF_6^- + AgCl \qquad (1.11)$$



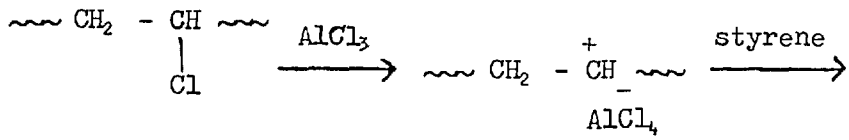
(1.12)

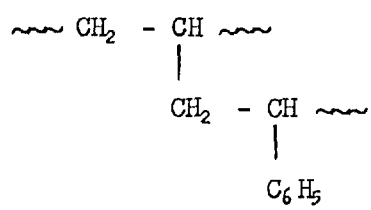




(1.13)

1.2.3. B. Grafting by Cationic Initiation. Synthesis of graft copolymers using conventional Lewis acid catalysts has been complicated by various side reactions. Chloromethylated polystyrene (91), poly(vinylchloride), vinyl chloride-vinyledene chloride copolymers (92) have been used in conjunction with Al-halides (91,92) and $TiCl_4$ (92) to produce macromolecular cations which initiated the polymerization of styrene and isobutylene,

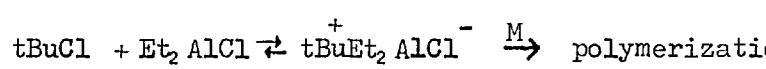




(1.14)

Side reactions resulted in degradation of the backbone polymer, homopolymerization of the graft monomers and cross-linking.

Synthesis of graft copolymers by cationic initiation has been developed by Kennedy. His method (88) of developing macromolecular cations was based on the discovery that certain alkyl-Al compounds, such as Et_2AlCl and Et_3Al, initiate the polymerization of cationically active monomers only in conjunction with purposely added alkyl halides such as t-BuCl (93). An important feature of these polymerizations was that Et_2AlCl or Et_3Al alone was unable to initiate polymerization and the addition of the cationogen such as t-BuCl, was essential for initiation. In this sense, the cationogen is the initiator and the role of the alkyl-Al is to assist in generating the initiating entity,



(1.15)

So, according to this technique, suitable polymeric halides, in conjunction with an alkyl-Al compound, can initiate the polymerization of cationically active monomers such as styrene, dienes and isobutylene. It has been found that polymeric halides containing tertiary or allylic halogens provided the most suitable sites for graft initiation (93). Thus poly[(ethylene-co-propylene)-g-styrene] was prepared using chlorinated ethylene-propylene rubber (94). A number of graft copolymers such as poly(vinylchloride-g-isobutylene) (95), poly(vinylchloride-g-butyl rubber) (96), poly[(isobutylene-co-isoprene)-g-styrene] (97) have been prepared by this technique. Some of these graft copolymers, e.g. poly[(ethylene-co-propylene)-g-styrene] and poly[(isobutylene-co-isoprene)-g-styrene] are interesting thermoplastic elastomers. A number of bi-graft copolymers (98,99) were also prepared by the selective sequential initiation of different monomers with polymeric halides containing different types of halogen atoms. These halogen atoms, within the same polymer molecule, had significantly different labile character.

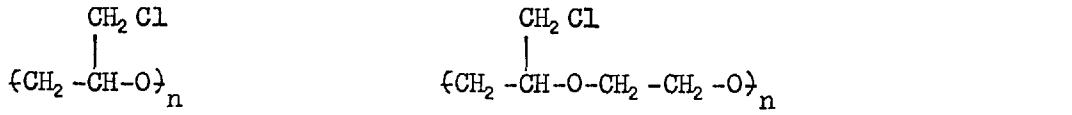
One peculiar feature of grafting by cationic initiation is that whereas graft copolymers with hydrocarbon grafts have been synthesized, grafting of cyclic ethers is unknown. The situation is just the opposite in the case of block copolymers (35).

1.3. Graft Copolymers of Epichlorohydrin Polymers

1.3.1. Introduction

High molecular weight amorphous polyepichlorohydrin and amorphous epichlorohydrin copolymers with other epoxides are very good elastomers and form a class of speciality synthetic rubbers (100,101). Two of this class of synthetic rubbers, amorphous polyepichlorohydrin homopolymer and a 1:1 molar copolymer of epichlorohydrin and ethylene oxide, have been developed commercially by Hercules Incorporated under the names

'Herchlor H' and 'Herchlor C' respectively. These are saturated polyethers having the following structures:



polyepichlorohydrin (PECH)

poly(epichlorohydrin-co-ethylene oxide) P(ECH-co-EO), 1:1 molar

These polyether elastomers are superior in some respects to the other speciality rubbers such as neoprene and nitrile rubbers (102). They are vulcanized by diamines or suitable difunctional reagents through the pendant chloromethyl groups.

Impact modification of a rigid brittle polymer with a rubbery polymer is now well known. This modification has been achieved sometimes by blending a glassy polymer with a rubbery polymer and sometimes by controlled block and graft copolymerization of the two component polymers. On the other hand, reinforcement of elastomers by blending or copolymerization with a rigid polymer is also a common practice. Because a graft copolymer provides the necessary interface for preparation of a finer polymer dispersion, it is always preferred for blending purposes than mere blending of the homopolymers.

Synthesis of graft copolymers with the epichlorohydrin polymers as elastomeric backbone polymers looks very fascinating.

In the literature there are examples of a good number of graft copolymers prepared with PECH, P(ECH-co-EO) and some other halogenated polyether polymers as backbones. All these except one involved a radical mechanism of grafting and the other method involved the anionic coupling technique (59). A list of the initiators/catalysts used for the radical method of grafting in these copolymers is given below with some references.

1.3.2. Initiators/Catalysts Used for Grafting by Free Radical Mechanism

(a) Organic peroxides such as benzoyl peroxide (103,104) and lauryl peroxide (105).

Different vinyl monomers such as styrene, MMA, acrylonitrile (103,104) and vinyl chloride (105) were graft copolymerized onto the chlorinated polyether backbone.

(b) Transition metal labile ligand complex catalysts Two types of catalysts under this heading referred to by Bamford (106) have been used.

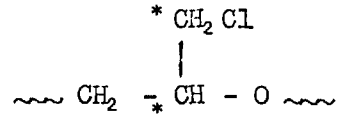
(i) Transition metal labile ligand complex catalyst with the metal in a low oxidation state

Metal carbonyls (107,108) such as $Fe(CO)_5$ and Ni-complexes (109) such as bis(triphenyl phosphite) (1,5-cyclooctadiene) Ni(0) have been used.

(ii) Transition metal-chelate complex catalysts with the metal in a high oxidation state (110) such as Mn(III) acetyl acetonate. These catalysts have been used either alone or in coordination with a co-catalyst such as dimethyl sulphoxide.

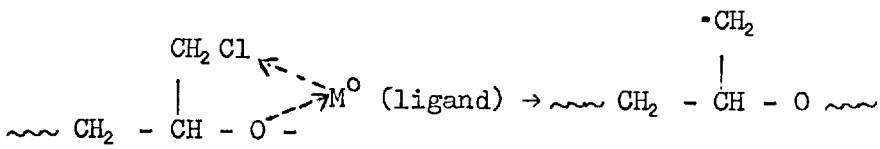
Different vinyl and diene monomers have been graft copolymerized onto epichlorohydrin polymer backbones with the complex catalysts mentioned above. Graft copolymers with a wide range of properties, from mouldable vulcanizable rubbers to tough solids were prepared (107,108,110). The references are mostly in the patent literature. No mechanisms for the generation of free radical sites have been mentioned.

When organic perocides are used as the initiator, generation of free radicals at the C-atoms marked by asterisks,



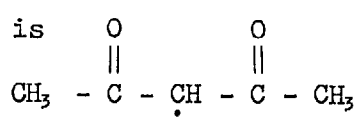
probably occurs. Grafting from these carbon atoms is associated with the greater labile character of Cl and tertiary hydrogen.

When a transition metal ligand complex catalyst such as $Fe(CO)_5$ is used, the formation of a free-radical may be assumed to have taken place at the C-Cl bond according to the mechanism proposed by Bamford (106). Though the chlorine atoms in epichlorohydrin polymers are not very active for reaction with complex catalysts, they are probably activated by the formation of a ligand between the metal of the complex and the etheral oxygen in the epichlorohydrin polymer. Thus ligand formation may help to donate an electron by a metal atom to a chlorine atom, thus helping to split the C-Cl bond



$$+ M^{\oplus}Cl^{\ominus} \text{ (ligand)} \qquad (1.16)$$

The primary radical from the metal-acetylacetonate chelate complex catalyst is



(106) which probably extracts Cl or tertiary hydrogen from PECH to form the macroradical.

1.4. Chemical Modification of Epichlorohydrin Polymers

1.4.1. Introduction

In order to impart certain special characteristics to a polymer, chemical modification of the polymer is sometimes necessary. Synthesis of polymers with desired groups is not always possible. In these cases, the desired groups can be introduced into a preformed polymer by suitable chemical reactions. Thus, by introducing polar groups onto the backbone

of a polymer, its solubility in polar solvents, adhesive character, electrolytic and other properties may be improved to a great extent. The main difficulty in such modifications is in finding suitable non-reactive solvents in which the polymer substrate and the other reagents are soluble and in which the desired modifications can be achieved with little degradation to the polymer.

Epichlorohydrin homo- and copolymers contain pendant $-CH_2Cl$ groups with primary halogen. From a chemical point of view, these polymers should undergo reactions characteristic of alkyl halides, such as nucleophilic substitution, dehydrohalogenation with a strong base, and reaction with Mg (in dry ether) to form Grignard reagents. However, these reactions may not be as simple with epichlorohydrin polymers as they are with simple alkyl halides because of the structural variations of these halogenated poly-ethers from simple alkyl halides. These variations are the presence of (i) a tert-H atom in the C-atom attached to the $-CH_2Cl$ group, (ii) ether linkages in the polymer, and (iii) a large number of functional groups close to one another in the same substrate.

1.4.2. Modifications Involving Substitution Reactions

Epichlorohydrin homo- and copolymers are usually vulcanized through the pendant $-CH_2Cl$ groups by means of diamines (100,111). The vulcanization reaction probably involves nucleophilic substitution. A number of modification reactions mostly involving substitution of Cl atoms of $-CH_2Cl$ groups are listed below.

(a) Substitution by -OH group

Direct substitution of -Cl by the -OH group was achieved by Bortel and Lamot (112) by heating the polymer dissolved in DMF or other solvents with KOH in presence of $NaHCO_3$ and allyl alcohol at 150°C. Substitution was quantitative but the polymer underwent some degradation.

Indirect substitution of -Cl by -OH was observed by Cohen (113) in an attempt to substitute -Cl by the acetate group. This was achieved by heating the polymer dissolved in methyl carbitol with potassium acetate at 175°C.

It was suggested that the halogens were first replaced by acetate groups which were then replaced by hydroxyl groups in an ester interchange reaction with the methyl carbitol. Potassium acetate thus acted as the catalyst in the reactions.

(b) Substitution by $-NH_2$ group

Treatment of PECH, as a low molecular weight syrup with NH_3 at $\geq 80^{\circ}C$ was found to cause cross-linking resulting in an elastomer insoluble in common solvents (114). Cross-linking was accelerated by NaOH. NH_3, like diamines, probably acted as a difunctional reagent with the polymer.

(c) Substitution by $-NHR$, $-N\begin{matrix}R\\R'\end{matrix}$, $:N-R'$ (R'' above)

In this type of substitution, R, R' and R'' are either simple alkyl or aryl groups or alkyl or aryl groups substituted at the end with hydroxyl, carboxyl or other groups.

High molecular weight PECH was modified with amino compounds containing polar substituents by Bortel and Lamot (112) with little degradation of the polymer. The reagents used for substitutions were diethanol amine, triethanol amine and immino diacetic acid. The reaction was carried out in DMF, DEF or dioxan at 150°C under nitrogen. Nucleophilic substitutions of Cl through the formation of -C-N bond was achieved. Thus, water-soluble high molecular weight elastomeric polyelectrolytes were prepared. Substitution achieved was 45-88% and degradation was by a factor of 2 to 8 depending on the solvent and modifying agent.

N'Guen and co-workers (115) carried out substitution of Cl in PECH, and P(ECH-co-EO) using different primary and secondary amines. They used phase-transfer catalysts such as tetrabutyl ammonium hydrogen sulphate to enhance substitution reactions. The reaction was carried in a biphasic mixture of the polymer in an organic solvent and aqueous NaOH in presence of the nucleophilic modifying agent and the phase transfer catalyst at a temperature of 60°C. The degree of substitution was found to depend on the nature of the nucleophilic reagent, solvent and the type of the phase-transfer catalyst.

(d) Substitution through formation -O- and -S- linkages

This was accomplished with metal salts of alcohols, phenols, thiols, thiophenols and other substituted compounds. With respect to the nucleophilic character, the anions from these compounds may be roughly placed in the order of nucleophilicity: mercaptide > thiophenoxide > alkoxide > phenoxide. The overall activity of such a group to act as a nucleophile will, of course, depend on the other substituents linked to it.

K-salts of several substituted phenols such as 4-hydroxy styryl phenyl ketone were used by Nishikubo (116). By heating the reagents in DMF at 100°C for 10 h. 96.8% etherification was achieved. Quantitative substitution of Cl in low molecular weight PECH and other chlorinated polyethers was made even under milder conditions (117). The reagents for substitution were several mercapto substituted alkanol such as $HSCH_2-CH_2OH$ in the presence of NaOH and the reaction was performed in Iso-PrOH at 60°C for 2 h. Polymers with pendant polar groups, useful as protective colloids for water soluble resins were formed. Substitution took place through formation of thioether linkages. The substituted product was useful as a stabilizer for other polymers. Substitution

of Cl in PECH by C_6H_5 S- and similar such groups were also done using alkali metal salts of HSC_6H_5 and other mercapto compounds (118).

Vandenberg (119) used alkali metal salts of various mercapto carboxylic acids, such as mercapto-acetic acid ($HSCH_2COOH$) and some mercapto-phosphorous compounds such as $(C_2H_5O)_2$ P(S) SH for modification of epichlorohydrin polymers. By heating the polymer in DMSO solution with the modifying agents, polar groups such as $-SCH_2-COOH$ and $(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S-$, were introduced. Substitution up to 90% was claimed in some cases. Viscosity data indicated very high degradation of the polymer. It was not suggested whether the mercapto nucleophile or the NaOH used in situ for the formation of the salt of the modifying agent was responsible for degradation.

(e) Substitution with alkyl carbanions (119)

The reagents used for substitution of Cl with alkyl carbanions were alkali metal salts of (i) α-alkali-metallo carboxylic acids, such as α-sodio-sodium acetate, $NaCH_2COONa$, (ii) alkyl sulphinyl carbanions such as $CH_3-\overset{O}{\overset{\uparrow}{S}}-CH_2^-Li^+$. The substitution reaction was performed in different solvents. The substituent $-CH_2COONa$ on acid treatment was converted to a pendant $-CH_2COOH$ group.

Thus polyethers were prepared containing highly polar groups with a wide range of properties from tough rubbers to tacky liquids and with a wide variation of solubility in water.

(f) Substitution by carboxylate groups, $-O-\overset{O}{\overset{\|}{C}}-R$ (through formation of ester linkages)

Substitution of Cl by an acetate group was achieved by Cohen (113) by heating the polymer in DMF solution with K-acetate at 150°C. Quantitative substitution was achieved although the polymer underwent some degradation.

Conversion of a similar polymer to polyepichlorohydrin, that is, poly[3,3-bis(chloromethyl)oxetane] ("Penton" polymer) to the corresponding acetate by reaction with Na-acetate at 150°C in DMSO was reported (120). A conversion of 78% was claimed on the basis of residual chlorine content. Other reagents used for substitution reactions with the same polymer were NaCN, PhONa, MeONa, Na-thiophenolate, Na-diethyl malonate and K-phthalimide.

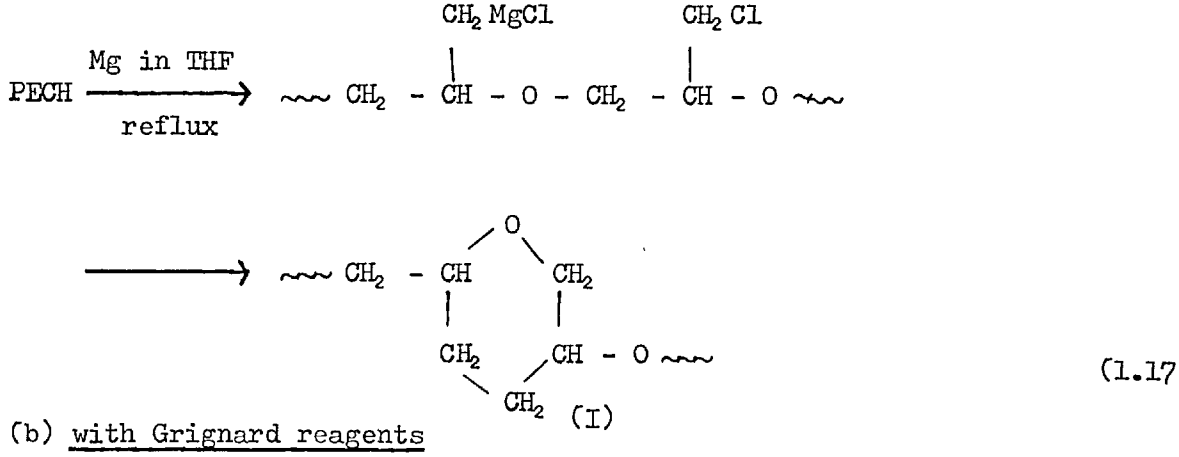
(g) Substitution with some specific reagents

Epichlorohydrin polymers were also modified with some specific reagents such as (i) a metal azide, e.g. N_3Na (121), (ii) Na-thiosulphate (122), (iii) thiourea (123), (N) K-O-tert-butyl thiocarbonate (124).

1.4.3. Reaction with Mg and Grignard Reagents (125)

(a) with Mg

In an attempt to prepare a polymeric Grignard reagent from polyepichlorohydrin by refluxing the polymer with Mg in dry THF, Minoura and co-workers observed dechlorination. The following reactions were suggested on the basis of I.R. spectrum of the recovered polymer.



(1.17)

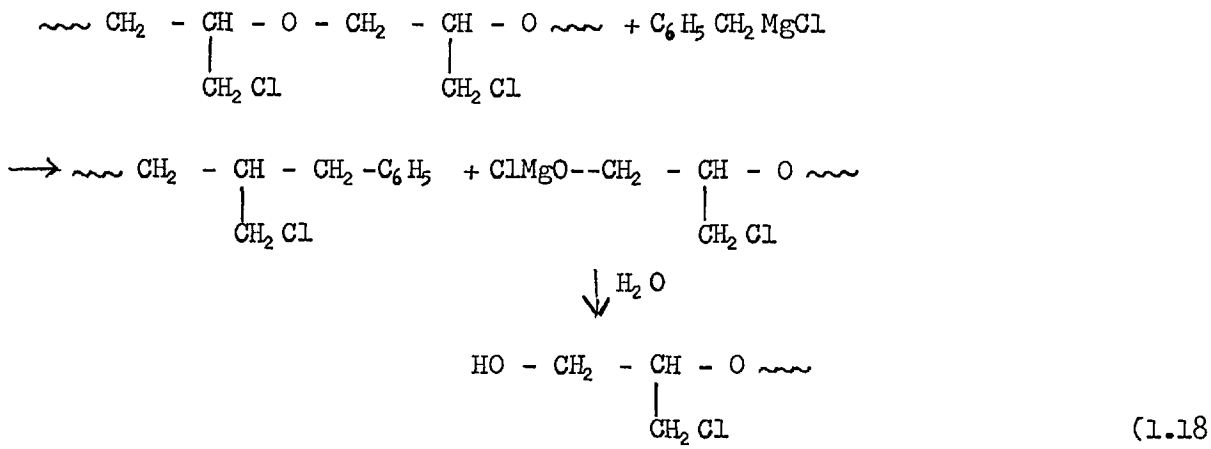
(b) with Grignard reagents

PECH in dry THF was refluxed with Grignard reagents such as $C_6H_5CH_2MgCl$ and $CH_2 = CH - CH_2MgCl$. The following reactions were found to take place.

(i) Substitution of Cl by benzyl and allyl groups by coupling (major reaction).

(ii) Formation of cyclic ethers as (I) above, through the formation of a polymeric Grignard reagent, formed by exchange reactions.

(iii) Cleavage of ether linkages



(1.18)

CHAPTER 2

SYNTHESIS OF POLYSTYRENE BY ANIONIC MECHANISM

2.1. Introduction

A. Anionic polymerization - general

Anionic polymerization proceeds through a carbanionic chain carrier and in its simplest form, consists of two stages, that of chain initiation and chain propagation. It is more suitable for the polymerization of vinyl monomers with electronegative substituents.

The initiation may be accomplished by two mechanisms. In one mechanism, the negative end of an ionic or ionogenic molecule adds to the double bond of the monomer with the formation of a carbanion in contact with the positive end of the initiator forming the gegen-ion, for example

$$B^-M^+ + CH_2 = \underset{\displaystyle R}{\overset{\displaystyle |}{CH}} \longrightarrow BCH_2 - \underset{\displaystyle R}{\overset{\displaystyle |}{CH}}{}^-M^+ \qquad (2.1)$$

Typical initiators of this type of initiation include KNH_2, n-BuLi and Grignard reagents.

The second mechanism involves the formation of a radical anion by the direct transfer of an electron from a donor species to the monomer. This occurs, for example, in the sodium-naphthalene-styrene system. A dianion is finally formed capable of initiation from both ends.

The scope and details of anionic polymerization have been discussed in a number of papers and reviews (126-132). Under suitable experimental conditions, in the absence of chain transfer to monomer or solvent and in the absence of all adventitious impurities, there is no termination reaction and the polymerization continues until a very small equilibrium

concentration of monomer remains unreacted (133). The ability of growing chain to remain active and continue polymerization upon further addition of monomer led to the name "living polymerization" (40,41).

As a consequence of the absence of termination reactions in living polymers, the number of growing chains remains constant. The number average molecular weight in such a case is

$$\bar{M}_n = \frac{[M]}{[I]} \times M \qquad (2.2)$$

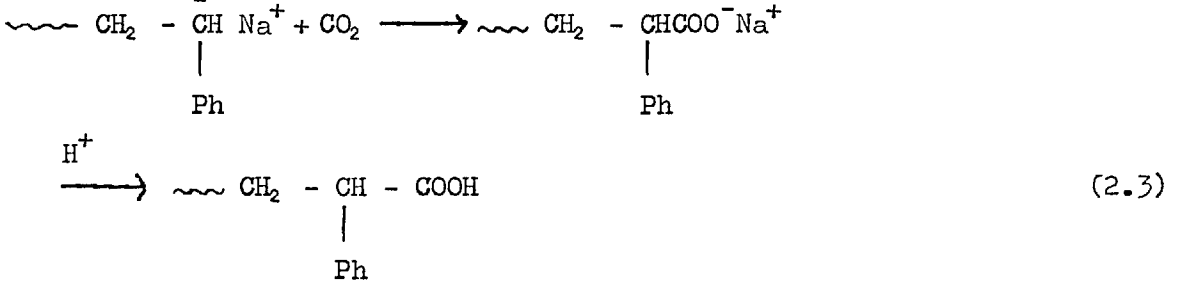
where [M] is the molar concentration of monomer consumed, [I] is the molar concentration of initiator and M is the molecular weight of the monomeric repeat unit. When the initiation is fast compared to propagation, all the active centres start to propagate simultaneously and a polymer of narrow molecular weight distribution, MWD, (Poisson distribution) (134) is produced.

Anionic polymerization is of great practical significance for the following reasons:

(1) It enables polymerization to be carried out to a high conversion and with the formation of polymers of pre-determined molecular weight.

(2) The living polymer can initiate polymerization of a second suitable monomer resulting in the formation of a block copolymer (1 - 5,7).

(3) Anionic chain-ends behave as typical nucleophiles and enable a polymer to be capped with suitable functional end-groups (127,135-138), for example, carboxyl group.



(2.3)

Living polymers contain very reactive carbanionic end groups. The following experimental conditions have to be met in order to avoid earlier termination of reactive species and prepare a polymer of narrower molecular weight distribution.

1. All impurities capable of destroying the highly reactive carbanionic species such as water, oxygen, carbon dioxide must be completely excluded from all the materials and the system used in the polymerization (135). The reaction therefore, must be carried out either in a high vacuum system or in an atmosphere of purified inert gas.

2. The reaction conditions, such as temperature, concentration of the monomer and initiator must be uniform throughout the polymerization system. Thus stirring must be efficient, particularly when the propagation is rapid (135).

3. Depropagation and transfer of active sites to monomer or solvent must not occur. Theoretical considerations of the effects of depropagation and of the chain transfer to monomers (135) on the MWD have been discussed.

4. Monodisperse polymers are obtained only when the initiation is fast compared to propagation so that all the growing chains become available from the beginning and each chain has an equal chance to add to monomer (135).

B. Anionic polymerization of styrene with organo-alkali metal initiators

Among the various anionic initiators used for the polymerization of styrene and other vinyl and diene monomers, organo-lithium and other organo-alkali metal initiators are the most widely used. In absence of association, an organo-metallic compound exists in solution in an equilibrium of four possible forms, a covalent compound (I), an intimate

ion-pair (II), a solvent-separated ion-pair (III) and solvated free-ions (IV), depending on the polarity of the solvent.

$$\underset{\text{I}}{B\text{-}M} \rightleftharpoons \underset{\text{II}}{B^-M^+} \rightleftharpoons \underset{\text{III}}{B^- \,\vdots\, S \,\vdots\, M^+} \rightleftharpoons \underset{\text{IV}}{B^-\text{---}S\ M^+\text{---}S} \qquad (2.4)$$

In polar solvents, the equilibrium favours the free ions. The initiation step involving an organo-metallic initiator in a highly polar solvent is therefore a simple addition of the anion to a monomer molecule (Eqn 2.1).

In non-polar solvents, with the initiators existing mostly as covalent compounds or tight ion-pairs, the initiation proceeds through the formation of a π coordination complex. Coordination activates the monomer by inducing a partial positive charge in it. On rearrangement of the π-complex, the initiator migrates as an anion to the positive end of the polarized double bond while the negative end attaches itself to the metal ion

$$B\text{-}M + CH_2{=}CH\,R \rightleftharpoons B\text{-}M\text{---}\underset{CH\,R}{\overset{CH_2}{\|}} \longrightarrow B\,CH_2\text{-}\underset{R}{\overset{}{\underset{|}{CH}}}\text{-}M \qquad (2.5)$$

Another complication in initation reactions in non-polar solvents involving covalent or intimate ion-pair species is the tendency of these species particularly those containing a lithium cation to associate into larger aggregates and this may cause various kinetic complications (139,140). Thus it seems that n-BuLi is hexamerically and the growing chain dimerically associated in the n-BuLi-styrene-benzene system. The association-dissociation equilibria may be labile, since the synthesis of polymers of narrow MWD in the system is possible (141).

Polymerization of styrene in different polar solvents such as THF, dioxan, and dimethoxyethane involving lithium, sodium, potassium and

other alkali metal counter-ions has been studied (142-144). Polymerization rates involving polystyryl lithium generally increase with the dielectric constant and solvating power of the solvent medium (145).

Apart from the solvents, the gegen-ions have also a pronounced influence on the rates of anionic polymerization. The influence of gegen-ions on the polymerization rates of styrene in THF at 298°K has shown (142) that the smaller Li-ions can be solvated to a greater extent than the larger ions.

The synthesis of polystyrene as described in the present and the succeeding chapters, was conducted using n-BuLi in non-polar solvents, benzene and toluene and also by cumyl-K in the polar solvent, THF. In pure THF, both initiation and propagation steps in the polymerization reactions by any of the organo-alkali metal initiators are fast and the reaction is complete within minutes even at -78°C (146). Polymerizations by the author were therefore performed at -78°C and styrene was added dropwise, with vigorous stirring of the reaction mixture. In pure benzene, initiation is slow compared to propagation which is itself much slower than that in THF but in the presence of small amounts of THF, the initiation rate is rapid (147). Small amounts of THF were therefore added to most polymerizations of styrene in benzene conducted in these laboratories. However, some samples of polystyrenes were also prepared in pure benzene and longer periods of time were allowed for the completion of the polymerization reaction.

2.2. Experimental Procedures

2.2.1. The Vacuum Line and the Argon Line

(a) The vacuum line. An outline of the vacuum line used is given in figure 2.1. It was constructed and used according to the instructions

given elsewhere (148). The pumping system comprised a high vacuum rotary pump (A) and a mercury diffusion pump (B). The device used for measuring the pressure was a conventional McLeod gauge (C). Stopcocks used in the line were all-glass high vacuum stopcocks. Two liquid nitrogen traps (D,D') were used and stopcocks in the pumping system were normally greased with Apiezon 'N' High Vacuum grease. Silicone High Vacuum grease was used with stopcocks in the purification system. Rhodin splash-heads (E) were used between flasks and outlets of the purification system. The use of splash-heads reduced the stripping of grease by solvents and also gave better control of distillation. Fine particles of calcium hydride were also trapped when distillation was performed from this drying agent.

A vacuum of approximately 10^{-5} Torr as measured by the McLeod gauge, was readily regained after each distillation.

(b) Argon line. Materials were sometimes handled under Argon (British Oxygen Co., High Purity Grade) which was passed through a long column of activated silica gel before use. The silica gel did not show any change of colour even after considerable use. The supply line for dry argon is shown in figure 2.2. One arm of the line was terminated by a Luer-lock 4 cm syringe needle while the other arm was connected to the vacuum line through a bulb (F) and a mercury manometer (M) (figure 2.1).

2.2.2. Purification of Materials

(a) n-Butyl lithium (Alpha Products). n-BuLi was supplied as a 2.5 M solution in n-hexane in a 500 cm^3 bottle stored under nitrogen. It was used without further purification. The solution was transferred to a number of calibrated dispensers shown in figure 2.3 as follows. A dispenser with a rubber septum placed at its side-arm was thoroughly evacuated, flamed out and cooled and then the screw-cap of the stock-

bottle was opened. The syringe needle from the argon supply line and the sharpened end of a long (1 metre) piece of dried steel tubing (19 gauge) were pushed through the rubber cap very carefully. Argon was passed for about a minute, and the other end of the steel tubing was then inserted into the dispenser through the rubber septum. By lowering the end of the steel tubing below the surface of the n-BuLi solution in the stock bottle, the solution was transferred to the dispenser under a pressure of argon. The operation is shown in figure 2.3. On taking out the steel tubing, the solution in the dispenser was frozen and degassed to 10^{-5} Torr and the side-arm was sealed off. On further degassing, the solution was thawed and the dispenser was filled with dry argon while still attached to the vacuum line. On closing the stopcock, the dispenser was taken off the vacuum line. With a rubber septum placed over the top of the cone and the stopcock closed, it was stored in a glove-box filled with dry oxygen-free nitrogen in a cool place. Samples were later conveniently withdrawn under argon pressure by a syringe after the syringe and the space above the stopcock had been properly flushed with argon.

(b) Dilution of stock n-BuLi solution. The concentration of the stock n-BuLi solution was too high for direct use as an initiator solution. The stock solution was therefore diluted by a factor of 5 by adding 20 cm^3 of stock solution to approximately 80 cm^3 of pure n-hexane in another dispenser similar to the one in figure 2.3.

(c) n-Hexane (BDH). The reagent was stirred over powdered calcium hydride (BDH) for about 24 h and then fractionally distilled. The middle fraction distilling at 67-68°C (1 atm) was degassed on the vacuum line, thawed and distilled into a flask containing about 1 cm^3 of stock n-BuLi solution. After further degassing, the solvent was distilled

into the dispenser. The technique for degassing solvents by freeze-thaw cycles has been described elsewhere (148).

(d) Estimation of n-BuLi concentration. Both stock and dilute solutions of n-BuLi were analysed by the "Double titration" method (149). Two 50 cm^3 dried conical flasks were thoroughly flushed with argon. A 2 cm^3 sample of n-BuLi solution was added dropwise by a syringe to approximately 10 cm^3 distilled water in one of the conical flasks. The water converted alkyl lithium to lithium hydroxide. Another 2 cm^3 sample was added dropwise through a rubber septum to the other conical flask containing 5 cm^3 of pure THF and 2 cm^3 of freshly distilled benzyl chloride. The solution was properly mixed and then quenched with 10 cm^3 distilled water.

The two resulting solutions from the n-BuLi treatment were titrated against a standard solution of sulphamic acid (Hopkin and Williams, GPR) with phenolphthalein as indicator. The concentration of active n-BuLi was determined from the difference in the lithium hydroxide concentrations, as obtained from titration results. The method is based on the fact that benzyl chloride couples with n-BuLi to form lithium chloride, whereas the other compounds such as n-BuOLi and LiOH produced by reaction of n-BuLi with impurities such as oxygen and water respectively, do not undergo the coupling reaction and are converted to LiOH by water.

The purification and storage of THF used in this and other experiments is described in section 2.2.2 (i). Benzyl chloride (Hopkin and Williams) was dried over phosphorous pentoxide for 12 h and then distilled in the vacuum line. The middle fraction was collected and stored in a flask wrapped with Al-foil under dry argon before use.

(e) Cumyl potassium (Orgmet Inc., Hampstead, N.H., U.S.A.). The reagent was used from an old stock bottle. It was kept in suspension in n-heptane in the presence of excess of metallic potassium. The reagent is extremely sensitive to moisture and air. It was stored and handled in a glove-box in an atmosphere of argon. The reagent was diluted with pure THF and filtered as described below.

(f) Dilution, filtration and storage of cumyl potassium. A 100 cm^3 storage ampoule (figure 2.4), a sealed flask containing approximately 100 cm^3 purified THF, a specially designed sintered glass filter of porosity 3 (figure 2.4), a 10 cm^3 syringe with a 15 cm needle, a 150 cm^3 flat bottomed flask with a stopper and the cumyl potassium stock bottle, were left in the glove-box. Dry nitrogen was flowed through for 3 h and dry argon for 1 h. All glassware used for the preparation of the initiator were also flushed with argon. The THF in the sealed flask was transferred to the flat bottomed flask by breaking the capillary in the former. The cumyl potassium stock bottle was shaken, its screw-cap removed and 10 cm^3 of the slurry was withdrawn and transferred into the flat bottomed flask containing the THF. The mixture was well-mixed and filtered through the sintered glass filter into the storage ampoule.

The initiator solution had a cherry red colour. The greased stopcock of the storage ampoule was closed and a rubber septum placed at the mouth of the open arm. The flask was then connected to the vacuum line, the solution was frozen and degassed and the side arm sealed off at the capillary constriction. On further degassing, the solution was thawed and the ampoule was filled with dry argon. With the stopcock closed and a rubber septum placed at the cone, the flask was kept in a deep freeze at -20°C to prevent any slow reaction of cumyl potassium with THF.

(g) Estimation of cumyl potassium concentration. The method was based on the reaction of cumyl potassium with n-butyl bromide to form potassium bromide which was estimated by titration with a standard silver nitrate solution in presence of fluorescien acid indicator. The details of the procedure have been described elsewhere (150).

(h) Benzene (Koch-Light Laboratories Ltd). The required volume of benzene was stirred over powdered calcium hydride for about 24 h and then fractionally distilled. The middle fraction distilling at 79 - 80°C (1 atm.) was collected. Sodium wire was pressed into the flask containing the solvent by means of a sodium press. The flask was then connected to the vacuum line and the contents were degassed to 10^{-5} Torr. After thawing, the solvent was stirred over sodium wire overnight. On further degassing, the solvent was distilled into a flask containing living polystyrene prepared as follows.

About 1 cm^3 of styrene, freed from the stabilizer and purified by fractional distillation as described in section 2.2.2 (j), was syringed into a dry calibrated flask equipped with a rubber septum and flushed with argon beforehand. To this was added 1 cm^3 of stock concentrated n-BuLi solution (for purification of 150 cm^3 of benzene). The mixture was stirred under a flow of argon for about 20 minutes at room temperature. A low molecular weight polystyrene was produced. The mixture was then degassed on the vacuum line.

Benzene, over sodium wire, was distilled onto living polystyrene, degassed, thawed and stirred overnight by means of a magnetic stirrer. The benzene was finally distilled into the polymerization flask (figure 2.6). Before final distillation into the polymerization flask, the solvent was once again degassed.

(i) Tetrahydrofuran (Hopkin and Williams). THF was stored over Linde 4A molecular sieve before use. Required volume of the solvent was stirred over powdered calcium hydride for 28 h and then fractionally distilled in a dry nitrogen atmosphere. The middle fraction distilling at 64 - 66°C (1 atm.) was collected. Na-wire and a few crystals of benzophenone were introduced into the flask. The contents were degassed and thawed in the vacuum line. The solvent was stirred in the presence of sodium wire for 15 - 16 h. A blue colour due to the sodium-benzophenone complex developed in half an hour. This ensured the drying of the solvent. The solvent was once again dried over Na/K alloy, a very efficient drying agent for solvents containing traces of water. The Na/K alloy was prepared as follows. Freshly cut sodium and potassium (1:2 by weight, about 0.6 g for 200 cm^3 solvent) were placed in a flask, evacuated to 10^{-5} Torr, and then heated gently under vacuum so as to melt, vapourize and form a mirror.

The flask was cooled and THF was distilled in from over Na-wire, degassed, thawed and stirred for about 4 h. The solvent was finally distilled into a number of calibrated ampoules (figure 2.5) whose side-arms, closed with rubber septa, were previously sealed off under vacuum at constriction 'a'. After repeated degassing in two cycles, the ampoules were sealed off the vacuum line at constrictions 'b'. These were stored in a deep-freeze at -20°C until used.

When THF was used as the solvent for polymerization, it was directly distilled into the polymerization flask (figure 2.6) from Na/K alloy.

(j) Styrene (BDH). The styrene supplied contained .001 - .002% w/v tert-butyl catechol as stabilizer. No special treatment was made for the removal of the stabilizer by washing with NaOH as suggested (151) because of the problems, experienced by workers in this laboratory before

(39,150) created by the water saturating the monomer. Instead, the monomer was stirred with powdered calcium hydride for 24 h and then fractionally distilled at reduced pressure. The middle fraction distilling at 42 - 45°C was collected. The high boiling stabilizer (b.p. 285°C at 1 atm.) was expected to remain in the still. The distilled monomer was degassed over powdered calcium hydride in the vacuum line, thawed and stirred for about 14 h and then distilled onto fresh calcium hydride. Here again the middle fraction was collected. On further degassing, the monomer was stirred over the calcium hydride for 3 - 4 h and finally distilled into calibrated ampoules which were degassed and sealed in the way described before (section 2.2.2 (i)).

2.2.3. Polymerization Procedure and Isolation of Polymers

(a) Polymerization in benzene initiated by n-BuLi. The polymerization was carried out in benzene in the presence of a small amount of THF, and also in pure benzene.

The reaction flasks (figure 2.6 and flask A, figure 4.1) were assembled with the THF and styrene ampoules and evacuated to 10^{-5} Torr for 2 h in the vacuum line. The polymerization flask and the part of the vacuum line used for the distillation of the solvent were flamed with a gas flame for about 20 minutes and allowed to cool. The vacuum pressure was measured as about 10^{-5} Torr. A required volume of benzene from over living polystyrene in a calibrated flask was distilled into the polymerization flask, degassed to 10^{-5} Torr, thawed and the flask was then filled with dry argon. With the tap closed, the flask was taken off the vacuum line. A rubber septum was placed at the cone and the space above the tap was flushed with argon. A calculated volume of dilute n-BuLi solution was introduced through the rubber septum by means of a syringe flushed with argon. The flask was rotated sideways to

neutralize any moisture adsorbed on the surface of the flask by the n-BuLi. It was then connected to the vacuum line, the mixture frozen and degassed to 10^{-5} Torr. The flask was then sealed from the vacuum line at the capillary constriction 'a'.

The mixture was thawed and stirred. The breakseal in the styrene ampoule was broken at this stage by the glass-encapsuled iron breaker being directed from outside by a horse-shoe magnet. When the styrene had drained in, the solution was cooled in an ice bath. Before the mixture started freezing, the ampoule of THF was opened. On addition of THF, the yellow colour of the polymerization mixture immediately became deep orange-red. The mixture was vigorously stirred and the polymerization carried out at room temperature for 8 h.

The living polymer thus prepared was used for coupling with polyepichlorohydrin described in section 4.2.2. A portion of the polymer was also separately terminated by degassed MeOH.

For polymerization in pure benzene, an apparatus similar to that in figure 2.6 or figure 4.1 (flask A) was used, except that the opening for THF ampoule was sealed. The operation of addition of initiator and monomer was similar to that described previously and the polymerization was usually continued for 24 h.

(b) Polymerization in THF, initiated by cumyl potassium. The apparatus and the technique were similar to those for the n-BuLi initiated polymerization of styrene in benzene. The flask used was the same as that in figure 2.6 or figure 4.1, with the opening for THF ampoule closed. As the rate of propagation was very fast in THF, the polymerization reaction was carried out at $-78^{\circ}C$ by cooling the flask in a methylated spirit/dry ice slurry. The monomer was added dropwise by placing the iron breaker at the opening towards the flask (at the position C,

figure 2.6 or 4.1). The mixture was stirred vigorously during the addition of the monomer. On complete addition of the monomer over a period of 15 minutes, the temperature was raised to 0°C and the polymerization continued usually for 4h at this temperature, with efficient stirring. The polymerization was terminated as before.

(c) Precipitation and purification of the polymers. The terminated polymer solution was filtered through a porosity 3 sintered funnel and the polymer was precipitated by adding the polymer solution dropwise to a ten-fold excess of stirred methanol. The precipitated polymer was collected on a pre-weighed sintered funnel (porosity 3) and dried to a constant weight in a vacuum overn at 50°C. The polymer was redissolved in toluene to make an approximately 4% solution and this solution was filtered. The polymer was then reprecipitated in MeOH, collected by filtration and dried to constant weight as before.

2.2.4. Characterization of Polymers.

Gel Permeation Chromatography (GPC). Gel permeation chromatography is a technique which separates polymer samples into fractions according to their molecular size and can give molecular weight distributions and various average molecular weights, after suitable calibration.

GPC of the samples prepared in this work were carried out by the Rubber and Plastics Research Association, (RAPRA). Polymers were analysed as 0.2% w/v solutions in THF at 20°C.

The molecular weight distribution and computer analysis of a sample of polystyrene prepared anionically in this work is shown in figure 2.7 and table 2.1 respectively.

2.3. Results and Discussions

Most of the living polystyrene samples prepared in this work were used in the synthesis of poly(epichlorohydrin-g-styrene) copolymers.

The polystyrene samples were also separately terminated and characterized. The experimental conditions, the number and weight average molecular weights ($\bar{M}n$ and $\bar{M}w$ respectively) and the corresponding $\bar{M}w/\bar{M}n$ values of the separately terminated polymer samples are reported and discussed in Chapters 4 and 5 along with graft copolymers.

Table 2.1. Computer Analysis of a Sample of Polystyrene Prepared by Anionic Mechanism

Retention or elution volume (counts) [a]	Polymer H values [b]	dW/dV, % values [c]	Polymer M values [d]	log M values	dW/d log M values
84	0.00	0.00	0.4591E+05	4.6619	0.00
85	0.20	0.09	0.3376E+05	4.5284	0.08
86	2.10	0.96	0.2466E+05	4.3919	0.84
87	7.11	3.23	0.1841E+05	4.2650	2.89
88	16.33	7.42	0.1398E+05	4.1456	6.83
89	28.56	12.98	0.1058E+05	4.0246	12.25
90	40.01	18.19	0.7898E+04	3.8975	17.61
91	46.17	20.99	0.6142E+04	3.7883	20.87
92	39.89	18.13	0.4722E+04	3.6741	18.53
93	21.53	9.79	0.3652E+04	3.5626	10.43
94	9.37	4.26	0.2865E+04	3.4572	4.65
95	3.74	1.70	0.2250E+04	3.3522	1.96
96	1.82	0.83	0.1771E+04	3.2482	1.00
97	1.12	0.51	0.1443E+04	3.1591	0.65
98	0.82	0.37	0.1158E+04	3.0637	0.49
99	0.41	0.19	0.9578E+03	2.9813	0.27
100	0.31	0.14	0.7971E+03	2.9015	0.22
101	0.21	0.09	0.6731E+03	2.8281	0.17
102	0.21	0.09	0.5755E+03	2.7601	0.17
103	0.10	0.05	0.5159E+03	2.7125	0.10
104	0.00	0.00	0.4478E+03	2.6511	0.00

a One count = 2.5 mls

b $H \propto \Delta n$, the change in refractive index of eluted polymer solution

c Weight per cent of the polymer eluting at the respective elution volume

d Molecular weight of the polymer eluted at the respective elution volume computed from the standard calibration curve for polystyrene.

Mark-Houwink constants in equation $[\eta] = KM^{\alpha}$ used for conversion via universal calibrations,

$K = 1.2 \times 10^{-2} cm^3 g^{-1}$ $\quad \alpha = 0.71$

$\bar{M}_n$ (Number average molecular weight) $= 5.45 \times 10^3$

$\bar{M}_w$ (Weight average molecular weight) $= 7.40 \times 10^3$

$\bar{M}_v$ (Viscosity average molecular weight) $= 7.11 \times 10^3$

$\bar{M}_w/\bar{M}_n = 1.36$

Figure 2.1. The Vacuum Line

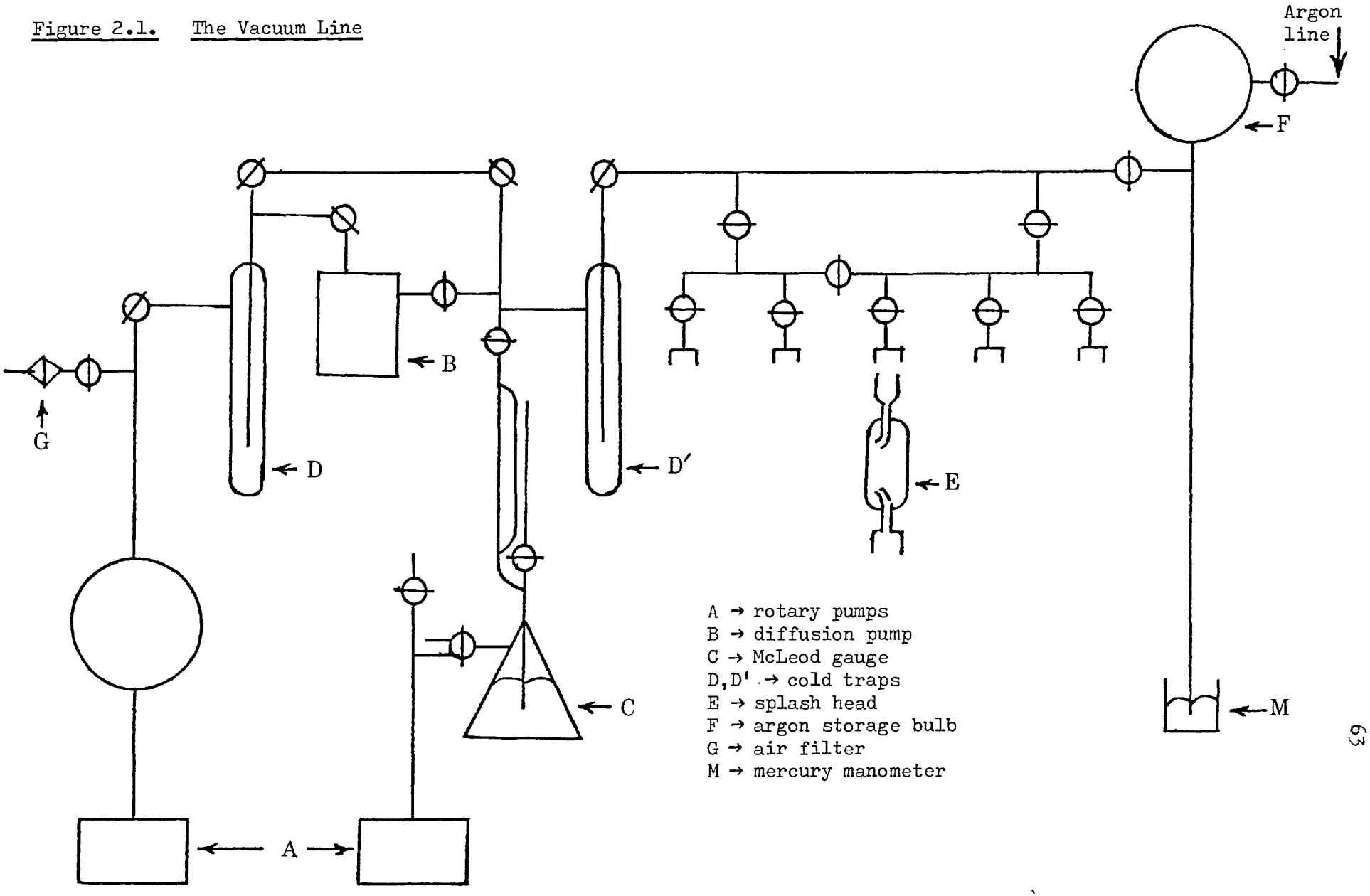


Figure 2.2. The Argon Supply Line

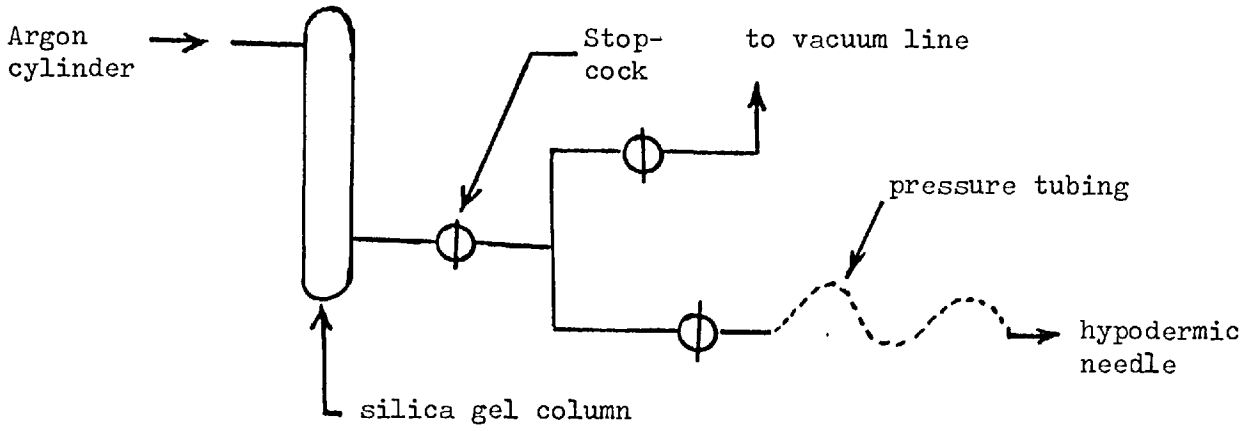


Figure 2.3. Transfer of n-BuLi to a Dispenser under Argon Pressure

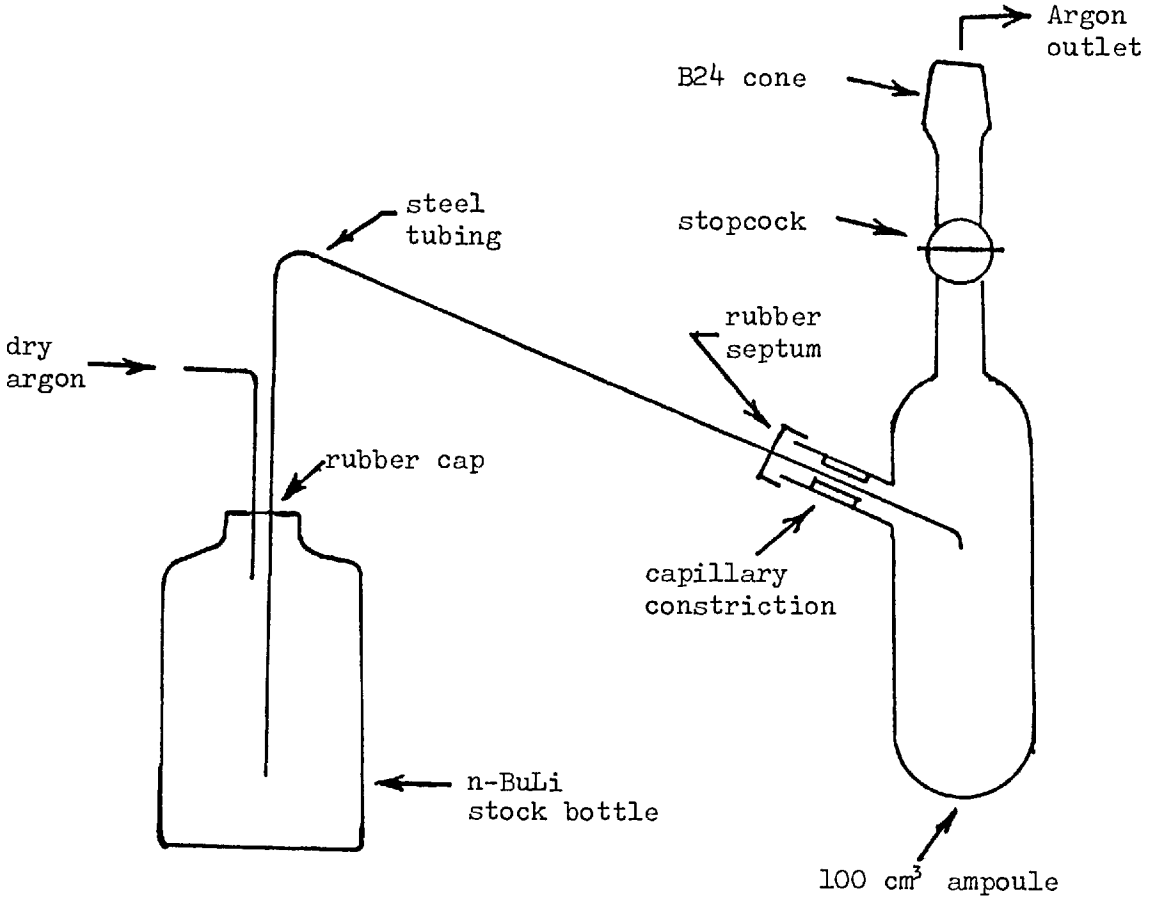


Figure 2.4. Filtration of Cumyl Potassium Initiator Solution into the Storage Ampoule

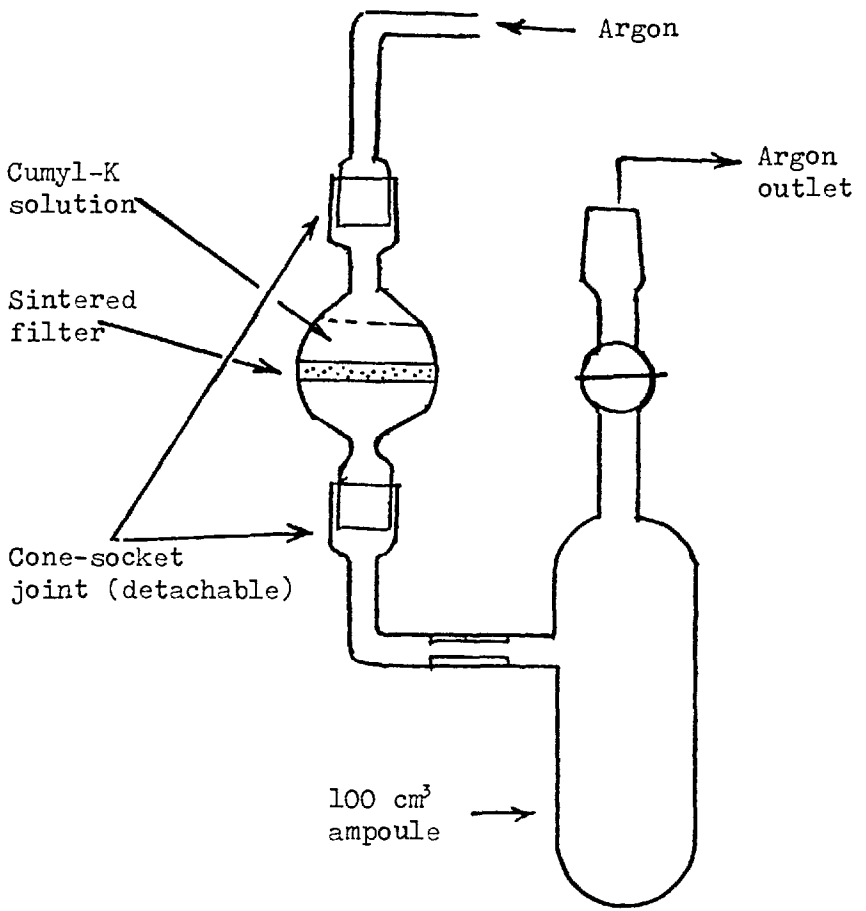


Figure 2.5. Storage Ampoule for THF and Styrene

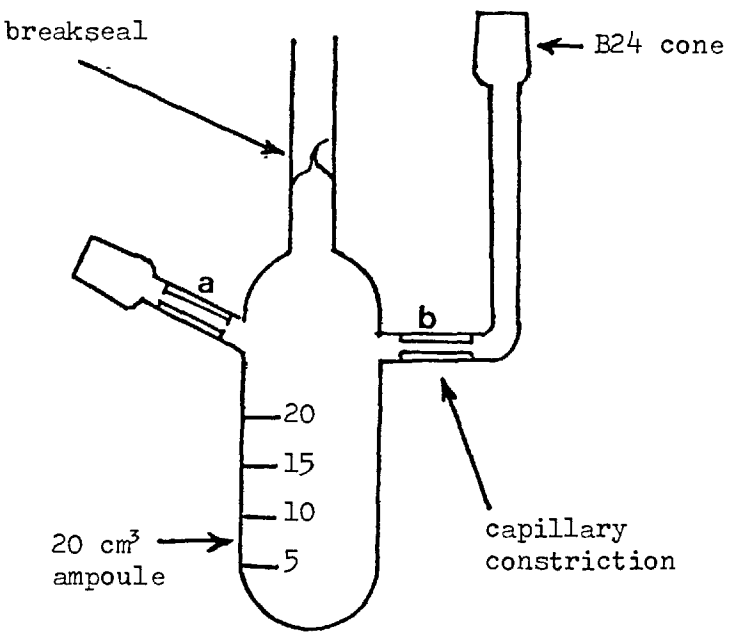


Figure 2.6. Apparatus for Polymerization of Styrene

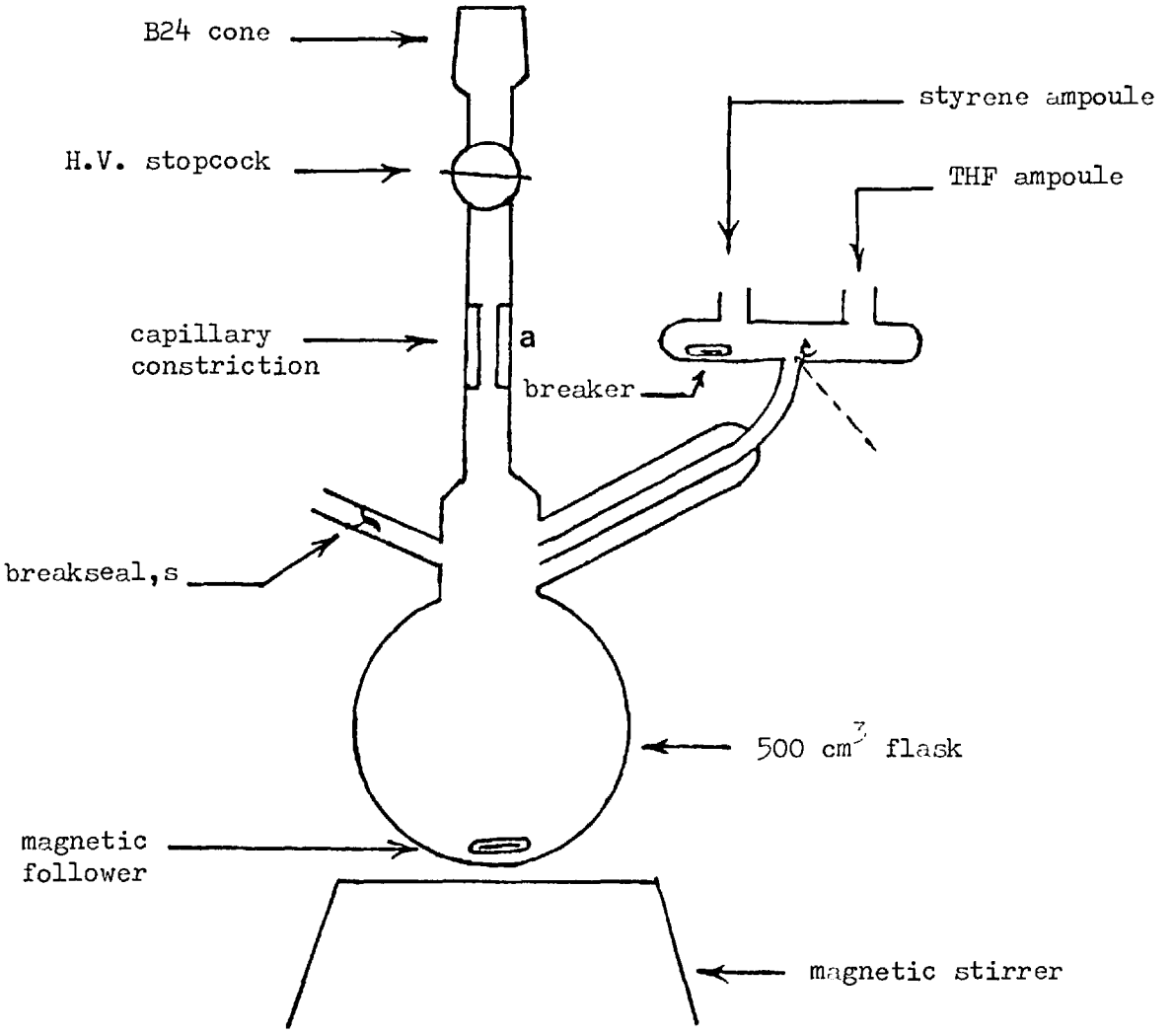
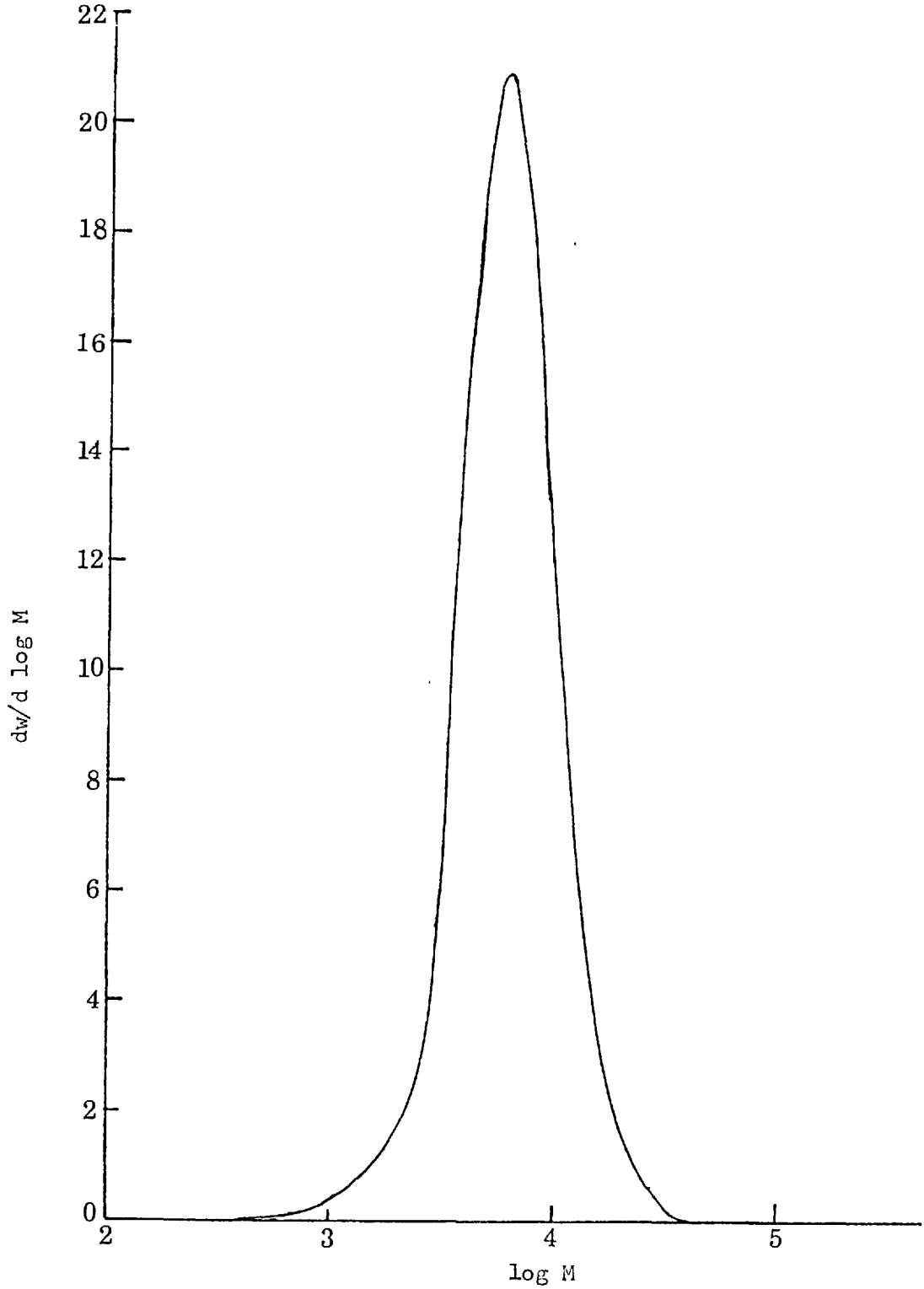


Figure 2.7. Differential Molecular Weight Distribution for a Polystyrene Sample Prepared Anionically (see Table 1.1)



CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND STABILITY STUDY OF POLYEPICHLOROHYDRIN

A. POLYMERIZATION OF EPICHLOROHYDRIN

3.1. Introduction

Epichlorohydrin and other 1,2-epoxides or oxiranes undergo ring opening polymerization. The angle strain in the three membered ring is the main driving force for the polymerization of epoxides (152).

The polymerization of 1,2-epoxides can be described in terms of three different mechanisms:

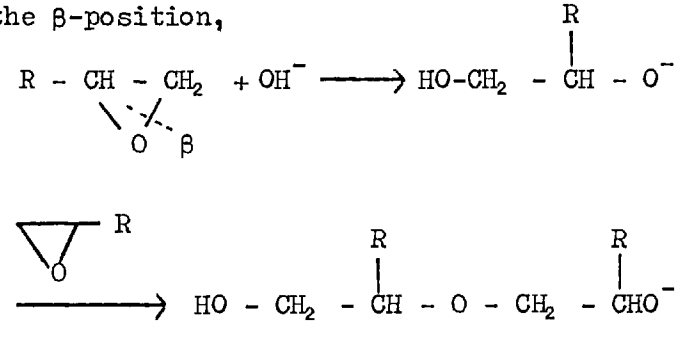
(i) anionic (base catalysed)

(ii) cationic (acid catalyzed) and

(iii) coordination.

The catalysts used for the polymerization are tentatively divided into three groups on the basis of their role in the polymerization reaction.

(i) Anionic or base-catalysed polymerization. The anionic polymerization occurs by nucleophilic attack of the anion on the epoxide, predominantly on the primary rather than secondary carbon atom in the unsymmetrically substituted epoxides (153) and the subsequent displacement of the ether-like oxygen in the strained three-membered ring with the ring opening at the β-position,



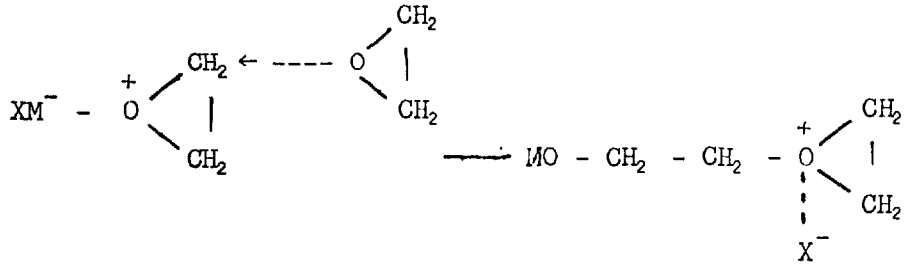
(3.1)

The catalysts used for anionic polymerization are alkali hydroxides (154) and alkoxides (155,156). Because of simultaneous elimination reactions, substituted epoxides do not form high molecular weight

polymers (157).

In base-catalysed polymerization of epichlorohydrin, there are other complicacies and the synthesis of epichlorohydrin polymers by anionic mechanism is unknown.

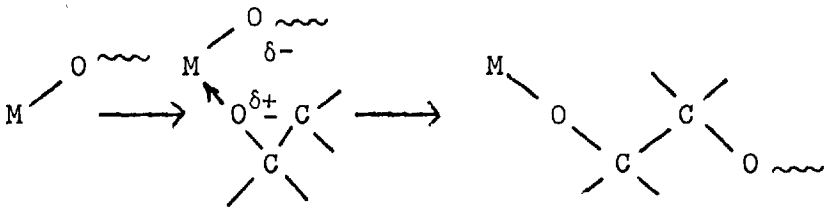
(ii) Cationic or acid-catalysed polymerization. Cationic polymerization involves a rearward nucleophilic attack of an epoxide molecule on a carbon atom of the epoxide forming the propagating oxonium ion. The ether-like oxygen in the oxonium ion is displaced resulting in the ring opening



(3.2)

The conventional catalysts for cationic polymerization of epoxides are Lewis acids such as BF_3, $AlCl_3$, $SnCl_4$, $TiCl_4$ and other metal halides (158). Catalytic activity of certain metal alkyls and their water modified compounds in the polymerization of certain epoxides has also been explained in terms of cationic mechanism (159,160). Cationic polymerization has an important difference from anionic polymerization in that while alkyl substitutions in the ethylene oxide ring are detrimental to the anionic polymerization, they favour cationic polymerization (161).

(iii) Coordination polymerization. Coordination polymerization combines features of both the anionic and cationic mechanism (161). It involves coordination of the monomer oxygen at a Lewis acid catalyst site M as shown below, followed by attack on the activated monomer by a growing alkoxide already bound to the site,



(3.3)

A coordination catalyst regulates the mode of fitting of the monomer in the polymer backbone and thereby controls the stereoregularity and molecular weight of the polymer. Some of the very effective catalyst systems developed and studied for stereoselective polymerization of epoxides are $FeCl_3$-PO (162), usually called Pruitt-Baggett catalyst, Et_2Zn-H_2O (163) and Et_3Al-H_2O-acetylacetonate (164). Exact structure of the catalyst site in none of these catalyst systems has been conclusively established (161). However some authors (159-167) have made important contributions to the elucidation of the mechanisms of the epoxide polymerization with coordination catalysts. It has been established that a number of metal atoms form a single catalyst site and that the number of polymer molecules formed is small compared to the number of metal atoms used in the catalyst. In stereoselective polymerization using coordination catalysts, along with stereoregular isotactic polymers, substantial amounts of amorphous polymers are also formed.

In polymerization of 1,2-epoxides whether by anionic, cationic or coordination mechanism, the ring opening has been found to take place with inversion of configuration at the carbon atom undergoing nucleophilic attack (168,169).

The first epichlorohydrin polymer prepared with Friedel Crafts catalysts such as $SnCl_4$ was reported as early as 1949 (170) and was a low molecular weight viscous liquid. A solid crystalline polymer prepared from the monomer was also disclosed by Pruitt and Baggett in 1959 (171). Ishida (172) prepared low molecular weight amorphous

and relatively high molecular weight crystalline polymers using $FeCl_3$-PO, $FeCl_3$-epichlorohydrin complex catalysts and some other organometallic catalysts such as Et_3Al, Et_2Zn. Those crystalline and low molecular weight amorphous polymers were of little practical importance. It was Vandenberg (101) who first reported amorphous epichlorohydrin homo- and co-polymers of high molecular weights prepared by the use of modified alkyl-Al catalysts also developed by him (164). These high molecular weight polymers were elastomeric in nature. Two of these polyether elastomers amorphous polyepichlorohydrin and a (1:1) epichlorohydrin-ethylene oxide copolymer are now commercially available from Hercules Inc. under the names 'Herchlor H' and 'Herchlor C' respectively. In the preparation of these elastomers, a mixture of crystalline and amorphous polymers is produced. The composition of the catalysts, which are alkyl Al-H_2O and alkyl Al-H_2O-acetylacetonate, can be adjusted to get higher yields of either the amorphous or crystalline products (100,101). The exact mechanism of polymerization has not been established. However, as with other epoxides, a cationic mechanism was proposed for polymerization reactions using the alkyl Al-H_2O catalyst because of the high rates of the polymerization reactions. In polymerization reactions using alkyl Al-H_2O-acetylacetonate catalyst, where the rates of polymerization are slow, a coordination mechanism has been proposed (173).

3.2. Polymerization with Triethyl Al-H_2O Catalyst : Experimental Procedure

3.2.1. Purification of Materials

(a) n-Heptane (Koch-Light Lab.) was stirred over powdered CaH_2 overnight and then fractionally distilled. The middle fraction distilling at 98°C (1 atm.) was collected and used.

(b) Diethyl ether (M. and B.). Anhydrous diethyl ether from a fresh bottle was tested for peroxide. It was found free from peroxide and

was used without further purification.

(c) Epichlorohydrin (Aldrich Chemical Co.) was fractionally distilled under a N_2 atmosphere. The middle fraction distilling at 115 - 117°C (1 atm.) was collected and used.

(d) Triethyl-Al (Koch-Light Lab.) was supplied in an iron cylinder (assay ~ 90%; density, 0.887 g cm^{-3} at room temperature). It was used without further purification. The cylinder was provided with a screw cap and a side tube. A requisite volume of the catalyst was withdrawn with a dry syringe after the space below the screw cap and the syringe were properly flushed with argon. The catalyst was introduced directly into the polymerization flask for epichlorohydrin containing n-heptane. The flask was flushed with argon beforehand.

3.2.2. Polymerization and Separation of the Polymer into Amorphous and Crystalline Fractions

(a) Polymerization procedures adopted here have been described elsewhere (174). The ultimate composition of the reactants and solvents used for polymerization was as follows:

n-Heptane,	15 cm^3;
Diethyl ether,	120 cm^3;
Triethyl Al,	2.6 cm^3 ≡ .018 mole;
water,	0.18 g ≡ .01 mole;
Epichlorohydrin,	50 g;
Catalyst composition,	$[(C_2H_5)_3Al]/[H_2O]$ = 1:0.55
	$[ECH]/[(C_2H_5)_3Al]$ = 30

The reaction was carried out at 30°C for 24 h and then stopped by adding 20 cm^3 methanol.

(b) Purification and separation of the polymer into amorphous and crystalline fractions. The polymer was purified and then separated

into two fractions: one fraction soluble in acetone and the other, insoluble. The procedure for the purification and separation has been described elsewhere (175). No antioxidant was however used in the present experiment. The acetone soluble polymer was precipitated in MeOH in a Waring blender and dried to a constant weight in a vacuum oven at 45°C. This polymer was elastomeric, amorphous, soluble in C_6H_6, THF, $CHCl_3$ and acetone, but insoluble in alkanes. The acetone insoluble polymer was also dried to constant weight at 45°C. This polymer was a tough white solid insoluble in C_6H_6, $CHCl_3$, acetone and cold THF but soluble up to an extent of 0.2 - 0.3% w/v in hot THF. The polymer remained in solution even when cooled. This polymer was probably partly crystalline.

Total monomer converted into polymer = 75.6% w/w

Amorphous fraction = 30.7% w/w of the total polymer

Crystalline fraction = 69.3% w/w of the total polymer

The amorphous and the crystalline PECH samples prepared in this work were designated as E11 and E12, respectively. As the polymer samples were to be used for the synthesis of graft copolymers by anionic coupling reactions, they were not mixed with any antioxidant.

(c) Storage of the polymers. The polymer samples E11 and E12 were stored in a vacuum desiccator wrapped in black paper for future use. The samples sent to RAPRA for GPC analysis were also wrapped with Al-foil.

3.2.3. Characterization of the Polymers

(a) Infra-red spectra of the samples E11 and E12 (figures 3.1 and 3.2 respectively) were recorded using a film of the polymers on a NaCl plate with a Perkin-Elmer Model 157G Grating Infra-red Spectrophotometer. The film for E11 was cast from CH_2Cl_2 solution and that for E12 from THF solution. These were compared with those in the literature (172).

(b) Proton nuclear magnetic resonance (NMR) spectra of the samples E11 and E12 were recorded with a Varian HA-100 Spectrometer. The polymer E11 was freeze-dried from C_6H_6 solution for this purpose and analysed as a solution in deutro-chloroform. The spectrum of the dried sample E12 was recorded in deuterated DMSO. Neither of the spectra was properly resolved since a single broad peak was obtained.

(c) Elemental microanalysis of the polymers was carried out and compared with the composition of the purified commercially available polymer ('Herchlor H' supplied by Hercules Inc.). The purification of 'Herchlor H' is described in section 4.2.1.

(d) Thermal analysis. The PECH samples were analysed using a DuPont-900 Thermal Analyser, fitted with a Differential Scanning Calorimetry (DSC) cell. Instructions set out in the manual were followed. The sample E11 was freeze-dried and the sample E12 was dried in vacuo at 60°C for this purpose. The samples were cut into small pieces and placed in the DSC pan. Analysis was carried out under an atmosphere of nitrogen, at a heating rate of 10°C per minute and with an empty pan as reference. Indicated temperatures were corrected to give T_{corr} according to data given in the instruction manual.

(e) GPC analysis. The number and weight average molecular weights of the samples E11 and E12 and their $\bar{M}_w/\bar{M}_n$ ratios are given in table 3.1.

3.3. Results and Discussions

(a) I.R. spectrum of the crystalline polymer sample, E12 is different from that of the amorphous polymer sample, E11, by the sharpness of the peaks in the fingerprint region, 1350 - 900 cm^{-1}, in the former. There are also some extra peaks at wave numbers 1287 cm^{-1} (medium), 1238 cm^{-1} (medium), 1177 cm^{-1} (medium) and 1040 cm^{-1} (weak) in the crystalline polymer (figure 3.2). The spectra of the two polymers are similar to

those in the literature (172). But these are not of any practical significance for the elucidation of the microstructures of the polymers (176).

(b) NMR spectra. Because of the similar shielding effect of Cl and etheral O on the three different types of protons in PECH, the chemical shifts due to the protons were at the same position (3.63 ppm from TMS). That is why the spectra were not properly resolved.

(c) The elemental compositions of the polymer samples agreed reasonably with the calculated values (Table 3.1).

(d) Thermal analysis. The acetone insoluble polymer E12 was partly crystalline. It had a T_g at -25°C and a T_m at 108°C. The T_m was slightly lower than the literature T_m values (111°C- 120°C) of different crystalline polyepichlorohydrins measured by microscopic and dilatometric methods by Dreyfuss (176). The value of T_m will, of course, depend on the rate of heating in the measurement. In crystalline polymers like poly(propylene oxide), irregular structures were also found to disturb crystallization and thereby depress the melting point (177).

The acetone soluble polymer was virtually completely amorphous and had a T_g at -27°C. As expected, the T_g of the amorphous polymer was much sharper than that of the partly crystalline polymer. T_g values of 'Herchlor H' are -28.5°C measured by DTA and -27°C measured by dilatometry (178).

(e) Molecular weights and molecular weight distribution. The number and weight average molecular weights of the amorphous and crystalline polyepichlorohydrin samples prepared in this work (Table 3.1) were relatively high but similar to the literature values of polymers prepared under identical conditions (175). The broad distribution in molecular weights as measured by $\bar{M}_w/\bar{M}_n$, are characteristic of polymers prepared by cationic mechanisms.

B. STABILITY STUDY OF AMORPHOUS POLYEPICHLOROHYDRIN FREE FROM ANTIOXIDANT

3.4. Introduction

During the period of characterization of the amorphous polyepichlorohydrin sample E11, it was left exposed to sunlight. The polymer was found to become progressively brownish and after a month's exposure to sunlight it had a very irritating smell and gave off white fumes in air, probably HCl, when the bottle containing the polymer was unstoppered. The partly crystalline polymer E12 was found to be more stable and did not become brownish so quickly. No such phenomenon was observed with E11 kept in the dark. It appeared that the amorphous polymer was undergoing oxidative degradation in the presence of sunlight. Similar degradation was also observed with the purified commercial polyepichlorohydrin samples in the absence of antioxidant. Some stability experiments were, therefore, conducted on the polyepichlorohydrin E11.

3.5. Experimental

(a) A portion of the polymer E11 was kept in the dark (wrapped with Al-foil); another portion was left exposed to sunlight. Reduced viscosities, (η_{sp}/c) of a freshly made solution (conc. 4.0 g dm^{-3}) in distilled toluene of the samples were measured from time to time at 25°C (curves I and II, figure 3.4). Similarly a solution of the sample in toluene (conc. 4.0 g dm^{-3}) was kept in the dark; another solution of the same concentration was left exposed to sunlight. Reduced viscosities of the solutions were measured from time to time (curves II and IV, figure 3.4).

Toluene used for the preparation of the solutions was distilled at atmospheric pressure and the middle fraction distilling at 110 - 111°C

was used. The solutions were directly filtered into the viscometer under nitrogen pressure and a modified Ubbelohde viscometer was used.

A purified commercial sample, El3 (made free from antioxidant by twice precipitation into MeOH), was also exposed to sunlight and the reduced viscosity of a freshly made solution in toluene (conc. 4.0 g dm^{-3}) was measured from time to time. A solution of El3 in toluene (conc. 4.0 g dm^{-3}) was also exposed to UV light (from a medium pressure mercury discharge lamp with envelope removed) and the reduced viscosities were measured from time to time over a period of 24 h. The solution was kept in a pyrex bottle. The results are given in figure 3.5.

(b) The I.R. spectrum of the sample El1 exposed to sunlight for a month (measured on a film cast from CH_2Cl_2 solution on NaCl plate) is given in figure 3.3 (a). A similar spectrum of a film of the polymer exposed to UV light from a high pressure mercury discharge lamp for 4 h was also recorded (figure 3.3 (b)).

3.6. Results and Discussions

Viscosity results (figure 3.4) show that the amorphous solid polyepichlorohydrin sample El1 remained stable in the dark (curve I) up to 110 days. The same sample, when exposed to sunlight (bright sunlight during the period of these studies) underwent chain cleavage (curve II) initially at a slower rate and then at a faster rate. Similar cleavage was observed with the purified commercial sample El3 (curve V). Probably this type of degradation is autocatalytic. From many other experiments, it was noted that the rate of degradation depended both on the extent to which the polymer was free from antioxidant, and the intensity of sunlight.

Sample El1 in toluene solution also underwent chain cleavage in presence of sunlight (curve IV) but the rate of cleavage gradually

decreased. Possibly some cross-linking reaction was also operative together with cleavage. The same polymer in toluene solution kept in the dark did not show any marked change in reduced viscosity for about two weeks but then the reduced viscosity increased slowly (curve III). Here the cross-linking reaction might have occurred along with backbone cleavage, but the cross-linking was predominant.

The polymer sample, E13, in toluene solution on exposure to UV light (wavelength near 375 nm) also underwent cleavage showing a decrease in reduced viscosity (figure 3.5) although the extent of cleavage in 24 h was not very pronounced.

The I.R. spectrum of the solid polyepichlorohydrin degraded by sunlight (figure 3.3 (a)) showed a sharp peak at 1730 cm^{-1} due to the non-conjugated $>C = O$ group and a broad peak in the region 3600 - 3300 cm^{-1} due to hydrogen bonded OH absorption from hydroxide and also possibly from hydroperoxide. A film of the polymer exposed to UV light for 4 h also showed similar but relatively sharper peaks at the corresponding positions (figure 3.3 (b)). Thus the polymer degradation in the presence of sunlight is an oxidative type of degradation, induced by solar UV light. The polymer was found to absorb UV light in the wave length region increasing from 243 nm and had a maximum absorption at 260 nm (sp. extinction coefficient = 0.08 $dm^3 g^{-1} cm^{-1}$).

Oxidative photodegradation of polymers has been discussed elsewhere (179,180). Polymers widely studied in this connection are rubber modified polystyrene, polyolefins and polyvinyl chloride. The different chemical groups responsible for sensitization of polymers for photodegradation are mostly carbonyl and hydroperoxy groups and also unsaturation in the unsaturated polymers. In most cases, hydroperoxides are initially formed

and these undergo further reactions forming carbonyl and hydroxyl groups. Trace amounts of low molecular weight impurities such as initiators (peroxides, hydroperoxides), catalysts (metal salts, metal oxides, metals) inhibitors, solvents and other agents left in the polymer very often act as photo-initiators or photosensitizers. The initiation process in a photochemical degradation may be induced by impurities according to the following reactions:

$$\text{initiator (external)} + h\nu \longrightarrow 2R\cdot \qquad (3.4)$$

$$PH\ (\text{polymer}) + R\cdot \longrightarrow P\cdot + RH \qquad (3.5)$$

$$\sim\sim CH_2 - \underset{\displaystyle R'}{\overset{\displaystyle R'}{\underset{|}{\overset{|}{C}}}} - CH_2 - \underset{\displaystyle R'}{\overset{\displaystyle R'}{\underset{|}{\overset{|}{C}}}} \sim\sim + R^{\circ} \longrightarrow \sim\sim CH_2 - \underset{\displaystyle R'}{\overset{\displaystyle R'}{\underset{|}{\overset{|}{C^{\circ}}}}} + R - CH_2 - \underset{\displaystyle R'}{\overset{\displaystyle R'}{\underset{|}{\overset{|}{C}}}} \sim\sim \qquad (3.6)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (3.7)$$

$$PH + RO_2\cdot \longrightarrow P\cdot + ROOH \qquad (3.8)$$

$$S\ (\text{solvent, initiator or catalyst photosensitizer}) + h\nu \longrightarrow S^* \qquad (3.9)$$

$$S^* + \text{Polymer} \longrightarrow S + \text{Polymer}^* \longrightarrow \text{macroradicals} \qquad (3.10)$$

Macroradicals may also be formed by the cleavage of a polymer bond sensitized by direct absorption of energy greater than the respective bond dissociation energy. A macroradical thus formed reacts with oxygen to form the propagating peroxy macroradical. These reactions are followed by other reactions resulting ultimately in further cleavage of the polymer and the formation of carbonyl and hydroxyl groups.

In the absence of sufficient information it is difficult to make any conclusion about the mechanism of cleavage in PECH. The formation of -OH and $>C=O$ groups in the degraded polymer may be expected to have taken place in a similar way to that in the oxidative degradation in polyethylene and polypropylene (179). The formation of macroradicals in PECH may take place by cleavage of any C-H bonds or C-Cl bond or more

likely by the cleavage of C-O-C etheral bonds having relatively lower bond energy. Probably small amounts of solvent trapped in the polymer or other impurities such as metal salts coming from the catalysts act as photosensitizers. HCl was also probably formed by the degradation reactions. Other chlorine-containing polymers on exposure to UV light have been observed to evolve HCl. The present experiments are inconclusive about these possibilities. However, these experiments established that PECH, free from antioxidant and suitable for anionic coupling reactions was stable if stored in the dark.

Table 3.1. Molecular Weights and Elemental Composition of the Amorphous and Crystalline Polyepichlorohydrin Samples (Section 3.2.2 (b))

Sample	Type of polymer	GPC Results $\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Elemental % Composition [a] C	H	Cl	O
E11	Amorphous	1.61	12.0	7.48	38.74	5.53	38.13	17.60
E12	Crystalline	4.17	24.69	5.92	38.56	5.47	37.81	18.16
E13 [b]	Amorphous	1.30	13.16	10.09	38.80	5.62	37.47	18.11

[a] Theoretical composition C = 38.94%, H = 5.45%, Cl = 38.32%, O = 17.29%

[b] A purified commercial sample (made free of antioxidant by two precipitations)

Figure 3.1. Infra-red Spectrum of a Film of Amorphous Polyepichlorohydrin Sample E11

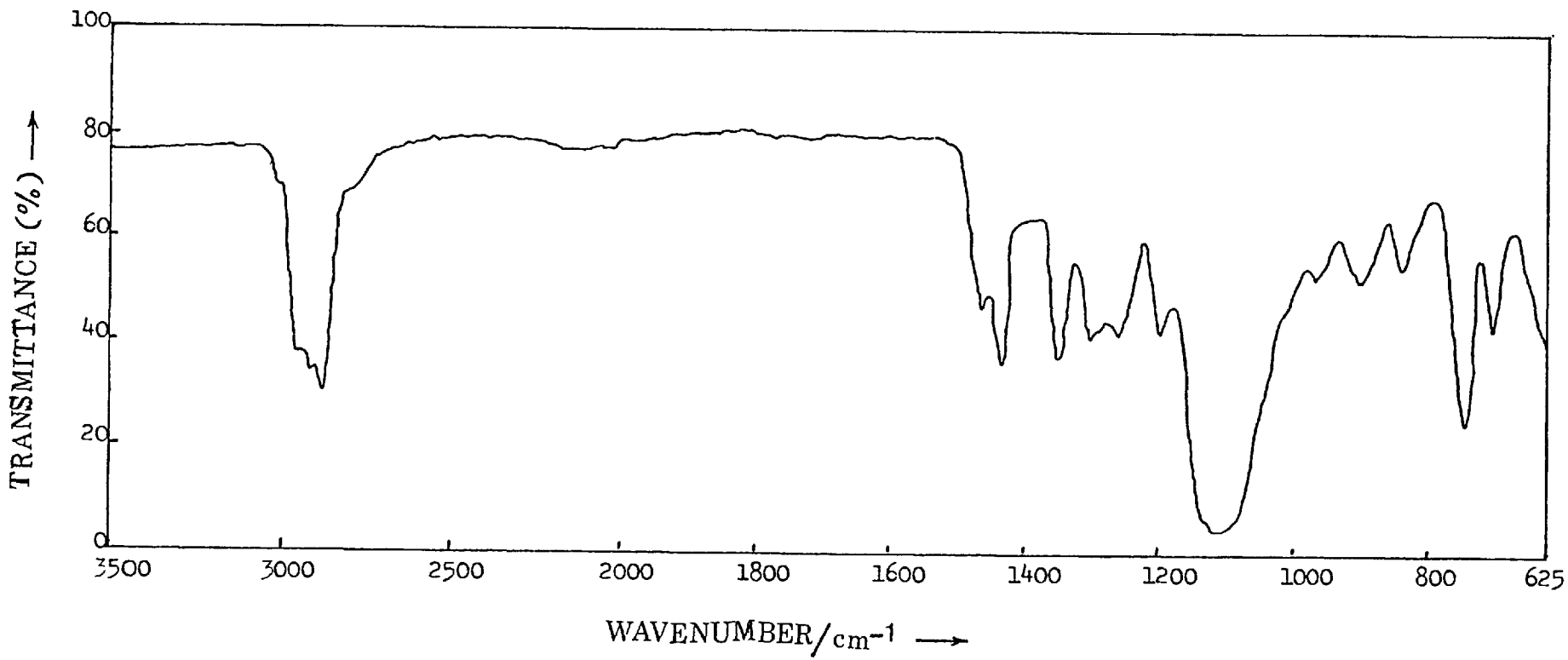


Figure 3.2. Infra-red Spectrum of a Film of Crystalline Polyepichlorohydrin Sample E12

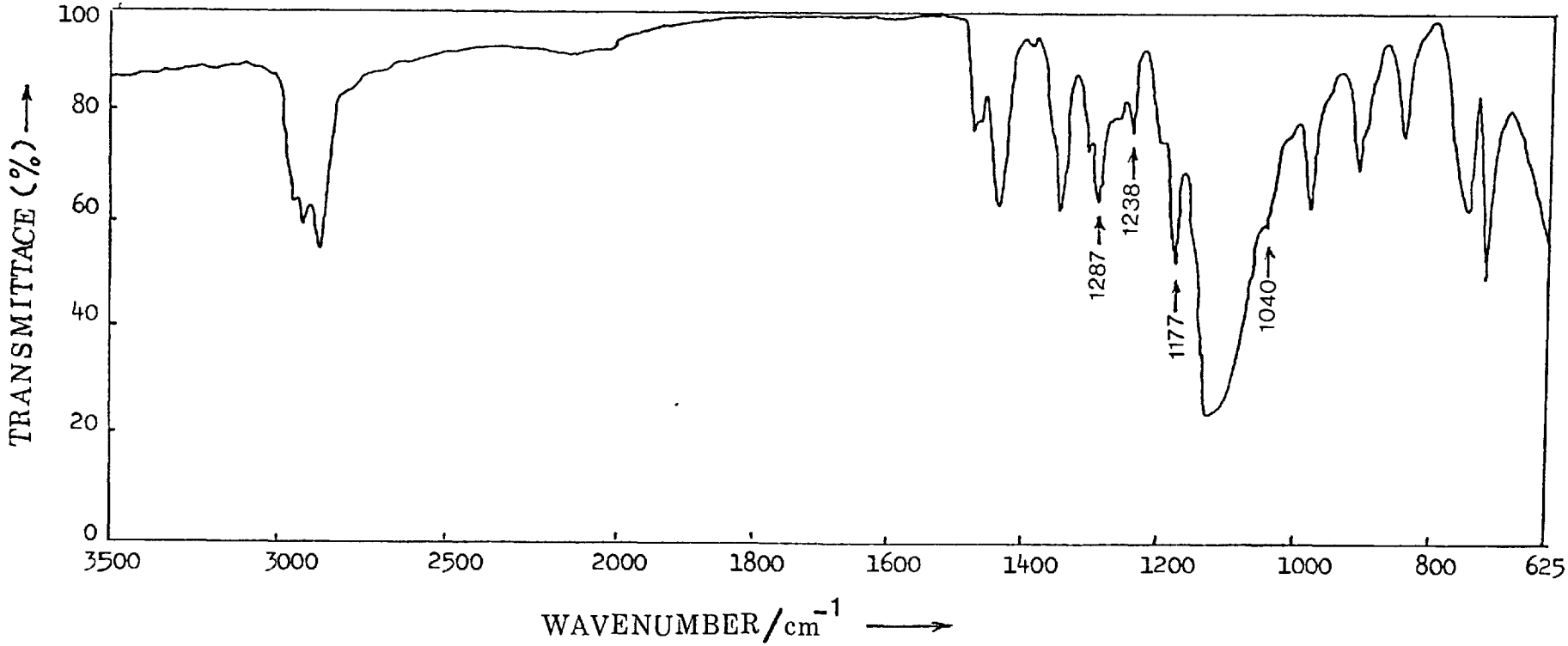


Figure 3.3. Part of the Infra-red Spectra of Amorphous PECH Degraded by UV Light

(a) a film, cast from the polymer exposed to bright sunlight for a month,

(b) a film of the polymer directly exposed to high pressure mercury discharge lamp.

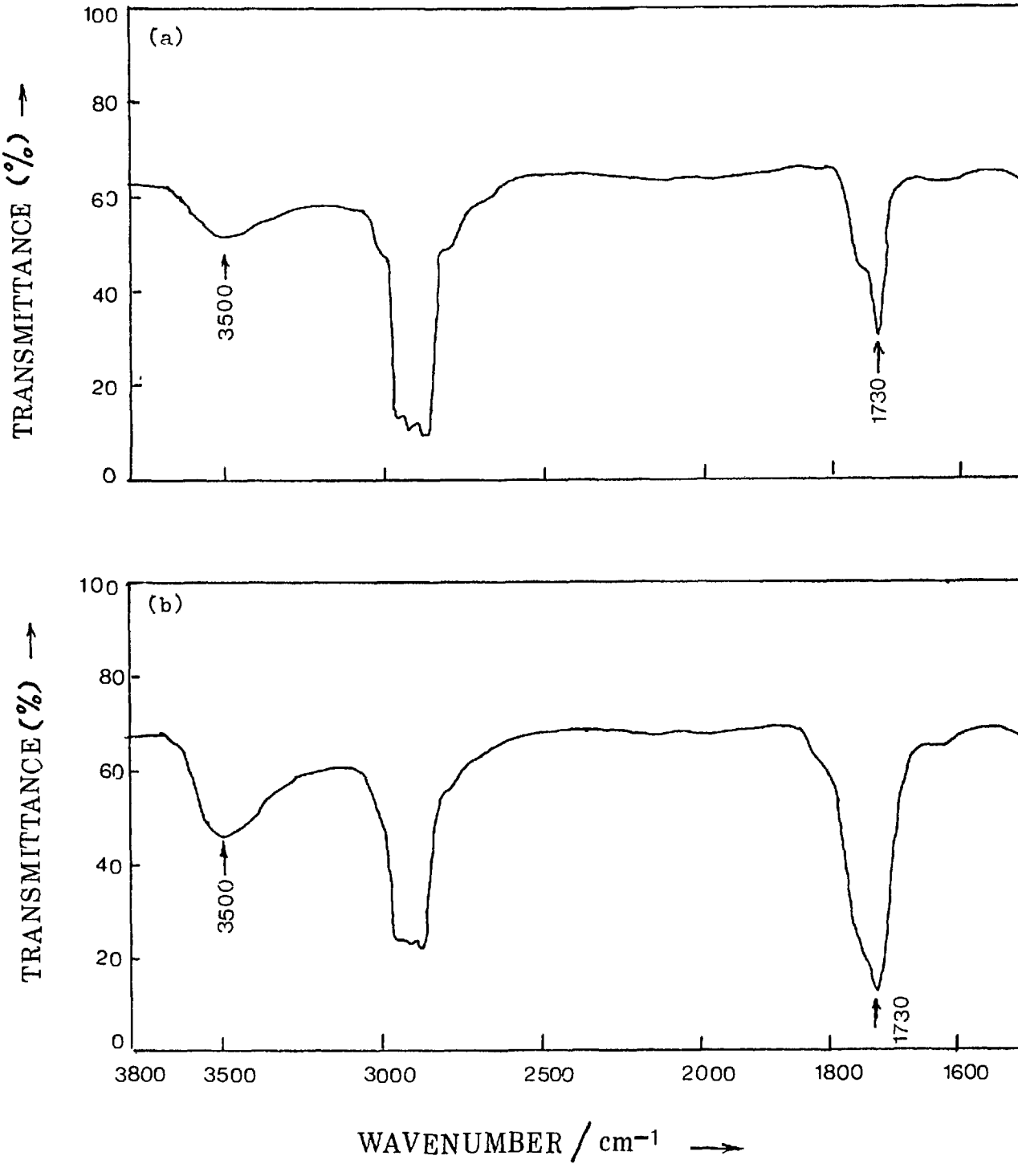


Figure 3.4. Reduced Viscosities of Amorphous PECH, Sample E11, Free from Antioxidant

[Solvent, Toluene; conc., 4.0 g dm^{-3}; Temp. of viscosity measurement, 25°C;
curves: (I) solid sample kept in the dark, (II) solid sample exposed to sunlight,
(III) sample in solution kept in the dark, (IV) sample in solution exposed to sunlight
(V) a commercial solid sample E13 (free from antioxidant) exposed to sunlight.]

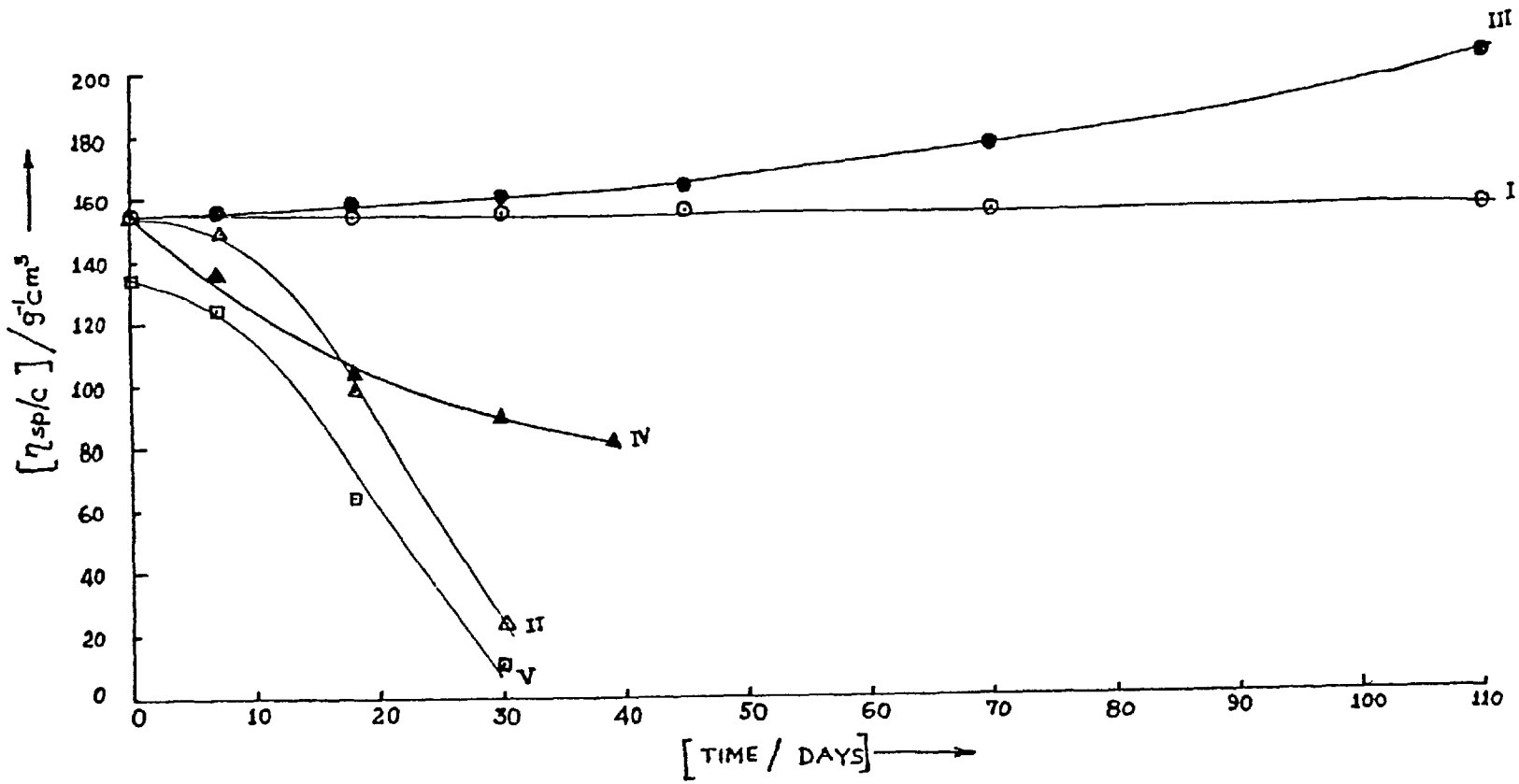
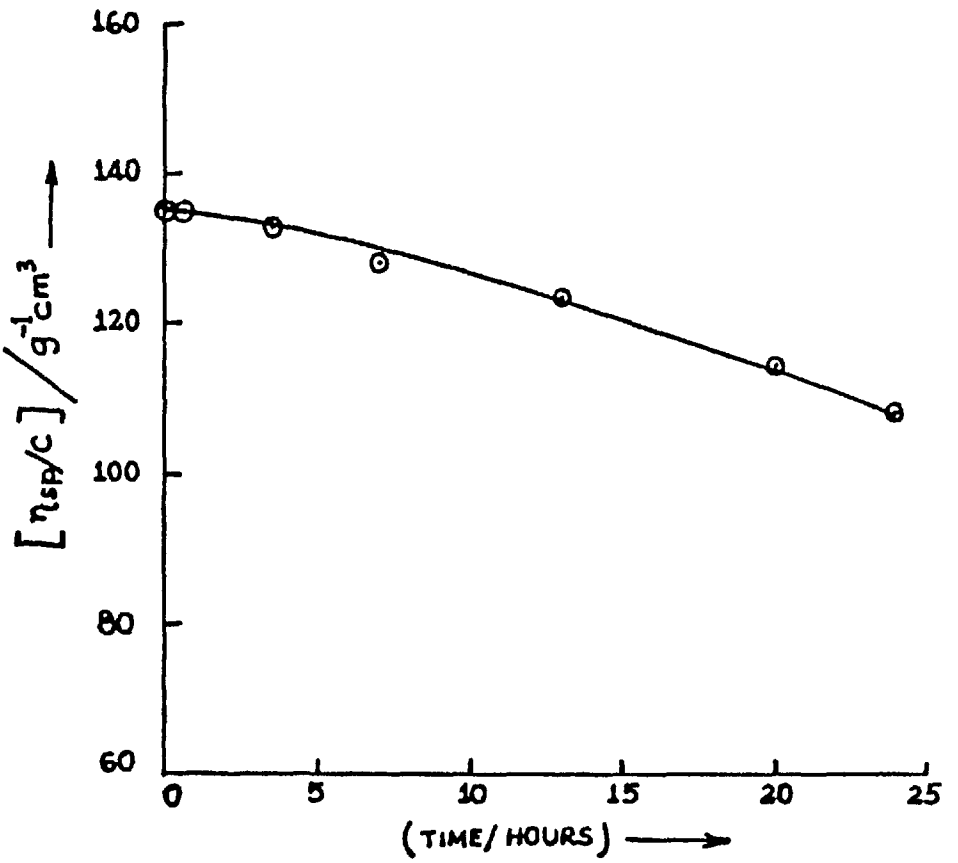


Figure 3.5. Reduced Viscosities of a Sample of Amorphous PECH in Toluene Solution Exposed to UV Light

[Conc., 4.0 g dm^{-3}; temp. of viscosity measurement, 25°C; type of lamp, medium pressure mercury discharge lamp with envelope removed; solution in pyrex vessel 35 cm away from the lamp]



CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF POLY(EPICHLOROHYDRIN-g-STYRENE) BY THE CARBANIONIC DEACTIVATION (ANIONIC COUPLING) TECHNIQUE AND CLEAVAGE OF POLYEPICHLOROHYDRIN BY n-BUTYL LITHIUM

A. GRAFTING OF POLYSTYRENE ONTO POLYEPICHLOROHYDRIN

4.1. Introduction

Synthesis of graft copolymers using multifunctional polymer backbone with halogen functions or other electronegative reactive functional groups by coupling reactions with nucleophilic living polymers has been surveyed in Section 1.2.2A. Epichlorohydrin homo- and co-polymers with pendant chloromethyl functional groups are good examples of multifunctional electrophilic backbone polymers which are used for the synthesis of graft copolymers by carbanionic deactivation or anionic coupling reactions. A literature survey showed only one example (59) of the synthesis of graft copolymers of epichlorohydrin polymers by this technique and this report lacked details of molecular weights of the products and possible side reactions occurring during grafting experiments.

In the synthesis of graft copolymers in the present experiments, the epichlorohydrin polymers used were polyepichlorohydrin (PECH), 'Herchlor H', supplied by Hercules Inc. Polymers prepared in this laboratory (Section 3.2.2) were also used. The living polymers used for the coupling reactions were polystyryl lithium and polystyryl potassium prepared according to the procedure described in Section 2.2.3.

A well-defined graft copolymer should obey the following criteria:

(i) the backbone polymer should be, as far as possible, of narrow molecular weight distribution (MWD)

(ii) the branches or grafts should be monodisperse

(iii) the degree of grafting should be uniform for all of the backbone polymer molecules.

In order to fulfil these conditions, care was taken to prepare and use monodisperse living polystyrene. As the commercial PECH, 'Herchlor H' had a very wide molecular weight distribution, it was roughly fractionated in some cases, although this did not narrow the dispersity greatly. However, all the PECH samples were carefully purified to remove the phenolic antioxidants and other possible additive impurities which might deactivate the living polymer. The coupling reactions were carried out at a constant temperature with dropwise addition of a solution of the living polymer to the PECH solution. Vigorous stirring of the reaction mixture was maintained to ensure uniform grafting of the PECH.

4.2. Experimental Procedures

4.2.1. Purification of Materials

(a) Commercial PECH, 'Herchlor H'. 'Herchlor H' was found soluble up to an extent of about 2% w/v in C_6H_6, toluene, acetone and 3 - 4% w/v in $CHCl_3$, CH_2Cl_2, THF and C_6H_5Cl on heating to about 50 - 60°. The solubility in most solvents was less than about 1% w/v at room temperature.

The polymer gum cut into small pieces was usually swelled in C_6H_6 overnight and then dissolved by heating at 60 - 65°C for 3 - 4 hours to make an approximately 2% w/v solution. About 5 - 10% w/w of the swollen polymer remained undissolved and was rejected by filtration. The polymer was twice precipitated from a clear benzene solution into a five-fold excess of methanol (BDH, Tech. grade) in a Waring blender, and dried to a constant weight in a vacuum oven at 45°C.

The purified dried samples were stored in a vacuum desiccator wrapped inside black paper in a cool place in a dark cupboard. This was necessary to avoid oxidative degradation of the purified polymers,

not containing antioxidant, in the presence of sunlight (Section 3.6). The purified polymer samples were used for the coupling reactions within a fortnight of purification. A portion of the polymer from each purified sample was washed with MeOH containing 0.1% w/v antioxidant, Topanol CA (ICI Ltd), dried and stored as described previously before characterization. This procedure was not observed, however, for the samples E5 and E7 (Table 4.1). Although degradation was not observed for E5 and E7, extensive degradation of other purified polymers was noticed in many cases within a month of purification when the samples were not stored in bottles wrapped with Al-foil or black paper.

(b) Topanol CA (ICI Ltd). This antioxidant, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butyl phenyl) butane was used as a 0.1% w/v solution in MeOH in the precipitation of different PECH and graft copolymer samples.

(c) Benzene used for dissolving polyepichlorohydrin and for freeze drying was distilled once and the middle fraction distilling at 79 - 80° (1 atm.) was collected. The solvent used for the preparation of living polystyrene and also for dissolving PECH for the coupling reaction was purified in the same way as described in Section 2.2.2.

(d) THF was purified and stored as described in Section 2.2.2.

(e) Styrene was purified and stored as described in Section 2.2.2.

(f) n-BuLi and Cumyl-K were estimated quantitatively and used as described in Section 2.2.2.

(g) Toluene (Koch-Light Laboratories Ltd) was dried over CaH_2 and then fractionally distilled. The middle fraction distilling at 110°C (1 atm.) was degassed on the vacuum line to 10^{-5} Torr and then distilled onto Na/K alloy. The solvent was stirred over Na/K alloy for 8 h, then degassed and finally distilled into the polymerization flask (Figure 4.1, flask A) for the preparation of $PS^{-}Li^{+}$ in toluene.

4.2.2. Grafting Procedure

For PECH samples and living PS samples used, see Table 4.1 and 4.2 respectively; for the experimental conditions of grafting reactions, see Table 4.3.

(a) Preparation of living polystyrene. The procedure used for the synthesis of living polystyrene has been described before (Section 2.2.3) and the experimental conditions for the preparation of different living polystyrene samples used have been outlined in Table 4.1. For graft copolymerization experiments G5, G7, G11 and G12, the living polystyrene samples S5, S7, S11 and S12 were prepared in flask 'A' (Figure 4.1). For graft copolymerization experiments G140 - G144, the living polystyrene sample S28 was prepared in a flask similar to that in Figure 2.6. In both cases, polymerization was conducted in flasks sealed under vacuum as before. A portion of living polystyrene was separated from each polystyrene sample used in the coupling reaction, terminated and precipitated separately as described in Section 2.2.3. The molecular weight of this polystyrene was regarded as the molecular weight of the living polystyrene used for the coupling reaction.

(b) Preparation of polyepichlorohydrin solutions for coupling reactions. A weighed amount of the purified PECH was dissolved in C_6H_6 and the mixture was filtered to remove insoluble additives and introduced into the coupling flask 'B' (Figure 4.1). The solution was frozen and the polymer freeze-dried in the vacuum line for 28 h. When a pressure of less than 10^{-5} Torr was attained, the required volume of the solvent was distilled into the flask 'B' from a calibrated flask. C_6H_6 was distilled over from living polystyryl lithium, THF and toluene from Na/K alloy, as the experiments demanded. When the polymer was dissolved in the solvent, the solution was degassed to 10^{-5} Torr and then

the flask was sealed off the vacuum line at constriction 'L'. For coupling experiments G140 - G144 different weighed amounts of PECH were freeze-dried from C_6H_6 solution in separate long necked flasks in the vacuum line. The flasks were filled with dry argon and then removed from the vacuum line. The required volume of the purified solvent was syringed into the flasks closed by rubber septa. The polymer in each experiment was completely dissolved in the solvent by heating the flask and contents at 35 - 40°C in a liquid paraffin bath while stirring the solution with a magnetic stirrer. The amounts and concentrations of PECH and the solvents used in different coupling experiments are given at the footnote of Table 4.3.

(c) Coupling reactions. For experiments G5, G11 and G140 both the PECH and the $PS^- Li^+$ were in C_6H_6 solution; for experiment G12 both polymeric reactants were in toluene with the flasks cooled at -78°C; for experiment G7, both polymeric reactants (PECH and $PS^- K^+$ in this case) were in THF and for experiments G141 - G144, the PECH was in THF and $PS^- Li^+$ was in C_6H_6 solution. In all cases, the living polymer solution was added drop by drop to the PECH solution. For experiments G5, G11, G7 and G12 a specially designed flask (Figure 4.1) was used. The coupling reaction was carried out by breaking the breakseal with an iron breaker covered by glass, regulated by a magnet and adding the living polymer solution dropwise from the flask 'A' to the PECH solution in the flask 'B' and thoroughly shaking the latter manually. As each drop of the living polymer solution was added to the PECH solution, the characteristic red colour of the latter disappeared almost instantaneously. Addition was complete in about 15 minutes.

In the experiments G140- G144, the living polymer solution was syringed out of the flask (Figure 2.6) through the breakseal 'S' under

a pressure of argon and then introduced into the PECH solution dropwise over a period of 10 minutes, while the mixture was stirred vigorously with a magnetic stirrer.

All of the reactions occurring in the reaction flask appeared visually to be very fast but nevertheless, the reaction mixtures were stirred for a total period of time before termination by methanol including the time of addition of the living polymer stated in Table 4.3.

In the experiments G5, G11 and G12, when either benzene or toluene was the solvent, the reaction mixture was colloidal. In experiment G140, where the coupling reaction was conducted in C_6H_6 but the living polymer contained a small amount of THF, the final reaction mixture was a little hazy. In experiments G7 and G141 - G144, where either THF or THF/C_6H_6 mixture (67:33 v/v), was the solvent, the final coupling reaction mixtures were clear.

When the reaction mixture from experiment G5 was allowed to settle for 1 h, a distinct jelly-like phase settled at the bottom of the flask. The clear solution from the top of the flask was decanted off and the polymers both in the clear solution and the jelly-like phase were separately precipitated and characterized. No jelly-like phase was separated from the experiments G11 and G12, although the reaction mixtures appeared colloidal.

After a definite reaction time, the polymer mixtures were terminated by methanol and recovered as described in the following section.

4.2.3. Purification of Polymers from the Coupling Experiments

(a) Isolation of the total polymer (Table 4.4, Preliminary treatment). The separation and isolation of different fractions of polymer from each coupling experiment are outlined in Table 4.4.

The jelly-like fraction G5-II from the experiment G5 was separated by decanting off the clear solution from the top of the flask. This

jelly-like fraction G5-II was dissolved in C_6H_6 by heating at about 50°, filtered off using a sintered funnel of porosity 3 and precipitated into an eight-fold excess of MeOH. The polymer was dried to constant weight in a vacuum oven at 45°C. The clear solution from the reaction flask containing the polymer fraction G5-I was filtered and the polymer precipitated and dried as before.

The colloidal polymer mixtures from experiments G11 and G12 were diluted with more benzene to give an approximately 2% w/v solution. On dilution, the colloidal nature of the reaction mixture almost disappeared. These solutions were filtered and the polymers G11-I, G12-I were recovered separately by precipitation in methanol and dried as described previously. Fractions G11-II and G12-II were soluble in the reaction solvent-excess methanolic mixture, so a portion of the filtered solution was evaporated to dryness to recover the brown coloured sticky polymer fractions G11-II and G12-II (trace amounts), respectively.

The solvent from experiments G7 and G141-G144 carried out in either THF or C_6H_6/THF mixtures was removed at room temperature by means of a rotary evaporator at low pressures using a water-pump. The respective isolated polymers were dissolved in C_6H_6 to give a 2 - 3% w/v solutions and the solutions were filtered before precipitation of the polymer into an eight-fold excess of MeOH. Evaporation of the THF and dissolution in C_6H_6 followed by filtration effectively removed any dissolved inorganic impurities and prepared relatively concentrated polymer solutions suitable for precipitation into methanol. The precipitated polymers from these experiments were designated G7, G141, G142, G143 and G144, respectively, corresponding to the experiment numbers.

The polymers eventually isolated from experiments G5 and G7 were

not treated with antioxidant but the polymers from all other experiments were washed with or precipitated into methanol containing 0.1% w/v Topanol CA, except the samples G11-II and G12-II from experiments G11 and G12 respectively. In the latter two cases, treatment with antioxident was not carried out so that IR spectra of the polymer samples could be studied without interference from antioxidant.

All the finally precipitated polymers were quantitatively collected on pre-weighed sintered glass crucibles and dried to constant weight in the vacuum oven at 45°C.

The amount of polystyrene used in each grafting experiment was calculated from the total weights of all the fractions recovered and the known amount of PECH originally used.

(b) Purification of the graft copolymers by extraction and fractional precipitation procedure (Table 4.4, Secondary treatment). Separation of the polymers into different fractions was performed in the light of the corresponding GPC results.

Diethyl ether and cyclohexane were found to be non-solvents for PECH but solvents for low molecular weight polystyrene with $\bar{M}_n \sim 5 \times 10^3$. These two non-solvents for PECH were expected to be non-solvents for the poly(epichlorohydrin-g-styrene) copolymers, but unfortunately were found to dissolve graft copolymers with relatively short branches containing more than 75% w/w polystyrene. Indeed, no successful extraction procedure was established for the separation of the graft copolymers from the homopolypolymers in these circumstances.

The polymer sample G5-II, separated from the insoluble jelly-like polymer from experiment G5, showed two peaks in the GPC trace. The higher molecular weight polymer in this sample was believed to be a graft copolymer and was extracted several times with diethyl ether at

room temperature to remove the low molecular weight polymer mixed with it. The ether insoluble polymer was reprecipitated from C_6H_6 solution into MeOH and dried to constant weight as before. This sample was designated as G5-IIA. Its polystyrene content was found to be about 3.3% w/w by UV analysis.

Sample G5-I showed a single GPC peak corresponding to an $\bar{M}_n$ value of 9.31×10^3 and contained 3.39% w/w Cl corresponding to 8.90% w/w PECH. Unsuccessful attempts were made to separate any graft copolymer present in G5-I by extraction with diethyl ether or cyclohexane. However, sample G5-I completely dissolved in these two solvents.

The methanol insoluble polymer G11-I from experiment G11 showed two overlapping GPC peaks corresponding to $\bar{M}_{n(1)}$ (0.49×10^5) and $\bar{M}_{n(2)}$ (7.99×10^3). The higher molecular weight polymer in this mixture was believed to be the graft copolymer. Three fractions G11-IA, G11-IB and G11-IC were separated from this mixture by two different techniques. Thus fractions G11-IA and G11-IB were obtained by extraction with cold cyclohexane while fraction G11-IC was obtained by fractional precipitation.

To separate the fractions G11-IA and G11-IB, about 5 g of the polymer G11-I was extracted three times with cold cyclohexane, each time with about 100 cm^3 of the solvent and then centrifuged. An insoluble polymer fraction deposited at the bottom of the centrifuge tube which was dissolved in benzene and precipitated in MeOH to recover the polymer fraction G11-IA (about 0.3 g). Fraction G11-IB, as a turbid solution, was recovered by evaporating off cyclohexane, dissolving the solid polymer in C_6H_6 and precipitating in MeOH. The separation of the graft copolymer by this extraction procedure was not completely successful however because of the fine colloidal nature of the mixture in cyclohexane.

The polymer fraction G11-IC from G11-I was separated by the fractional precipitation method according to the procedure described in the literature (181). A 1% w/v solution of the polymer was used and methanol was used as the precipitant. A suitable solvent-nonsolvent ratio was discovered for each sample which would dissolve the polystyrene used in the coupling reaction. Fractionation was conducted by dropwise addition of the precipitant from a graduated burette to a fast-stirred solution of the polymer in a special two-necked flask with a tap and a cone at the bottom as shown in Figure 4.2. The addition of non-solvent was stopped at the desired solvent/non-solvent ratio. The precipitated polymer was deposited in the cone of the flask as a gel on leaving overnight. It was redissolved and refractionated in a similar way using the same solvent and non-solvent as mentioned. In this way after two fractionations, the polymer fraction G11-IC was precipitated and dried as before.

A similar procedure was adopted for the separation of the graft copolymer sample G12-IA from the polymer mixture G12-I.

The polymer sample G7 showed two separate peaks (slightly overlapping) in its GPC trace. Only a high molecular weight fraction was separated from it by the procedure described above.

Separation of the desired fractions of the graft copolymers by fractional precipitation was successful in all the above cases as shown by the single GPC peaks of the separated samples. However, complete recovery of the graft copolymers from the respective mixtures of graft copolymers and homopolystyrene was probably not performed in these cases.

It was believed that a most successful and complete separation of the graft copolymers had been achieved for the samples G140G and G141G - G144G. The two GPC peaks in the samples G140 - G144 were widely

separated and hence a complete separation of the graft copolymers was relatively easy. As the PECH backbone and the living polystyrene samples used for the synthesis of graft copolymers in experiments G140 - G144 were the same, a standard procedure for the separation of graft copolymers could be used. A turbidimetric titration curve (Figure 4.3) described below was constructed using benzene and methanol by means of a spectrophotometric titration with a simple EEL Titrator.

Graft copolymer samples G140G - G144G were thus successfully separated, free of homopolystyrene by fractional precipitation techniques based on the information derived from the turbidimetric titrations. Each of the samples was precipitated twice from a 1% w/v solution in C_6H_6 with MeOH containing 0.1% w/v antioxidant.

No attempt was made to separate any unreacted homo-PECH from the graft copolymers since with the relatively large amounts of polystyrene of short chain length used in the grafting experiments, no PECH should be left unreacted. This assumption may not be correct for the grafting experiments G5, G11 and G12 however, where cross-linking and colloidal phase separation was observed. In this discussion, the composition of the graft copolymer samples G140G - G144G and G7G was assumed to be homogeneous.

(c) Turbidimetric titation. The turbidity of a 1% w/v solution of the polymer mixture in benzene for example, G142 was measured during progressive addition of the non-solvent, methanol, from a microburette by the use of a Model 49 EEL Spectrophotometer.

The solution (10 cm^3) was placed in a cell in the light beam of the spectrophotometer and stirred by a magnetic stirrer. After each successive addition of methanol, the absorbance was recorded directly from a type 200 EEL galvanometer connected to the photocell. The

instructions in the manual supplied (182) for the use of the instrument were carefully followed. On making concentration corrections to the absorbance, a turbidimetric titration curve was drawn (Figure 4.3) for the graft copolymer as well as for homopolystyrene. The curve for a graft copolymer showed a depression at the point at which its precipitation was complete, because of the coalescence of the precipitated graft copolymer particles.

4.2.4. Characterization of the Graft Copolymers

(a) Molecular weights $\bar{M}_n$, $\bar{M}_w$ and molecular weight distributions, MWD, by GPC. $\bar{M}_n$, $\bar{M}_w$ and MWD of the graft copolymers, P(ECH-g-S) and the component homopolymers, PECH and PS were measured by GPC. GPC traces for some samples are given in Figures 4.4 and 4.5. Molecular weights of PECH, PS and P(ECH-g-S) samples are given in Table 4.1, 4.2 and 4.7 respectively. Due to the fact that the GPC machine had not been calibrated using samples of PECH and P(ECH-g-S) copolymers, the molecular weights, $\bar{M}_n$ and $\bar{M}_w$ for these polymers are 'nominal' values. They are still, however, extremely useful in interpreting the results.

In this discussion, the $\bar{M}_n$ and $\bar{M}_w$ corresponding to the higher molecular weight peak in the GPC trace of the graft copolymer mixture with homopolystyrene was regarded as $\bar{M}_n$ and $\bar{M}_w$ of the graft copolymer. For example in Figure 4.4 (b), the graft copolymer is that with peak 'G'. Its molecular weight was therefore taken as the molecular weight of the graft copolymer. This was necessary to make a better assessment of the extent of degradation in the different graft copolymer samples during their synthesis. These molecular weights and also the molecular weights of some of the purified graft copolymers are given in Table 4.7. In most cases, these values agree reasonably well. This fact confirms the successful and alsmost complete separation of the graft copolymers

when this was attempted. In a similar way, the composition of any isolated and purified graft copolymer was assumed to be identical to the composition of the unpurified graft copolymer in its mixture with component homopolystyrene.

(b) Infra-red Spectra of the graft copolymers were recorded using films of the polymers cast on NaCl plates from either CH_2Cl_2 or $CHCl_3$ solutions. Spectra for the graft copolymer samples G141G, G144G (purified) and the MeOH soluble degraded product G11-II are given in Figures 4.9A, 4.9B and 4.10 respectively. Spectra of graft copolymers correspond to the sum of those of PS and PECH.

(c) Overall composition

(i) UV Spectroscopy. Overall composition of some of the graft copolymers were determined by UV spectroscopy (183). The samples were either extracted with or reprecipitated into MeOH without antioxidant, washed with this solvent and then completely dried. This step was necessary to make the samples completely free from any antioxidant before UV measurement.

Spectra of at least three solutions of different concentrations for each sample in spectroscopic grade chloroform (BDH Lab.) were recorded using a Perkin-Elmer 137 UV spectrophotometer. The specific extinction coefficient for a sample was estimated from the slope of the plot of absorbance at 262 nm, an absorbance maximum for polystyrene, against concentration. Thus from the specific extinction coefficient values for the graft copolymers and the separately measured values for polystyrene and polyepichlorohydrin, the weight fraction of polystyrene in the graft copolymer was measured from the equation

$$E^*_{graft} = yE^*_{PS} + (1-y)E^*_{PECH} \qquad (4.1)$$

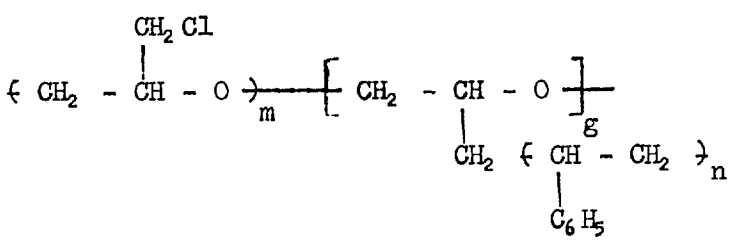
where y = weight fraction of PS in the graft copolymer,

E* = the respective specific extinction coefficient at 262 nm in $dm^3 g^{-1} cm^{-1}$.

Specific extinction coefficients for different PECH samples were found to vary from 0.06 to 0.08 $dm^3 g^{-1} cm^{-1}$. Similarly specific extinction coefficients for different PS samples varied from 2.12 to 2.24 $dm^3 g^{-1} cm^{-1}$. These variations were taken within the limits of experimental errors.

(ii) Elemental microanalysis and percentage of PS (w/w) content.

Elemental analysis of the graft copolymer samples for carbon, hydrogen and chlorine content were carried out. Taking the general formula of the graft copolymer as



$$\% \text{ Cl} = \left(\frac{35.45\ m}{92.53\ m + 104.15\ ng + 57.07g}\right) \times 100$$

$$\% \text{ PECH} = \left(\frac{92.53\ m}{92.53\ m + 104.15\ ng + 57.07g}\right) \times 100$$

So
$$\frac{\% \text{ Cl}}{\% \text{ PECH}} = \frac{35.45}{92.53} \qquad (4.2)$$

$$\% \text{ PS} = 100 - \% \text{ PECH} \qquad (4.3)$$

In equations (4.2) and (4.3), % PECH indicates the % of epichlorohydrin units by weight in the graft copolymers. Calculation of PS contents in the different graft copolymers (Table 4.5) based on UV and microanalytical results agree reasonably well for PS contents lower than 90% w/w. For PS contents higher than 90% w/w, the UV measurements gave relatively higher PS contents than the other method, probably because of absorbance

from various end groups caused by degradation discussed in Section 4.7. Hence microanalytical results were taken as more dependable.

(d) Calculations on composition, structure and molecular weights.

(i) Correction for % PS contents. Calculation of ether contents from chlorine content of microanalysis will give a lower value because of ignoring the existence of

$$\left\{ CH_2 - \underset{\displaystyle CH_2 -}{CH} - O \right\}$$

units in the graft copolymers having a very high degree of grafting. Hence calculation of PS contents by difference, that is, by the equation, % PS = 100 - % PECH will give a usually higher value of % PS content. A correction was therefore made for the existence of ether units with chlorine replaced, from the ratio m/g in the graft copolymer of the structure,

$$\left\{ CH_2 - \underset{CH_2\,Cl}{CH} - O \right\}_m \left[CH_2 - \underset{CH_2 \left\{ CH - CH_2 \right\}_n}{\underset{|}{CH}} - O \right]_g \qquad (C_6H_5)$$

where m is the number of epichlorohydrin units intact and g is the graft frequency.

From the relation,

$$\frac{\text{weight of } \left\{ CH_2 - \underset{CH_2\,Cl}{CH} - O \right\} \text{ units}}{\text{weight of } \left\{ CH_2 - \underset{CH_2 -}{CH} - O \right\} \text{ units}} = \frac{m \times 92.53}{g \times 57.07} \qquad (4.4)$$

and the weight per cent of PECH (unsubstituted epichlorohydrin units calculated from the % Cl), the weight per cent of ether units with chlorine replaced was calculated. The latter % by weight of substituted ether units, added to the % epichlorohydrin (unsubstituted) units calculated from the % Cl gives the total value for the % ether

(substituted and unsubstituted) and hence the correct % PS in the graft copolymers. The corrected and uncorrected % PS contents are given in Table 4.5. There is little difference between corrected and uncorrected % PS w/w contents in a graft copolymer. However, the correction gives a better estimation of the grafting efficiency of PS and the calculated $\bar{M}_n$ of the graft copolymers containing more than 80% PS w/w of short chain length based on the equations used. By percentage PS w/w content in a graft copolymer will be meant corrected % PS w/w content in any future discussion in this chapter, unless otherwise mentioned. The percentage by weight of PS in any graft copolymer or mixture will be written as % PS w/w or more simply as % PS.

(ii) Inverse graft frequency, λ. Because of side reactions, especially degradation reactions, calculations of graft frequency from the simple relation,

$$\bar{M}_n \text{ (graft copolymer)} = \bar{M}_n \text{ (backbone)} + \bar{M}_m \text{ (graft)} \times \text{graft frequency} \tag{4.5}$$

is not possible. Hence the inverse graft frequency,

$$\lambda = \frac{m + g}{g} \tag{4.6}$$

which is the number of ether units (substituted and unsubstituted) per graft was calculated from the following equation derived from the structural formula of the graft copolymer.

$$\% \text{ Cl} = \frac{35.45\ m}{92.53\ m + 104.15\ ng + 57.07\ g} \times 100$$

$$= \frac{35.45\ m}{92.53\ m + \bar{M}_n \text{ (PS)} \times g + 57.07 \times g} \times 100 \tag{4.7}$$

In these calculations, the elemental composition of PECH was assumed to be the same as that of its repeat unit.

(iii) Expected $\bar{M}_n$. These values of the graft copolymers were calculated from the relation

$$\bar{M}_n \text{ (graft)} = \bar{M}_n(\text{PECH}) + \frac{y}{x} \bar{M}_n(\text{PECH}) \qquad (4.8)$$

where x and y are the weight per cent of the ether units (substituted and unsubstituted) and PS respectively in the graft copolymers. $\bar{M}_n$(cal) will be used for expected $\bar{M}_n$ of the graft copolymers in the discussion.

(iv) Grafting efficiency of PS in the graft copolymers was calculated from the relation,

$$\text{grafting efficiency} = \frac{\text{PS per g polyether in graft copolymer}}{\text{PS used per g of PECH}} \times 100 \qquad (4.9)$$

where PS per g of polyether in the graft copolymer

$$= \frac{\text{weight of \% of PS}}{\text{weight \% of polyether}}$$

in the graft copolymer. The word polyether is used instead of PECH, because in the graft copolymers, the ether units are not only

$$\left\{ CH_2 - \underset{\displaystyle CH_2Cl}{\underset{|}{CH}} - O - \right) \quad \text{but also} \quad \left\{ CH_2 - \underset{\displaystyle CH_2 -}{\underset{|}{CH}} - O \right\}.$$

(v) Degradation factor, f. This value for a graft copolymer was calculated from the relation,

$$f = \bar{M}_n(\text{cal})/\bar{M}_n(\text{obs}) \qquad (4.10)$$

The term 'degradation' used in future discussion in this chapter signifies mostly the cleavage of a polymer.

Inverse graft frequencies, corrected % PS contents and hence the calculated $\bar{M}_n$ and grafting efficiencies of PS in the different graft copolymers were based on equations incorporating $\bar{M}_n$ of the separately terminated living PS. These values can be used for comparison purposes for any series of graft copolymers.

Composition of some of the well purified graft copolymers are given in Table 4.5 and their calculated and observed $\bar{M}_n$ values in Table 4.6.

(vi) Ratio R

$$R = \frac{\text{Number of moles of added } PS^-}{\text{Initial number of moles of Cl in PECH}}$$

used in a grafting experiment.

The number of moles of added PS^- was calculated from the $\bar{M}_n$ of the separately terminated living PS^- and the amount of PS^- used in a grafting experiment. This amount of PS^- was obtained from the total amount of the polymer isolated from a grafting experiment and the initial amount of PECH used. The molar ratio mentioned here will be in future written simply as 'R' and sometimes as (mole of PS^-/mole of Cl)

4.3. Results and Discussions

Information concerning the graft copolymers prepared in this work is contained in the Tables 4.1 - 4.7.

4.3.1. Molecular Weights and Molecular Weight Distribution of Starting Polyepichlorohydrin and Polystyrene Samples

The PECH samples (Table 4.1) used for the grafting experiments had different $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values because of the different treatment during purification of the samples mentioned in the footnote of Table 4.1.

The polystyrene samples (Table 4.2) used in this work were not completely monodisperse. The molecular weight distributions were relatively broader in the samples prepared in benzene and toluene without any added THF. In hydrocarbon media, the initiation reaction is comparatively slower than propagation (139,147) and all the chains do not start propagation at the same time. The molecular weights of all the samples were higher than the calculated values. This was probably because a fraction

of the initiator was killed by the moisture adsorbed on the surface of the polymerization flask. For preparation of truly monodisperse polystyrene, purging of the flask with living polymer solution is necessary. This was not done in the present experiments. Another reason for obtaining polymers with molecular weights higher than the calculated values may be the killing of some of the propagating chains by traces of impurities left in the monomer. Distributions of molecular weight were narrower in cases when polymerizations were done in the presence of small amounts of THF (sample S28, Table 4.2).

4.3.2. Molecular Weights and Composition of Graft Copolymers and Side Reactions in Grafting Experiments

(a) Coupling reaction in pure hydro carbon solvents (Experiments G5, G11, G12, Table 4.3). The molecular weights ($\bar{M}_n$) and the composition of the different fractions of the graft copolymerization reaction products (Table 4.4) show that the synthesis of P(ECH-g-S) copolymers by the carbanionic deactivation or anionic coupling reactions in pure hydrocarbon solvents using polystyryl lithium as the living polymer is complicated by two distinct side reactions, (i) cross-linking and subsequent colloidal phase separation, and (ii) degradation.

Initially, gradual addition of the red living polymer solution to the PECH solution caused an insoluble colloidal substance to be formed with instant disappearance of the red colour characteristic of polystyryl lithium. Observations during experiments G5, G11 and G12, indicated that the insolubility of this colloid increased with an increase in the initial concentration of PECH for approximately equal amounts of $PS^- Li^+$ added. Hazy solutions and sometimes curd-like suspensions were produced in these experiments. However, in experiment G140, in which the initial PECH concentration was relatively low

and the solvent mixture on adding $PS^- Li^+$ contained a small amount of THF, no colloidal suspension was formed, although the solution remained slightly hazy. The red colour of the living polymer always disappeared very rapidly on its addition.

When certain of the reaction mixtures such as G5 were allowed to stand for about an hour, the colloidal particles settled and an insoluble jelly-like phase was formed at the bottom of the reaction flask. This effect was particularly noticeable when the initial PECH concentration was high.

Separation of the reaction products from experiment G5, for example, as described in Section 4.2.3 and Table 4.4 gave as one product, G5-IIA. Its PS content of about 3.3% showed that it was only very slightly grafted. The number average molecular weight, $\bar{M}_n$ of G5-IIA was 8.1×10^5 and was thus higher than that of the PECH sample E5 of 2.36×10^5 (Table 4.1). Sample G5-IIA appeared to be a partially cross-linked PECH which although not soluble in the reaction mixture, dissolved in C_6H_6 and other common solvents for PECH. The insolubility of G5-IIA and the colloidal suspension produced during experiments G5, G11 and G12 was partly due to a cross-linking process and may also be due to the salting out effect on PECH by the LiCl, formed in the simultaneous grafting reactions. In a separate experiment, salting out of PECH was observed when a LiCl solution in THF was added to a PECH in C_6H_6.

This cross-linking presumably occurs by lithium halogen interchange reactions and has been observed before to some extent when PECH was treated with n-BuLi (184) and to a greater extent when chloromethylated polystyrene was coupled with $PS^- Li^+$ in pure hydrocarbon solvents (43,48).

In experiment G5 both grafting and degradation reactions took place simultaneously with cross-linking. Sample G5-I (Table 4.4) gave a single

peak in the GPC trace corresponding to an $\bar{M}_n$ of 9.31×10^3 which is higher than the $\bar{M}_n$ of separately terminated living PS ($\bar{M}_n = 5.75 \times 10^3$) and much less than that of the original PECH ($\bar{M}_n = 2.36 \times 10^5$). This sample G5-I was thus either a degraded graft copolymer mixed with homopolystyrene or a mixture of degraded polyepichlorohydrin and homopolystyrene. It was found to be completely soluble in diethyl ether and cyclohexane, two non-solvents for PECH but solvents for low molecular weight PS and also for graft copolymers with a very high degree of short chain grafting. This indicated that the graft copolymer present in the mixture G5-I was heavily grafted and also extensively degraded.

The very high degradation of this graft copolymer in comparison to those prepared in other experiments (G11 and G12) in hydrocarbon solvents may be due to the relatively large concentration of $PS^- Li^+$ responsible for degradation in the phase containing the dissolved PECH.

The composition of the two fractions, G11-IC and G12-IA (Table 4.4) separated from the grafting experiments G11 and G12 carried out in benzene at 20°C and toluene at -78°C, suggest that very high extents of grafting took place in spite of degradation, cross-linking and colloidal phase separation. The samples G11-IC and G12-IA had corrected PS contents of 83.79% and 86.22% respectively (Table 4.5) and showed single peaks in their respective GPC traces.

(b) Heterogeneous nature of grafting and degradation reactions in pure hydrocarbon solvents. In pure hydrocarbon solvents, a portion of PECH is phase separated due to cross-linking and also probably due to the salting out effect. There is therefore a relatively high build up of concentration of living polymer in the phase containing the dissolved PECH. This may cause considerably more degradation and more grafting

in the soluble PECH than might otherwise be expected. With a relatively high amount of living polymer added to the system, the insoluble phase also becomes degraded and grafted. This is the reason why the two different fractions G11-IA and G11-IC (Table 4.4) were so widely different in composition.

(c) Coupling reactions in benzene (living polymer, $PS^- Li^+$) with a small amount of THF in the coupler solution (Experiment G140, Table 4.3)

In this grafting experiment, no colloidal phase separation was observed. Cross-linking was probably largely avoided due to the small amount of THF in the living polymer solution ($[THF]/[PS^- Li^+] = 41.8$). A similar effect of a polar solvent in reducing cross-linking due to lithium halogen interchange reactions in coupling reactions between chloromethylated polystyrene and either $PS^- Li^+$ or polyisoprenyl lithium in benzene has been observed (48,52).

The degradation of the graft copolymer G140G was also quite marked. For example, the degradation factor, $\bar{M}_n(cal)/\bar{M}_n(obs)$ in G140G is less than in G11-IC for comparable ratio of R = (mole of PS^-/mole of Cl) (Table 4.6) used in the grafting experiments G140 and G11. This comparison is just an approximation because of the heterogeneous nature of grafting and cross-linking in G11-IC and incomplete separation of this graft copolymer from the mixture G11-I.

The marked reduction in cross-linking and also the relatively less degradation in experiment G140 was probably due to the presence of a small amount of THF in the $PS^- Li^+$ used for coupling reaction.

One possible reason for greater degradation in the graft copolymer samples from experiments G5, G11 and G12 than from G140 may be the presence of small amount of unreacted n-BuLi in the $PS^- Li^+$ prepared in the absence of THF. It was thought, however, that most of the

degradation was due to $PS^- Li^+$ rather than n-BuLi. The presence of small amounts of unreacted n-BuLi in the $PS^- Li^+$ of $\bar{M}_n$ less than 5,000 prepared in the absence of THF has been reported in the literature (62). The cleavage action of BuLi as well as $PS^- Li^+$ on PECH has been described in Section 4.7.

(d) Coupling reaction in THF using potassium counter-ion (Experiment G7, Table 4.3). The grafting reaction in THF using the potassium counter-ion was found to occur without any noticeable degradation and appeared to be as fast as in benzene using the lithium counter-ion. The fraction G7G is a highly grafted sample with a corrected PS content of 86.45% and grafting efficiency of PS as 51.58% (Table 4.5). Its molecular weight ($\bar{M}_n = 3.62 \times 10^5$) is greater than that of the original PECH (nominal $\bar{M}_n = 0.44 \times 10^5$). The $\bar{M}_n$ calculated for the graft copolymer agrees with $\bar{M}_n$ measured by GPC (Table 4.6). The absence of degradation in this case may be related to the greater metallic character of the K^+ counter-ion for reaction with the chlorine of the $-CH_2Cl$ in PECH. Other experiments indicated that PECH, dissolved in a polar solvent like THF was less prone to degradation induced by the PS^--counter-ion than when dissolved in a non-polar solvent. This may also be due to the higher polarity of the C-Cl bond which leads to a higher rate of nucleophilic substitution in a polar solvent. The low grafting efficiency in the sample G7G may be due to termination of the living PS^- anions by some non-degradative side reactions or impurities in the system.

(c) Coupling reactions in THF/C_6H_6 (final composition 67:33 v/v) using Li-counter-ion (Experiment G141 - G144, Table 4.3). In the synthesis of the series of graft copolymers G141G - G144G, the PECH used was dissolved in THF and the living polymer was $PS^- Li^+$ in C_6H_6. The PS contents in the series of graft copolymers (G141G - G144G) increased

gradually from 46.6% to 94.1% with an increase in the molar ratio, R used in their synthesis (Table 4.5). The grafting efficiency of PS also increased from about 44% to about 64% when plotted against the molar ratio, R (Figure 4.6).

The reason for the gradual increase in grafting efficiency with an increase in R may be due to the decreasing % impurity contents in the PECH-solvent mixture with increasing R values. Thus a decreasing fraction of PS^- added was terminated by a non-degradative reaction with impurities as the value of R increased.

The $\bar{M}_n$ of all the graft copolymers of the series were higher than that of the starting PECH backbone polymer (Table 4.6 and Figure 4.7). Figure 4.8 shows a plot of the degradation factor, $f = \bar{M}_n(cal/\bar{M}_n(obs)$ against R and indicates that the extent of degradation increased with an increase in the amount of living polymer used. For a ratio R of less than 0.1, the amount of degradation was negligibly small.

The average inverse graft frequency in the most degraded graft copolymer sample G144G, as calculated from % Cl by eqns (4.6) and (4.7) is 4.1 which means that there is one polystyrene graft for every four repeat units in PECH backbone. A 10% error of the % Cl for G144G gives an inverse graft frequency of 4.1 ± 0.3. The average inverse graft frequencies in the samples G141G - G144G (Table 4.6) indicate that PECH can be grafted without severe degradation in a polar solvent such as THF using living anions either conjugated to lithium or potassium counter-ions.

Of the two reactions, substitution and degradation, the former appears to be faster in a polar solvent. Degradation reaction becomes noticeable in the heavily grafted molecules when the remaining chlorine atoms are less accessible for substitution due to shielding by the PS grafts.

(f) Grafting efficiencies of PS^- in C_6H_6 and THF/C_6H_6 mixtures (67:33 v/v)

A comparison of the grafting efficiency in G140G prepared in C_6H_6 to those in the graft copolymers prepared in THF/C_6H_6 under closely similar conditions (Table 4.5 and Figure 4.6) shows that the grafting efficiency in the former was higher in spite of greater degradation involved in its production (Figure 4.8). Similarly, grafting efficiencies of PS^- in the two other samples G11-IC and G12-IA, prepared in pure benzene and toluene, respectively, were also very high in spite of heavy degradation and cross-linking. As discussed in Section 4.7 every degradation reaction should result in the termination of a living polymer chain. Hence the higher grafting efficiencies in hydrocarbon solvents are surprising.

The most probable reason is that both coupling and degradation reactions are relatively fast and both involve a contact ion-pair in hydrocarbon solvents with the former reaction a little faster than the latter. The termination of living polymer is mainly due to its degradative reaction with PECH.

In the THF/C_6H_6 mixture, because of the greater polarity of C-Cl bond, the coupling reaction is faster than in hydrocarbon solvents. Degradation reactions are suppressed to a greater extent. The relatively lower grafting efficiencies in the graft copolymer samples G141G - G144G compared with G140G were probably mainly due to the greater extent of the non-degradative termination of the living polymer chains in the synthesis of the series G141G-G144G. The extents of the degradative termination reactions may also be different, however.

Another less likely reason for the higher grafting efficiency in G140G compared with G141G - G144G is the contribution from grafting at the carbonyl groups formed on degradation by the reaction:

$$O = CH - \underset{}{\overset{CH_2Cl}{\overset{|}{CH}}} - O \sim\sim + PS^- Li^+ \longrightarrow Li^+O - \underset{PS}{\overset{|}{CH}} - \overset{CH_2Cl}{\overset{|}{CH}} - O \sim\sim \qquad (4.11)$$

(g) Chemical nature of side reactions Besides cross-linking in pure hydrocarbon solvents, degradation reactions were also noticed in some grafting experiments, especially in those carried out in C_6H_6 and toluene. Degradation also took place in experiments carried out in THF/C_6H_6 mixture at higher values of R (Figure 4.8). A methanol soluble sticky brown polymer, G11-II (Table 4.4), when recovered by solvent evaporation from experiment G11, carried out in C_6H_6, showed some extra peaks in its I.R. spectrum (Figure 4.10), apart from the usual peaks for PECH and PS. These extra peaks were at 3680 - 3320 cm^{-1} (broad) due to -OH (hydrogen bonded), at 3295 and 2120 cm^{-1} due to $-C \equiv C-H$, at 1725 cm^{-1} due to $> C = O$, at 1665 cm^{-1} due to α,β-unsaturated aldehyde or ketone, and at 1630 cm^{-1} due to $>C = C<$ conjugated to etheral oxygen (as in a vinyl ether). A similar spectrum was recorded for the polymer sample G12-II recovered from the grafting experiment carried out in toluene at -78°C. Formation of the groups mentioned above due to cleavage of PECH by $PS^- Li^+$ is described in Section 4.7. The degradation of PECH in C_6H_6 and C_6H_6/THF mixture by $PS^- Li^+$ may be expected to be of a similar chemical nature.

(h) Molecular weights, $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ ratios of the graft copolymers. The $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values of the polymer corresponding to the higher molecular weight GPC peak in a non-fractionated graft copolymer mixture with homopolystyrene corresponds to the graft copolymer. Thus purification of the graft copolymers G140G - G141G from homopolystyrene by fractional precipitation based on tubidimetric titrations (Section 4.2.3 (c)) gave quantitative separation and the graft copolymers consequently showed single peaks in their GPC traces.

A comparison of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values for certain purified graft copolymers giving a single GPC peak with the values corresponding to the higher molecular weight of the GPC peak of the mixture is shown in Table 4.7. The two sets of values agree reasonably well except unexpectedly for G141G. All the graft copolymers of the series G140G - G141G were purified under identical conditions.

The differential molecular weight distribution curves for the graft copolymer mixture G140 and the purified graft copolymer G140G are given in Figure 4.4; those for G143 and G143G in Figure 4.5. G140G and G143G have a similar composition (PS contents 84.57% and 83.77% respectively). The distribution curve for the parent PECH sample E19 is also given in Figure 4.4 (a), for comparison.

$\bar{M}_w/\bar{M}_n$ galues for different graft copolymers (Table 4.7) show that the distribution is usually narrower for those graft copolymers which had undergone considerable degradation. Thus the $\bar{M}_w/\bar{M}_n$ value for G140G with more degradation is smaller than that of G143G. Figures 4.4 and 4.5 also illustrate this fact. If the degradation reaction is random the distribution will become narrower compared to that of the original PECH and in the absence of grafting "a most probable distribution", with $\bar{M}_w/\bar{M}_n$ equal to 2 would ultimately result. On grafting with chains of narrow distribution, the ultimate distribution of the degraded graft copolymer would become still narrower.

B. BUTYL LITHIUM CLEAVAGE OF POLYEPICHLOROHYDRIN

4.4. Introduction

In the course of the synthesis of P(ECH-g-S) copolymers by anionic coupling reactions between $PS^- Li^+$ and PECH, either in C_6H_6 or toluene solution, small amounts of methanol soluble sticky degraded graft copolymers, (or possibly degraded PECH mixed with low molecular weight

homopolystyrene), G11-II and G12-II were recovered. The infra-red spectra of these polymers (Figure 4.10) showed some extra peaks due to -OH, -C ≡ C-H, >C = O, α,β-unsaturated aldehyde or ketone and >C = CH_2 apart from the usual peaks for PECH and PS. It was thought that the $PS^- Li^+$ which caused grafting by nucleophilic substitution was also responsible for the cleavage of the PECH backbone. In order to investigate the effect of a smaller molecular weight compound on the cleavage of PECH, n-BuLi was used. However, benzyl lithium or α-phenyl ethyl lithium would have been better analogues for the purpose but these were unavailable. Another objective was to ascertain whether any stable metalated polymer was formed due to lithium-halogen interchange reactions and whether any such stable metalated polymer could initiate polymerization of a monomer such as styrene. After this work had been completed, it was discovered that the cleavage of PECH by different organo-lithium compounds including BuLi and C_6H_5Li had also been studied by Vandenberg (184).

4.5. Experimentals

4.5.1. Purification of Materials

(a) PECH was purified as before (Section 4.2.1). Sample E9 (Table 4.1) was used for the cleavage reaction and this sample was free from antioxidant.

(b) Benzene, used as solvent for the cleavage reaction, was dried over CaH_2 and the middle fraction after distillation at atmospheric pressure was used.

(c) n-BuLi used had an original concentration of 0.483 mol dm^{-3} in n-hexane. The handling of n-BuLi was as described before.

4.5.2. The Cleavage Reaction and the Recovery of the Products

(a) The cleavage reaction. 1 g of dried PECH was dissolved in 100 cm^3 of distilled benzene in each of the four experiments 1, 2, 3 and 4 (Table 4.8).

The flasks containing the solutions were carefully flushed with argon. 3.4, 7.9, 13.4 and 19.9 cm^3 of 0.483 molar n-BuLi solution in n-hexane were added to the flasks in experiments 1, 2, 3 and 4 respectively. The mixtures were stirred at room temperature for 6 h and then short-stopped with degassed water. The mixture in the flask assumed a brownish yellow colour during the reaction; the intensity of colour being more in those experiments containing the greater proportion of n-BuLi.
A small amount of antioxidant, 2,6-di-tert-butyl p-cresol dissolved in benzene was added to each flask so that the amount of antioxidant became 0.05% w/w of the total solid in the flask.

(b) Recovery of the degraded (cleaved) polymer. The solvent from each flask was rotary evaporated to remove water. The solid was dissolved in C_6H_6 and filtered through a porosity 3 sintered glass funnel. The clear solution was then evaporated to dryness to recover the degraded polymer. It was an elastomeric tacky solid in experiment I and a darker brown tacky liquid in the experiments 2, 3, 4 respectively. The solid was dried further in a vacuum desiccator in the dark, until used for characterization.

(c) Recovery and estimation of chlorine cleaved from PECH. The solid insoluble in C_6H_6 left on the sintered funnel was dried and then dissolved in dil HNO_3. The amount of chlorine cleaved in each experiment was determined as AgCl by gravimetric analysis described elsewhere (185). Analysis was done in subdued light so that the AgCl was not decomposed.

4.5.3. Characterization of Degraded Polymers

(a) Molecular weights The molecular weights of the degraded samples henceforth designated C_1, C_2, C_3 and C_4 from the corresponding experiments 1, 2, 3 and 4 were measured by GPC. The relationship between $\bar{M}_n$ and the values of R_1 is shown in Figure 4.13.

R_1 in future discussions will always indicate the ratio,

$$\frac{\text{number of moles of n-BuLi}}{\text{number of moles of Cl in initial PECH}}$$

used in a cleavage reaction.

(b) Limiting viscosity numbers. The limiting viscosity numbers of the initial PECH sample, E9 and the degraded polymers C_1 - C_4 were measured in toluene at 30°C using a modified Ubbelohde suspended level viscometer. Solvent and solutions were filtered directly into the viscometer under a pressure of nitrogen. The principles and practice of capillary tube viscometry have been described elsewhere (186). Solvent flow times were greater than 95 seconds, and kinetic energy and end-corrections were not made. A plot of viscosity number and logarithmic viscosity number against concentration for PECH sample E9 is shown in Figure 4.14. The limiting number, $[\eta]$, given by the relation

$$[\eta] = \lim_{c \to o} \eta_{sp}/c = \lim_{c \to o} \ln \eta_r/c \qquad (4.12)$$

where the symbols have their usual meaning, was obtained by extrapolation. A plot showing the drop in the limiting viscosity numbers in the degraded polymer samples against the values of R_1 is given in Figure 4.15.

(c) Percentage of chlorine loss. Chlorine cleaved from PECH at different values of R_1 used was determined as AgCl and hence the per cent loss of chlorine equal to

$$\left(\frac{\text{wt of Cl displaced}}{\text{wt of Cl in the polymer used}}\right) \times 100$$

was calculated. A plot of the weight % of chlorine displaced against the values of R_1 is shown in Figure 4.16.

(d) I.R. spectra of the cleavage products, C_1 - C_4 were recorded in $CHCl_3$ (BDH, Spectroscopic grade) using a variable path length cell. The solvent was eluted through a column of activated Al_2O_3 to make it free

from the stabilizer (ethanol). However, it was not completely free from the stabilizer and showed peaks due to -OH groups. A relative estimation of the amounts of the different groups formed by the cleavage of PECH was possible with correction for absorbance due to the solvent. A concentration of 38.48 g dm^{-3} of each of the samples, C_1 - C_4 was used with a cell path length of 0.5 mm. The I.R. spectra of the cleavage products as films on NaCl plates, cast either from CH_2Cl_2 solution or directly prepared from the pasty cleavage products were also taken.

The spectra in $CHCl_3$ solution (Figure 4.11) showed peaks at 3560 - 3360 cm^{-1} (broad strong) due to -OH, at 3305 cm^{-1} (sharp strong) due to -C ≡ C-H, at 1730 cm^{-1} (weak) due to normal aldehyde or ketone, at 1670 cm^{-1} (strong) due to an α,β-unsaturated aldehyde or ketone, at 1630 cm^{-1} (strong) due to H_2C = C< of a vinyl ether or conjugated to a carbonyl group and also peaks at 1605 cm^{-1}, 1580 cm^{-1}. The I.R. spectra of the films also showed peaks at approximately the same wave numbers with the exception that a weak but distinct peak due to -C ≡ C-H appeared at 2120 cm^{-1} and the peaks at 1605 cm^{-1} and 1580 cm^{-1} disappeared. The latter two peaks are probably characteristic of >C = C< conjugated to a carbonyl group and their appearance depends on the nature of the sample used in recording the spectrum.

The I.R. peaks for a BuLi cleavage product of PECH taken on a film appeared at almost exactly the same position as those in the cleavage products of $PS^- Li^+$ acting on PECH (Figure 4.10) except the peaks characteristic of PS in the latter.

(e) The relative amounts of different groups formed by cleavage reactions were measured as a function of the molar amounts of n-BuLi, Y per g PECH. From the I.R. spectra of the cleavage products in $CHCl_3$ solution (Figure 4.11), the relative absorbance due to a particular group at

each value of Y used for the cleavage reaction, was made with correction for absorbance due to the solvent. The relative absorbance was calculated from the following relations

$$A \text{ (absorbance)} = \log_{10} \frac{I_o}{I} \qquad (4.13)$$

$$\% \text{ light absorbed} = \left(\frac{I_o - I}{I_o}\right) x\ 100 \qquad (4.14)$$

when I and I_o are the intensities of the transmitted and incident radiation respectively. Percentage of light absorbed was measured from the base line to the peak height. For example, in Figure 4.11, h is the % of light absorbed due to OH groups in the cleavage product C_1, at the concentration and thickness of the cell used, including the % of light absorbed by the solvent. From the calculated total absorbance, the absorbance due to the solvent at the respective wave number for the same thickness of the cell (calculated from a different spectrum not shown in the figure) was deducted to obtain the absorbance for the particular group.

A plot of absorbance for the different groups against mmole n-BuLi per g PECH used in the cleavage reactions is shown in Figure 4.12.

(f) Unsaturation in the degraded polymers. An unsuccessful attempt was made to determine the extent of unsaturation in a cleavage product by the modified mercuric acetate method of Martin (187). The results were not reproducible and further attempts were therefore abandoned.

4.6. Results and Discussion

n-BuLi caused an extensive cleavage of PECH as evident from the drop in molecular weights and limiting viscosity numbers (Figures 4.13 and 4.15). These measurements reached a limiting value at a value of

R_1 greater than 0.5.

The cleavage of PECH by n-BuLi followed by subsequent treatment with water resulted in the formation of different end groups such as -OH, $-C \equiv C-H$, $O = CH-$, $O = CH - \underset{\underset{CH_2}{\|}}{C} - O \sim\sim$.

The reactions leading to the formation of these groups are discussed in Section 4.7.1.

The absorbance due to the different groups in I.R. spectra taken in $CHCl_3$ solution against the molar amounts of n-BuLi per g PECH used in cleavage reactions, shows that the concentration of these groups was proportional to the relative amounts of n-BuLi (Figure 4.12).

The limiting values in the molecular weights and the steady increase in the percentage loss in chlorine (Figure 4.16) with the ratio R_1 used suggested that at higher values of R_1 some reactions not resulting in the further cleavage of the PECH backbone, but in the abstraction of chlorine atoms, took place. However, the absorbance due to the different end groups suggested that all reactions were taking place simultaneously. These results may be explained by the fact that some low molecular weight volatile polymer molecules were lost in the most highly degraded samples. The actual loss measured in the samples C_3 and C_4 were 1.3% and 4.1% w/w of the total PECH used. This loss of low molecular weight volatile products might have resulted in a limiting value of the molecular weights. Moreover, the molecular weight difference in the very low molecular weight polymers might not be readily detected by viscosity measurements or by GPC.

4.7. Mechanism of Polyepichlorohydrin Cleavage by n-Butyl lithium and Polystyryl lithium

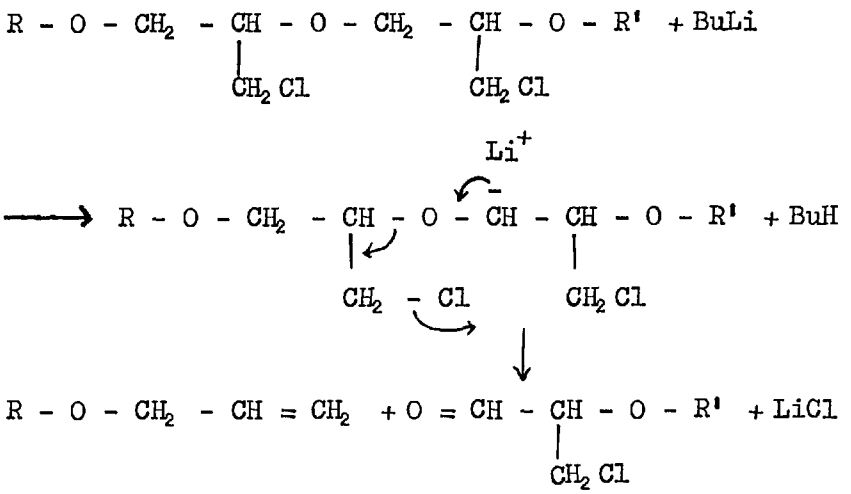
4.7.1. Cleavage by n-BuLi. The formation of different groups in the

cleavage products may be explained by the mechanism proposed by Vandenberg (184). Vandenberg in his cleavage studies of epichlorohydrin polymers, identified formation of the end groups, -OH, $-C \equiv C-H$ and $>C = O$ (normal aldehyde and ketone) and made a quantitative estimation of the different end groups.

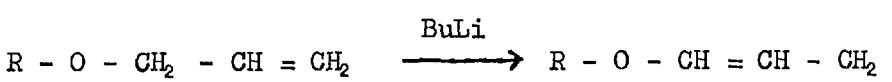
The products of the cleavage reactions in the present set of experiments were somewhat different from those of Vandenberg's experiments, These differences may be due to different experimental conditions and also the cleavage products were not acid hydrolysed.

The amount of normal aldehyde formed in the present experiments was small as evident by the low intensity of the peak at 1730 cm^{-1}, except in the sample C_4. The higher concentration of normal aldehyde in this sample may be from the action of sunlight as discussed before (Section 3.6). The reactions leading to the formation of several different groups, previously detected by I.R. measurements (4.5.3 (d)) are tentatively given below.

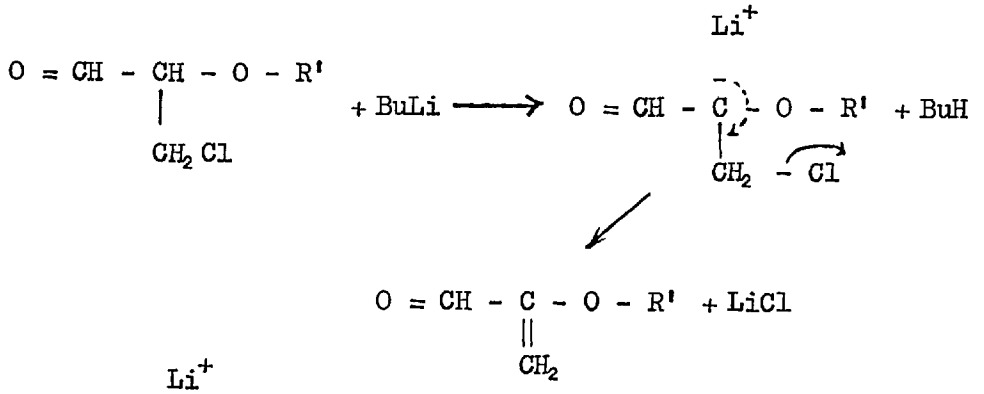
Route 1



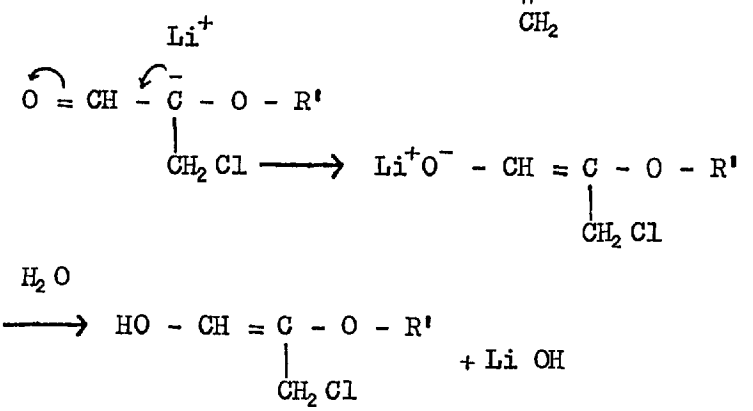
(4.15)



(4.16)

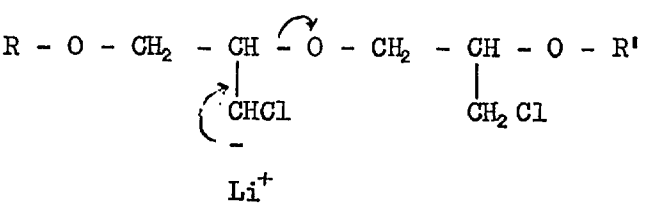


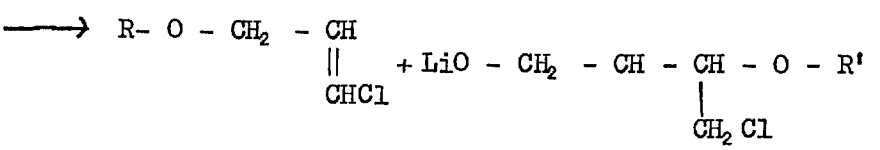
(4.17)



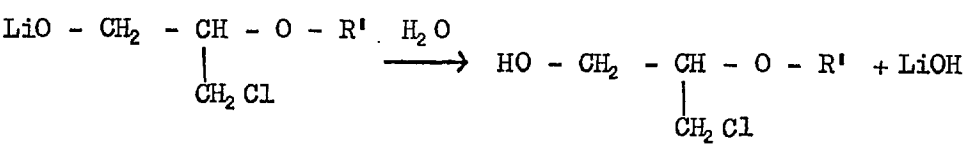
(4.18)

Route 2

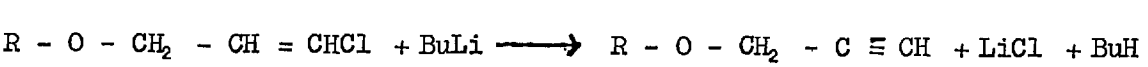




(4.19)

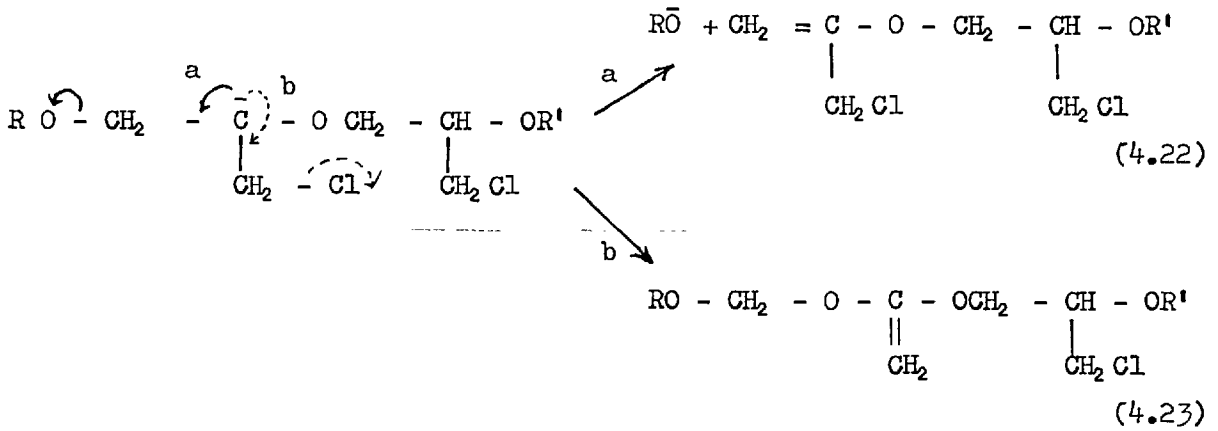


(4.20)



(4.21)

Route 3

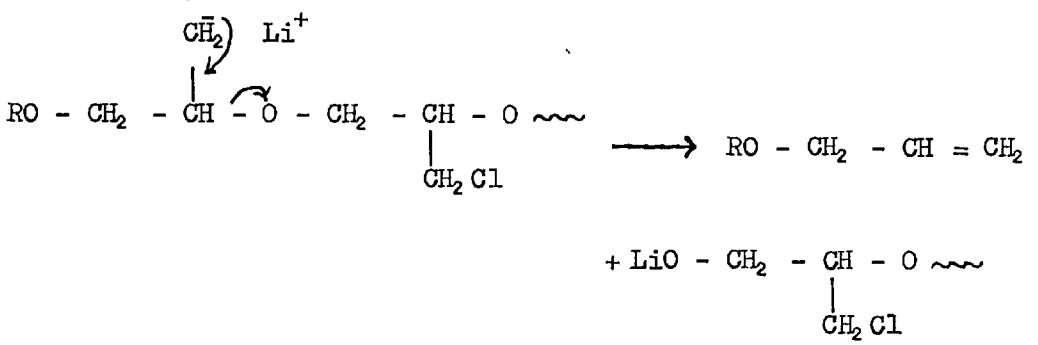


(4.22)

(4.23)

Route 4

Another possible reaction is cross-linking due to lithium-halogen interchange. A lithiated carbanion is first formed. The lithiated polymer then couples with the chloromethyl group of another chain, resulting in the cross-linking. No cross-linking was observed in the present experiments. Cleavage may also take place through formation of carbanion by this route.



(4.24)

4.7.2. Cleavage by $PS^- Li^+$. Similarity in the I.R. spectrum of the cleavage product of BuLi on PECH to that of the cleavage product of $PS^- Li^+$ on the polymer in hydrocarbon solvents suggests that the cleavage action by both reactants follows the same mechanism. Probably the nature of the cleavage in C_6H_6/THF by $PS^- Li^+$ is also similar. The extent of cleavage by $PS^- Li^+$, though very high in pure hydrocarbon solvents, was much less than by BuLi under similar conditions.

The basicity order of the organo lithium compounds (188), n-BuLi > C_6H_5Li > $C_6H_5CH_2Li$ suggests that $PS^-\ Li^+$, the polymeric analogue of $C_6H_5CH_2Li$ would be less basic than $C_6H_5CH_2Li$ and far less basic than BuLi, partly because of its greater size. $PS^-\ Li^+$ gives rise to the coupling reaction with the $-CH_2Cl$ group of PECH. It would be of great interest to check whether BuLi and $C_6H_5CH_2Li$ exhibit any coupling reactivity with PECH apart from the cleavage reaction.

Table 4.1. Molecular Weights of Polyepichlorohydrin Samples, Purified by Reprecipitation, Used for Grafting Reactions

Sample	Source	GPC Results		
		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
E5	Hercules Inc.	2.36	18.13	7.67
E7	"	0.44 [a]	2.35	5.35
E9	"	1.69 [b]	8.42	5.00
E13	"	1.30 [b]	13.16	10.09
E19	"	3.49 [c]	13.60	3.90
E11	prepared in our lab.	1.61	12.00	7.48

[a] A roughly fractionated polymer sample (a fraction of lower $\bar{M}_n$)

[b] The swollen polymer, insoluble in cold C_6H_6 was discarded

[c] A roughly fractionated polymer sample (a fraction of higher $\bar{M}_n$)

Table 4.2. Anionic Polymerization of Styrene for Coupling Reactions. Experimental Conditions

Sample	Initiator	Solvent	Temp./ °C	Time/ h	[Monomer]/ mol dm^{-3}	10^2 x [Initiator]/ mol dm^{-3}	$\bar{M}_n$ (cal) x 10^{-3}	Results		
								$\bar{M}_n$ x 10^{-3}	$\bar{M}_w$ x 10^{-3}	$\bar{M}_w/\bar{M}_n$
S5	n-BuLi	C_6H_6	20	24	1.045	2.398	4.54	5.75	10.67	1.86
S11	"	"	20	24	0.800	1.667	5.00	6.59	10.05	1.52
S12	"	$C_6H_5-CH_3$	20	24	1.044	2.660	4.09	5.75	9.63	1.67
S28	"	C_6H_6 [a]	20	8	1.104	2.269	5.07	5.45	7.40	1.36
S7	Cumyl K	THF	-78,0	4	1.183	1.227	10.04	13.37	20.27	1.52

[a] 10 cm^3 of THF in 130 cm^3 total volume was used

[THF]/[n-BuLi] = 41.8

Table 4.3. Grafting of PECH with Living Polystyrene by the Carbanionic Deactivation Technique. Experimental Conditions

Experiment	PECH sample used [a]	PS^- sample used [b]	Living Polymer	Weight of PS per g of PECH/g	$10^2 \times R$	Solvent	Temp/ ^oC	Time/ h [c]
G5	E5	S5	$PS^- Li^+$	6.821	10.98	C_6H_6	20	2
G11	E11	S11	"	9.250	12.99	"	20	1
G12	E11	S12	"	10.468	16.84	Toluene	-78	1
G7	E7	S7	$PS^- K^+$	12.369	8.56	THF	20	1
G140	E19	S28	$PS^- Li^+$	8.126	13.77	C_6H_6 [d]	20	$\frac{1}{2}$
G141	E19	S28	"	1.996	3.39	THF + C_6H_6 (67:33v/v)	20	$\frac{1}{2}$
G142	E19	S28	"	4.123	7.00	"	20	$\frac{1}{2}$
G143	E19	S28	"	10.848	18.45	"	20	$\frac{1}{2}$
G144	E19	S28	"	24.974	42.37	"	20	$\frac{1}{2}$

$$R = \left(\frac{\text{Number of moles of added } PS^-}{\text{Initial number of moles of Cl in PECH}} \right)$$

a PECH samples were those in Table 4.1. In experiments G141 - G144, the weights of PECH used were 1.001, 0.501, 0.2, 0.08 g respectively in 40 cm^3 THF in each case; about 20 cm^3 of living PS^- in C_6H_6 was added in each case. In experiment G140, there was 0.25 g PECH in 40 cm^3 C_6H_6; in experiment G5, 1 g PECH was in about 50 cm^3 of the solvent and in other cases 1 g of PECH was in about 100 cm^3 of the solvent.

b PS^- samples used were those mentioned in Table 4.2.

c The time for which the coupling reaction mixtures were stirred before termination by MeOH; the coupling reactions themselves appeared very fast.

d The solvent contained a small amount of THF on adding $PS^- Li^+$.

Table 4.4. Separation of the Products of Coupling Reactions for the Synthesis of Poly(epichlorohydrin-g-styrene) Copolymers

Experiment	Preliminary treatment (see Section 4.2.3 (a))	GPC results of the recovered samples[a]			Secondary treatment (see Section 4.2.3 (b))				Conclusion from different studies
		No. of peaks in GPC trace	$\bar{M}_n$ (1) x10^{-5}	$\bar{M}_n$ (2) x10^{-3}	Starting sample	treatment	Sample recovered	% PS (w/w) content	
G5 →	Sol. in reaction mixture, pptd in MeOH, G5-I	1	-	9.31	G5-I	No successful separation from homo-PS	G5-I	91.10	G5-I is a degraded graft copolymer mixed with homo-PS
	Insol. in reaction mixture, pptd in MeOH, G5-II	2 (separate)	8.10	9.57	G5-II →	Ether insol. →	G5-IIA	3.30	G5-IIA is partly cross-linked PECH with low grafting
						Ether sol. (discarded)			
G11 →	pptd in MeOH → MeOH insol., G11-I	.2 (over-lapping)	0.49	7.99	G11-I →	→ C_6H_{12} insol., trace →	G11-IA	18.36	G11-IA is a degraded graft copolymer with low grafting, $\bar{M}_n = 3.56 \times 10^4$.
						→ C_6H_{12} sol. →	G11-IB	-	G11-IB is a degraded graft copolymer mixed with homo-PS, with 2 GPC peaks
	→ MeOH sol. (trace). G11-II; I.R. spectrum (Fig. 4.10)	-	-	-	-	→ pptd higher M.wt fraction	G11-IC	84.52	G11-IC is a degraded graft copolymer with high overall grafting. $\bar{M}_n = 5.31 \times 10^4$
									G11-II is possibly an extensively degraded graft copolymer.

Table 4.4 (continued)

Experiment	Preliminary treatment (see Section 4.2.3 (a))	GPC results of the recovered samples			Secondary treatment (see Section 4.2.3 (b))				Conclusion from different studies
		No. of peaks in GPC trace	$\bar{M}_n$ (1) x10^{-5}	$\bar{M}_n$ (2) x10^{-3}	Starting sample	treatment	Sample recovered	% PS (w/w) content	
G12 →	pptd in MeOH → MeOH insol., G12-I; MeOH sol., (trace) G12-II; I.R. spectrum same as that of G11-II	2 (over-lapping)	0.52	7.37	G12-I →	→ pptd higher M.wt fraction	G12-IA	87.08	G12-IA is a degraded graft copolymer. $\bar{M}_n = 4.12 \times 10^4$ G12-II is possibly an extensively degraded graft copolymer.
		-	-	0.675		→ fractions of lower M. wts discarded			
G7	→ pptd in MeOH → G7	2 (slightly overlapping)	3.62	14.12	G7	→ pptd higher M.wt fraction	G7G	86.82	Discussed in the text (Section 4.3.2 (d))
G140	→ pptd in MeOH → G140	2 (separate)	1.50	5.46	G140	→ pptd higher M.wt fraction	G140G[c]	85.46	" (Section 4.3.2 (c))
G141	→ pptd in MeOH → G141	2 (separate)	6.19	5.30	G141	" " "	G141G[c]	47.09	" (Section 4.3.2 (e))
G142	→ " " " → G142	"	7.69	5.63	G142	" " "	G142G[c]	65.05	" "

Table 4.4 (continued 2)

Experiment	Preliminary treatment (see Section 4.2.3 (a))	GPC results of the recovered samples			Secondary treatment (see Section 4.2.3 (b))				Conclusion from different studies
		No. of peaks in GPC trace	$\bar{M}_n(1)$ $\times 10^{-5}$	$\bar{M}_n(2)$ $\times 10^{-3}$	Starting sample	treatment	Sample recovered	% PS (w/w) content	
G143	→ pptd in MeOH → G143	2 (separate)	7.90	5.51	G143	→ pptd higher M.wt fraction	G143G[c]	84.65	Discussed in the text (Section 4.3.2 (e))
G144	→ " " " → G144	"	4.97	5.36	G144	" " "	G144G[c]	95.09	" "

a $\bar{M}_n(1)$ and $\bar{M}_n(2)$ correspond to the higher and lower molecular weight peaks of the GPC traces of samples from preliminary treatment.

b % PS content corresponds to that of the fraction obtained on secondary treatment. It was calculated from % Cl obtained from elemental microanalysis (Section 4.2.4 (c) (ii)) except for G5-IIA for which it was based on U V analysis. All PS contents are uncorrected values for graft copolymers. Both corrected and uncorrected PS contents are given in Table 4.5.

c Complete separation of higher molecular weight polymer (graft copolymer) was attempted.

Abbreviation : Sol. → soluble; insol. → insoluble; pptd → precipitated; C_6H_{12} → cyclohexane.

Table 4.5. Composition (by weight) of the Purified Poly(epichlorohydrin-g-styrene) samples

Polymer sample	% PS (U V)	Results based on microanalysis						% PS used in grafting experiment
		% Cl	% PECH cal. from % Cl	% PECH (corrected)	% PS (uncorrected)	% PS (corrected)	Grafting a efficiency of PS	
G11-IC	-	5.93	15.48	16.21	84.52	83.79	55.88	90.24
G12-IA	-	4.95	12.92	13.78	87.08	86.22	59.77	91.28
G7G	-	5.05	13.18	13.55	86.82	86.45	51.58	92.52
G140G	86.57	5.57	14.54	15.43	85.46	84.57	67.45	89.04
G141G	46.69	20.27	52.91	53.40	47.09	46.60	43.74	66.62
G142G	65.28	13.39	34.95	35.63	65.05	64.37	43.82	80.48
G143G	85.65	5.88	15.35	16.23	84.65	83.77	47.58	91.56
G144G	98.14	1.88	4.91	5.90	95.09	94.10	63.86	96.15

a Grafting efficiency is based on corrected % PS content.

Table 4.6. Molecular Weights ($\bar{M}_n$), Composition and Structure of the Poly(epichlorohydrin-g-styrene) Samples. [a]

Graft copolymer sample	Initial PECH $\bar{M}_n \times 10^{-5}$	$10^2 \times R$	R'	Graft copolymer			f	λ	PS branch $\bar{M}_n \times 10^{-3}$
				% PS (w/w) (corrected)	$\bar{M}_n$ (cal) $\times 10^{-5}$	$\bar{M}_n$ (obs) [b] $\times 10^{-5}$			
G11-IC	1.61	12.99	7.70	83.79	9.93	0.49	20.26	14.2	6.59
G12-IA	1.61	16.84	5.94	86.22	11.68	0.52	22.46	10.3	5.75
G7G	0.44	8.56	11.68	86.45	3.24	3.62	-	23.0	13.37
G140G	3.49	13.77	7.26	84.57	22.62	1.50	15.08	11.1	5.45
G141G	3.49	3.39	29.50	46.60	6.54	6.19	1.06	67.8	5.45
G142G	3.49	7.00	14.28	64.37	9.80	7.69	1.27	32.9	5.45
G143G	3.49	18.45	5.42	83.77	21.50	7.90	2.72	11.8	5.45
G144G	3.49	42.37	2.36	94.10	59.15	4.97	11.90	4.1	5.45

$R = \left(\frac{\text{Number of moles of added PS}^-}{\text{Initial number of moles of Cl in PECH}}\right)$ used in the grafting experiment

$R' = \frac{1}{R}$

f (degradation factor) $= \bar{M}_n$ (cal)/$\bar{M}_n$ (obs)

λ = Average inverse graft frequency

a The reaction conditions and method of isolation of the graft copolymers are shown in Tables 4.3 and 4.4 respectively.

b $\bar{M}_n$ corresponds to that of the higher molecular weight peak in the GPC profile of the mixture of the graft copolymer with homopolystyrene.

Table 4.7. Molecular Weights and MWD ($\bar{M}_w/\bar{M}_n$) of the Graft Copolymers

Graft copolymer samples	Initial PECH		Purified Graft Copolymer			Graft Copolymer in the Mixture		
	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
G11-IC	1.61	7.48	0.53	1.47	2.77	0.49	0.80	1.65
G12-IA	1.61	7.48	0.41	1.20	2.91	.52	0.81	1.57
G140G	3.49	3.90	1.69	4.32	2.55	1.50	2.78	1.85
G141G	3.49	3.90	0.31	0.73	2.33	6.19	21.04	3.40
G142G	3.49	3.90	8.11	33.24	4.10	7.69	22.99	2.99
G143G	3.49	3.90	7.70	37.02	4.80	7.90	27.43	3.47
G144G	3.49	3.90	5.20	16.61	3.19	4.97	12.47	2.51

Table 4.8. BuLi cleavage of Polyepichlorohydrin [a]

Experiment No. [b]	Initial PECH/g	Y = (n-BuLi)/ m.mole	R_1	Z	Cleaved polymer				$[\eta]/g^{-1}cm^3$ in toluene at 30°C	Total % loss of polymer [c]
					Sample	GPC results				
						$\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$		
1	1	1.642	0.152	5.59	C_1	7.14	597.2	83.64	87.0	0.39
2	1	3.816	0.353	14.31	C_2	1.88	5.68	3.02	8.5	0.51
3	1	6.472	0.599	28.80	C_3	0.920	3.29	3.59	6.0	1.3
4	1	9.612	0.890	41.25	C_4	0.790	2.14	2.72	5.9	4.10

a PECH sample used was E9 (Table 4.1); $\bar{M}_n = 1.69 \times 10^5$; $[\eta] = 125\ cm^3g^{-1}$ at 30°C in toluene.

b 1 g of PECH dissolved in 100 cm^3 C_6H_6 in each experiment; reaction time = 6 h; temp. = 20°C.

c Percentage of unrecovered polymer

Y = m.mole n BuLi used per g PECH

R_1 = (Number of moles of n-BuLi/number of moles of Cl in initial PECH) used in a cleavage reaction.

$$Z = \text{Weight \% Cl displaced from the cleaved polymer} = \frac{\text{wt of Cl displaced}}{\text{wt of Cl in the polymer used}} \times 100.$$

Figure 4.1. Apparatus for Anionic Coupling Experiments, G5, G7, G11 and G12. (Section 4.2.2)

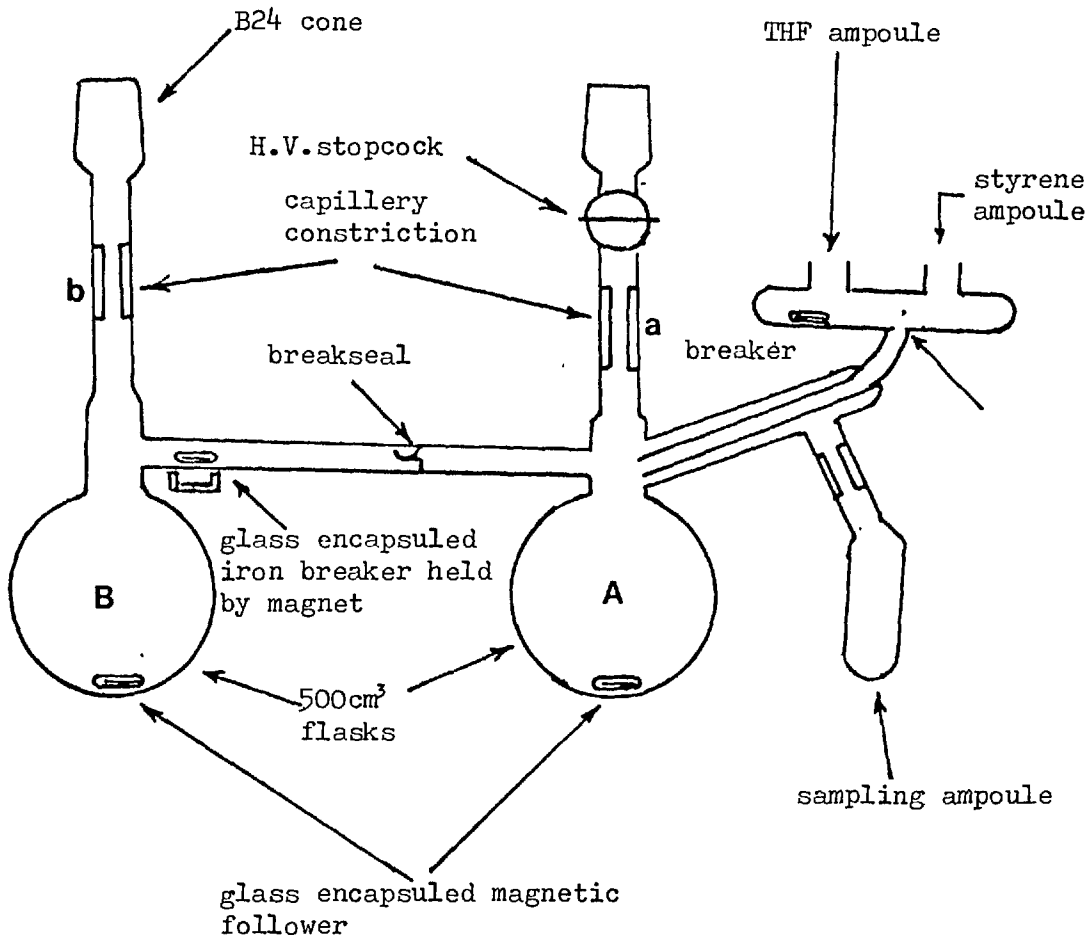


Figure 4.2. Apparatus for Fractional Precipitation

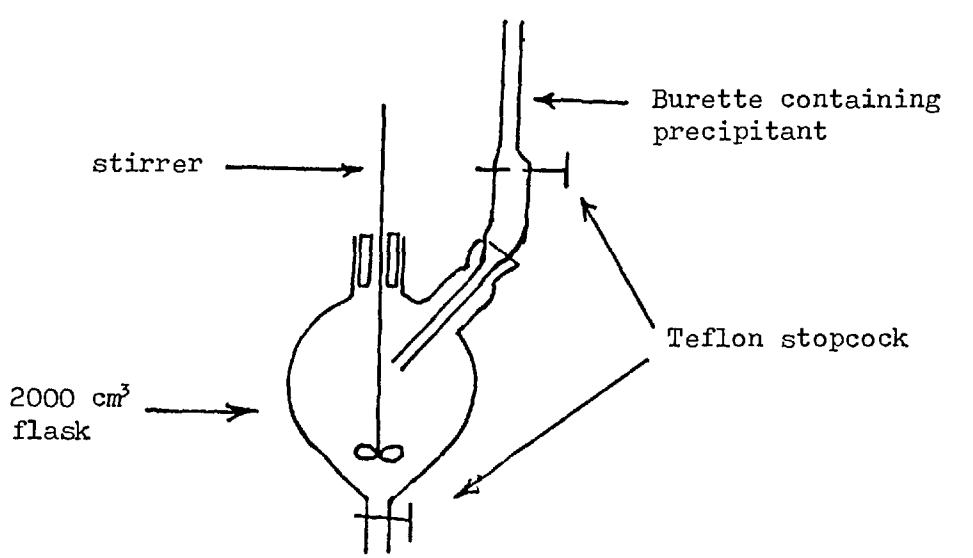


Figure 4.3. Turbidimetric Titration Curves for the Polymer Samples G142 and S28 in C_6H_6 Solution (1% w/v) on Titration with MeOH

[o G142, a P(ECH-g-S) copolymer mixed with homo-PS;
Δ S28, homo-polystyrene]

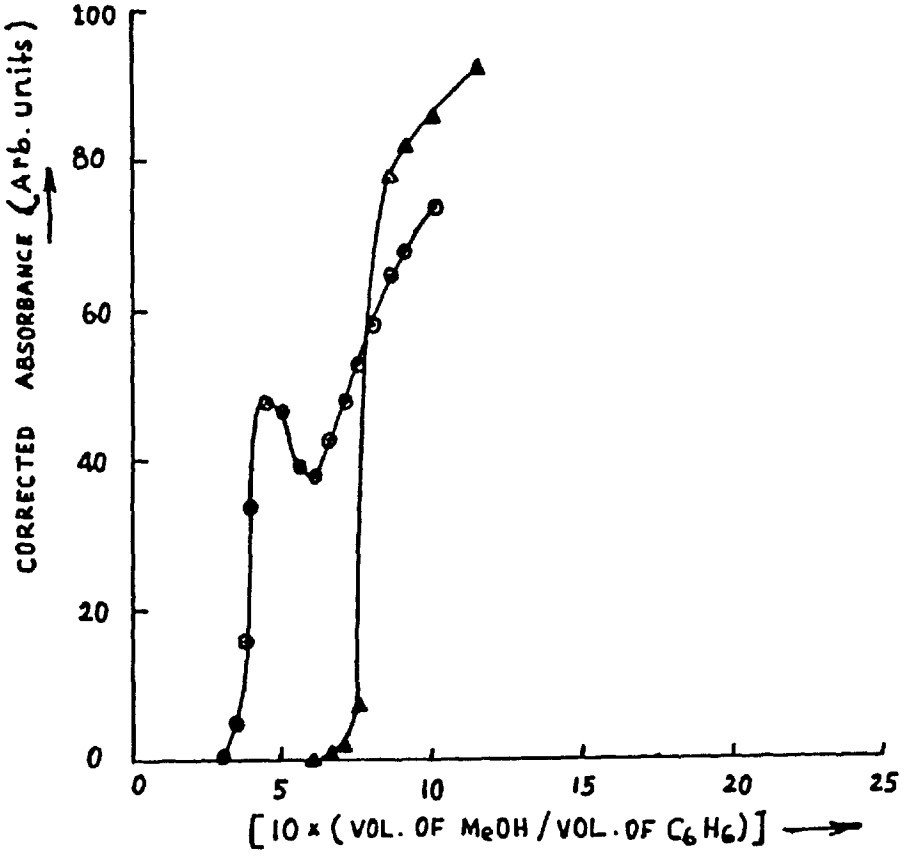


Figure 4.4. Gel Permeation Chromatograms

(a) Sample E19, PECH
(b) Sample G140, P(ECH-g-S) mixed with homo-PS
(c) Sample G140G, P(ECH-g-S) purified by fractional precipitation from G140; Δn = change in refractive index of the eluted polymer solution.

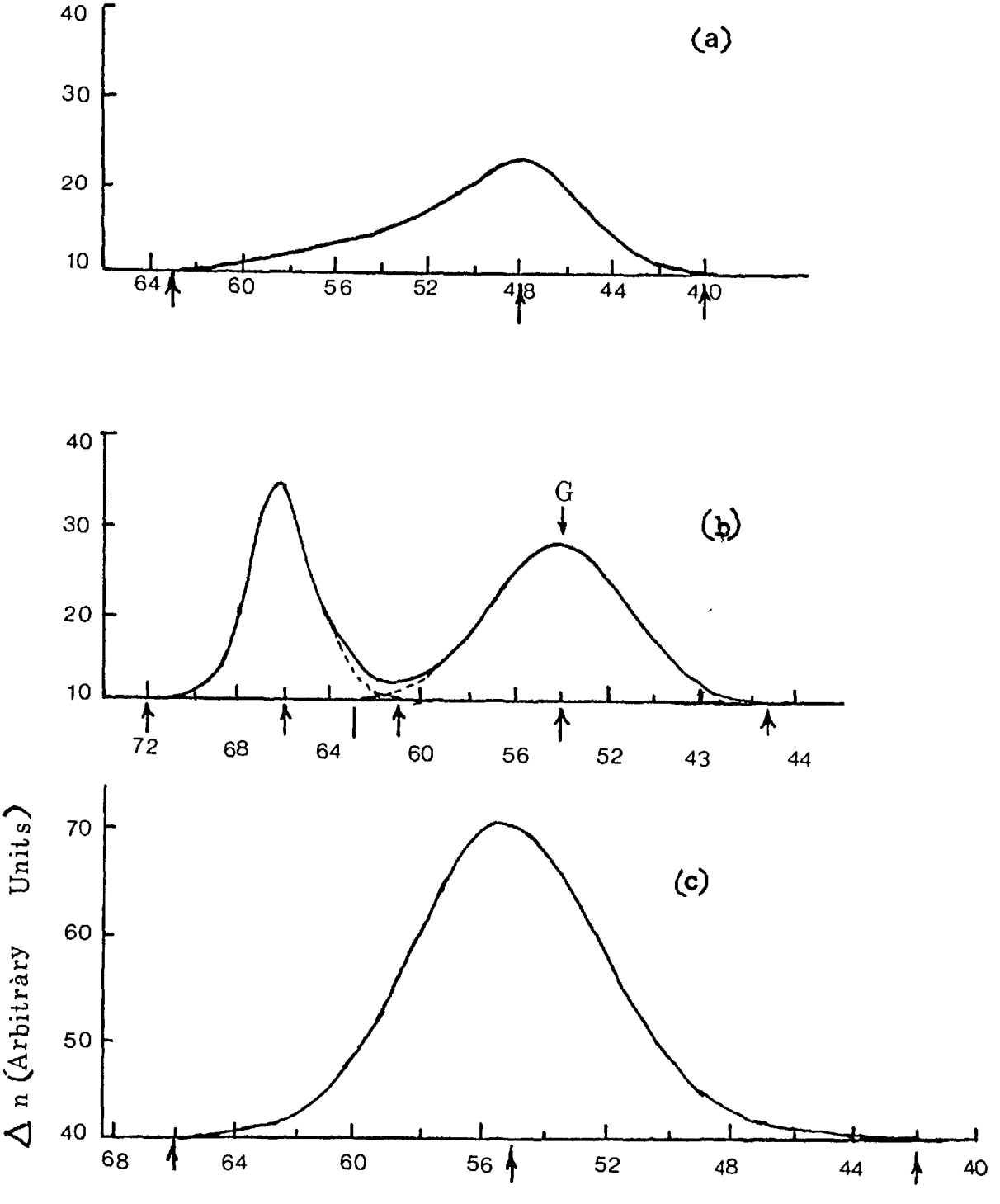


Figure 4.5. Gel Permeation Chromatograms

(a) Sample G143, P(ECH-g-S) mixed with homopolystyrene

(b) Sample G143G, P(ECH-g-S) purified by fractional precipitation from G143

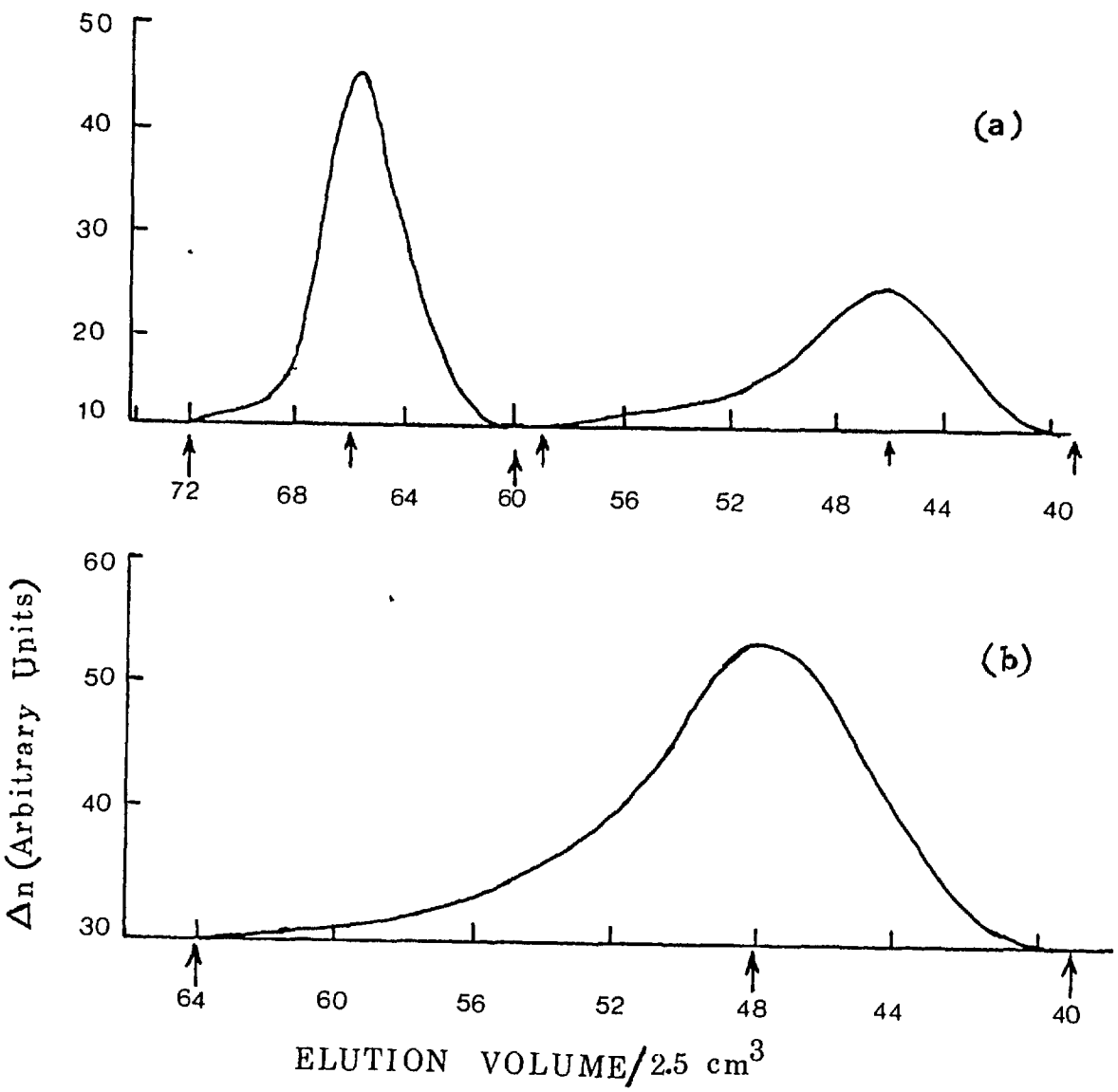


Figure 4.6. Grafting Efficiency of Polystyrene (% of total PS w/w grafted) in Graft Copolymer Samples G140G - G144G as a function of Molar Ratio R

$$R = \frac{\text{Number of moles of added } PS^-}{\text{Initial number of moles of Cl in PECH}}$$

⊙ Graft copolymers, G141G - G144G prepared in THF/C_6H_6 67/33 v/v

△ Graft copolymer G140G prepared in C_6H_6 containing a small amount of THF]

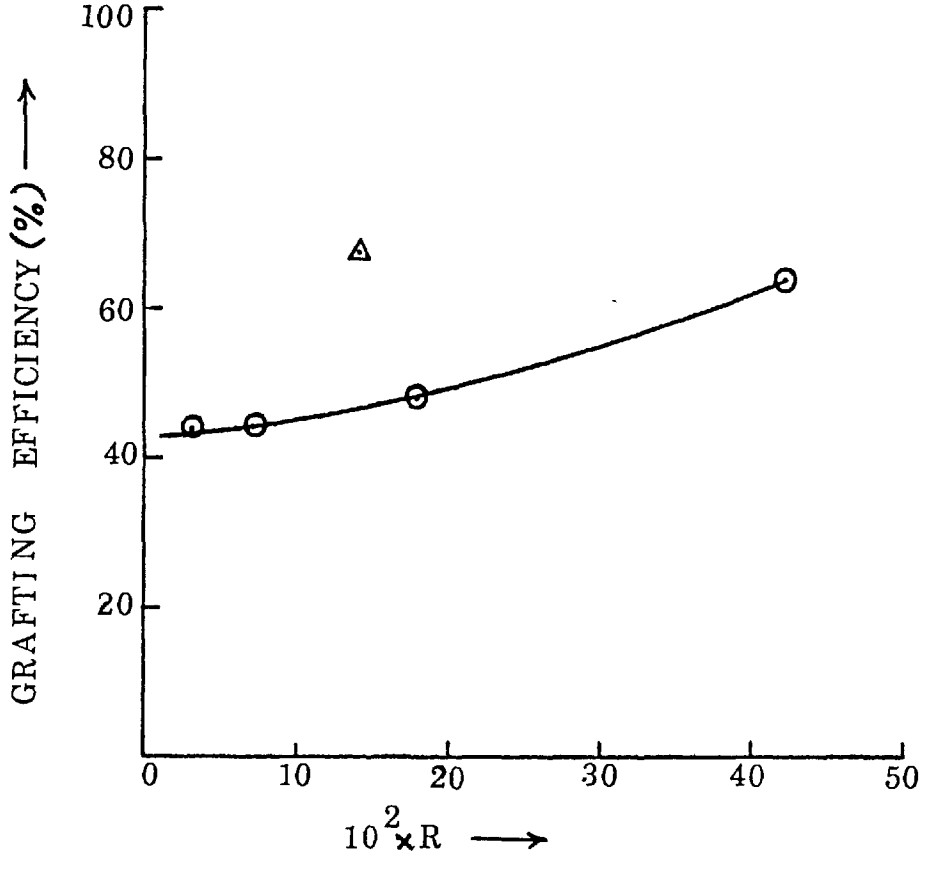


Figure 4.7. Relationship between $\bar{M}_n$ of the Graft Copolymer Samples G140G - G144G and the Molar Ratio 'R' used in Their Synthesis

[⊙ G141G - G144G prepared in THF/C_6H_6, 67:33 v/v;
△ G140G prepared in C_6H_6]

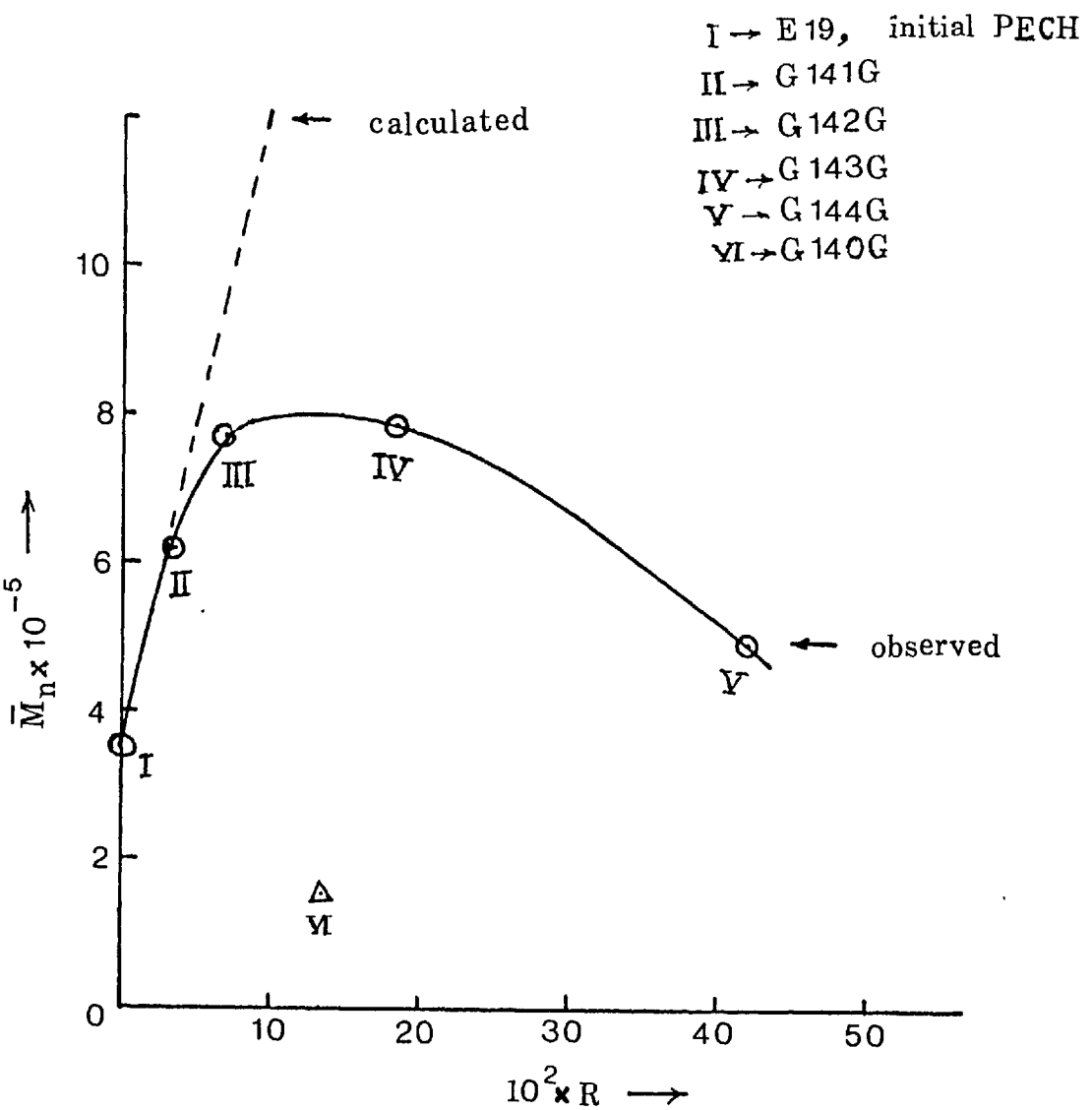


Figure 4.8. Relationship between Degradation Factor, $f = \bar{M}_n$ (cal)/$\bar{M}_n$ (obs) in the Graft Copolymer Samples G140G - G144G and the Molar Ratio 'R' used in their Synthesis

[G141G - G144G prepared in THF/C_6H_6, 67:33 v/v; G140G prepared in C_6H_6]

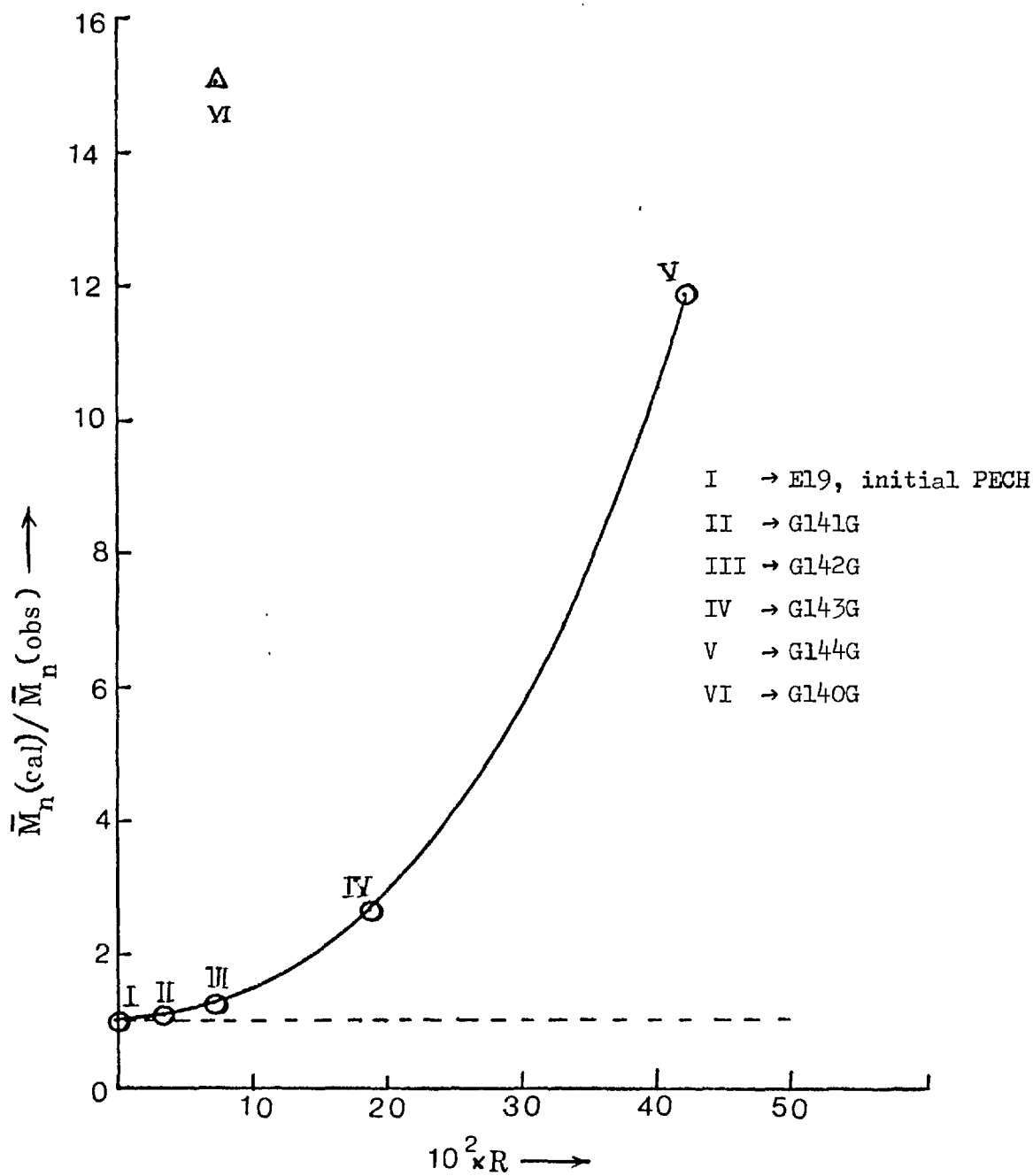


Figure 4.9A Infra-red Spectrum for P(ECH-g-S) Sample G141G (film) (PS content, 46.6% w/w)

[See Figure 3.1 for I.R. spectrum of amorphous PECH]

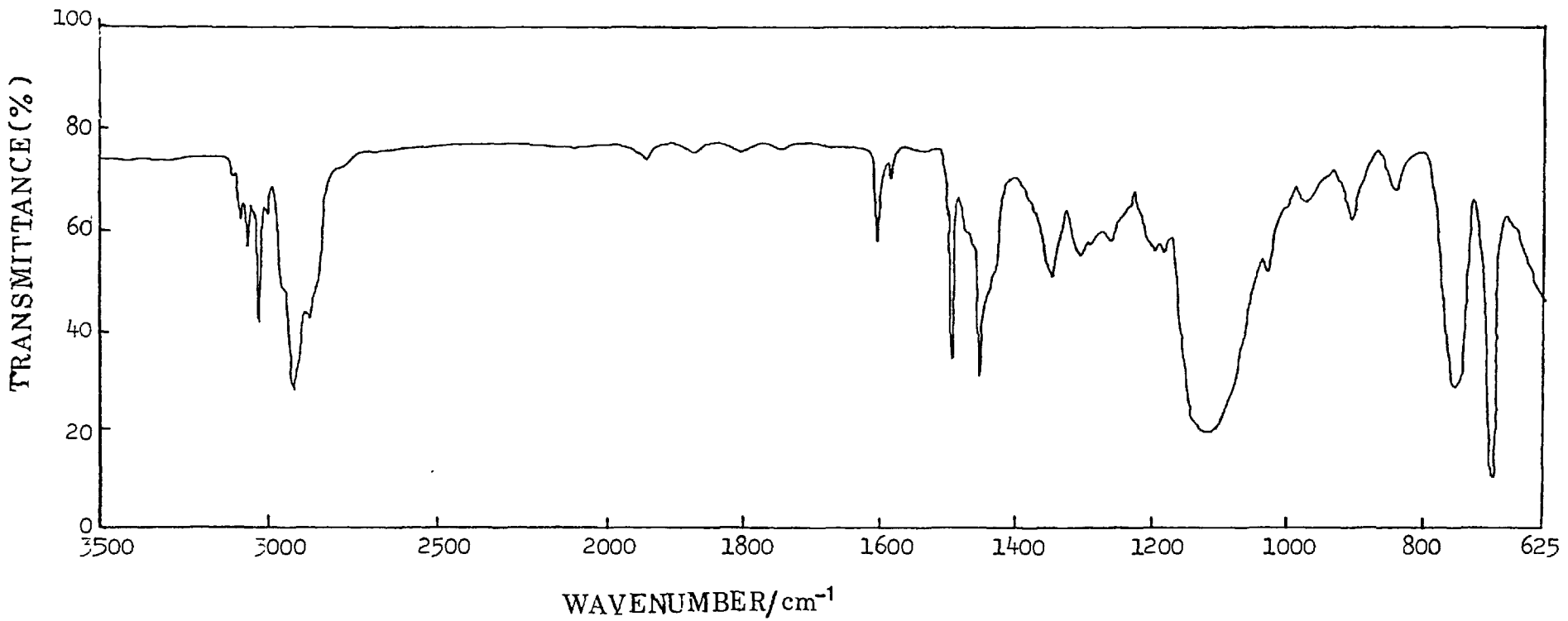


Figure 4.9B Infra-red Spectrum for P(ECH-g-S) Sample G144G (PS content, 94.1% w/w)

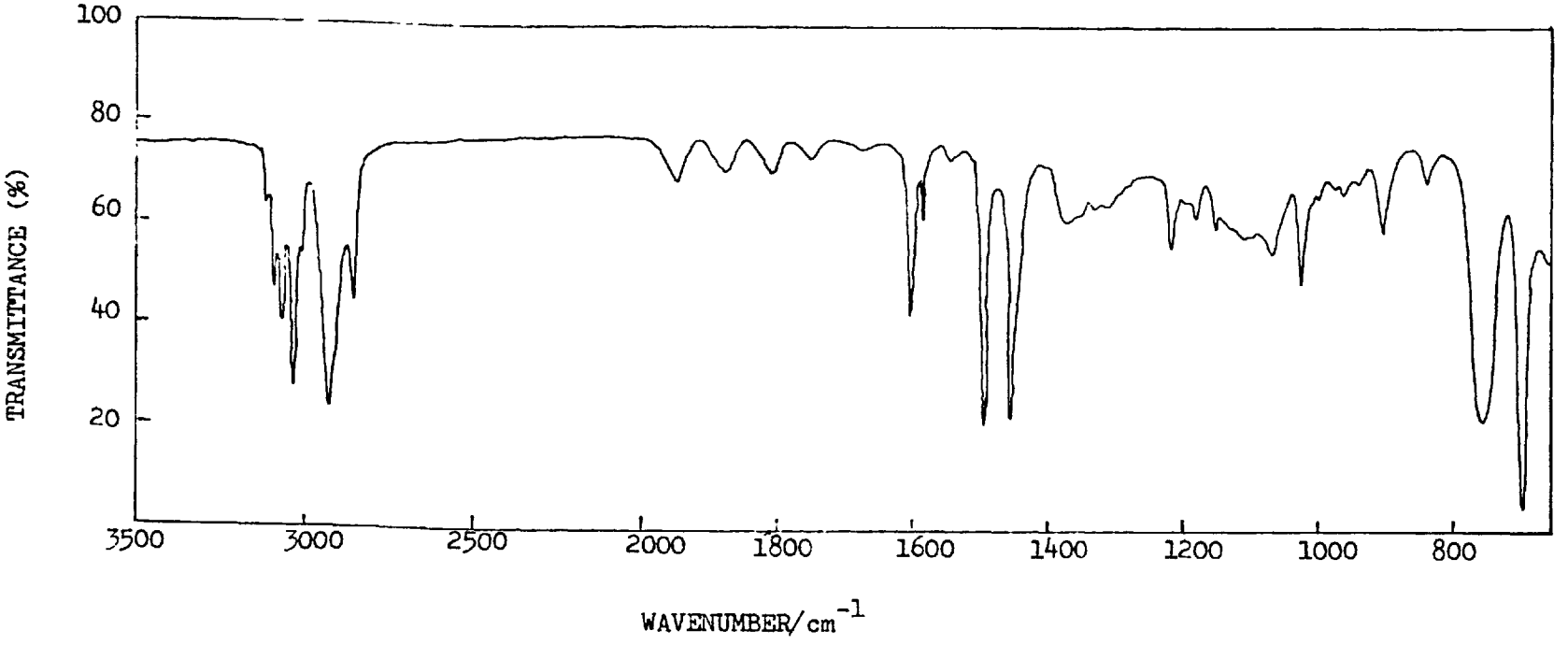


Figure 4.10. Infra-red Spectrum of the Cleavage Product G11-II Recovered from the Grafting Experiment G11 (see Section 4.3.2(g))

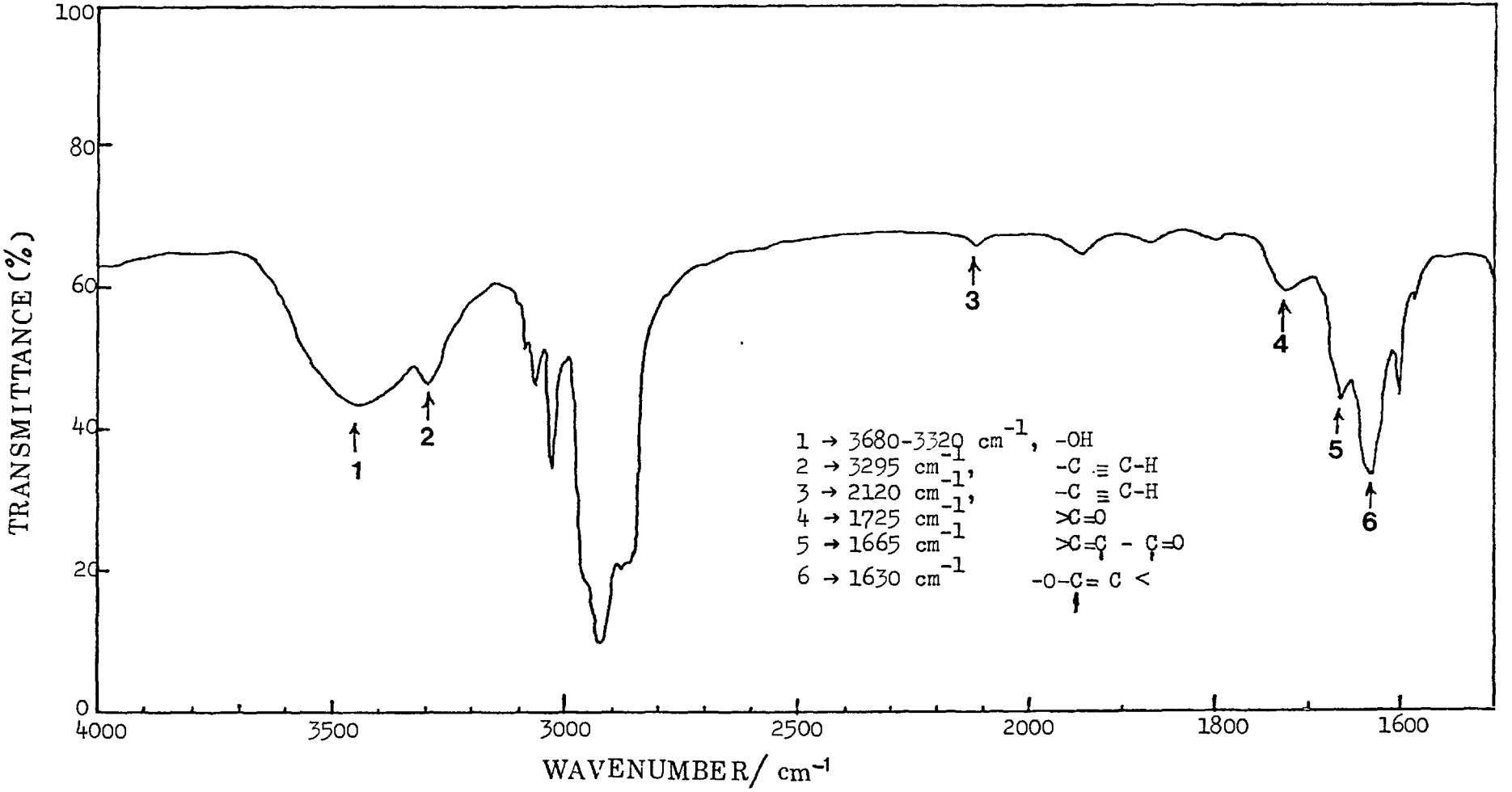


Figure 4.11. Infra-red Spectra of the BuLi Cleavage Products of PECH, C_1-C_4 in $CHCCl_3$ Solution

[Concentration, 38.48 mg cm^{-3}; cell thickness, 0.5 mm]

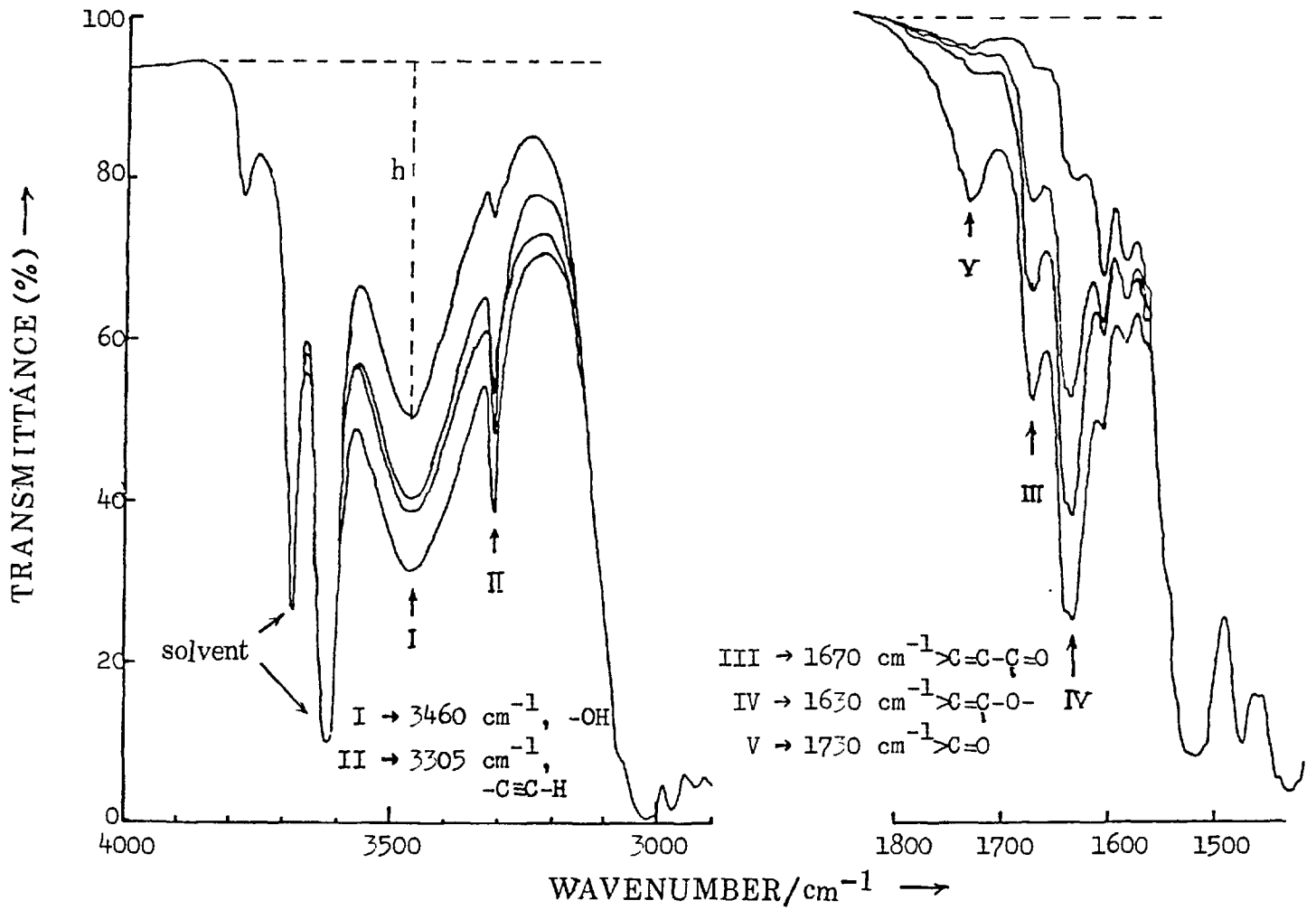


Figure 4.12. Relative Absorbance of Different Groups formed in the BuLi Cleavage Products (C_1 -C_4) of PECH as a Function of the Amounts of n-BuLi used for Cleavage Reactions

[Calculated from I.R. spectra in Figure 4.11]

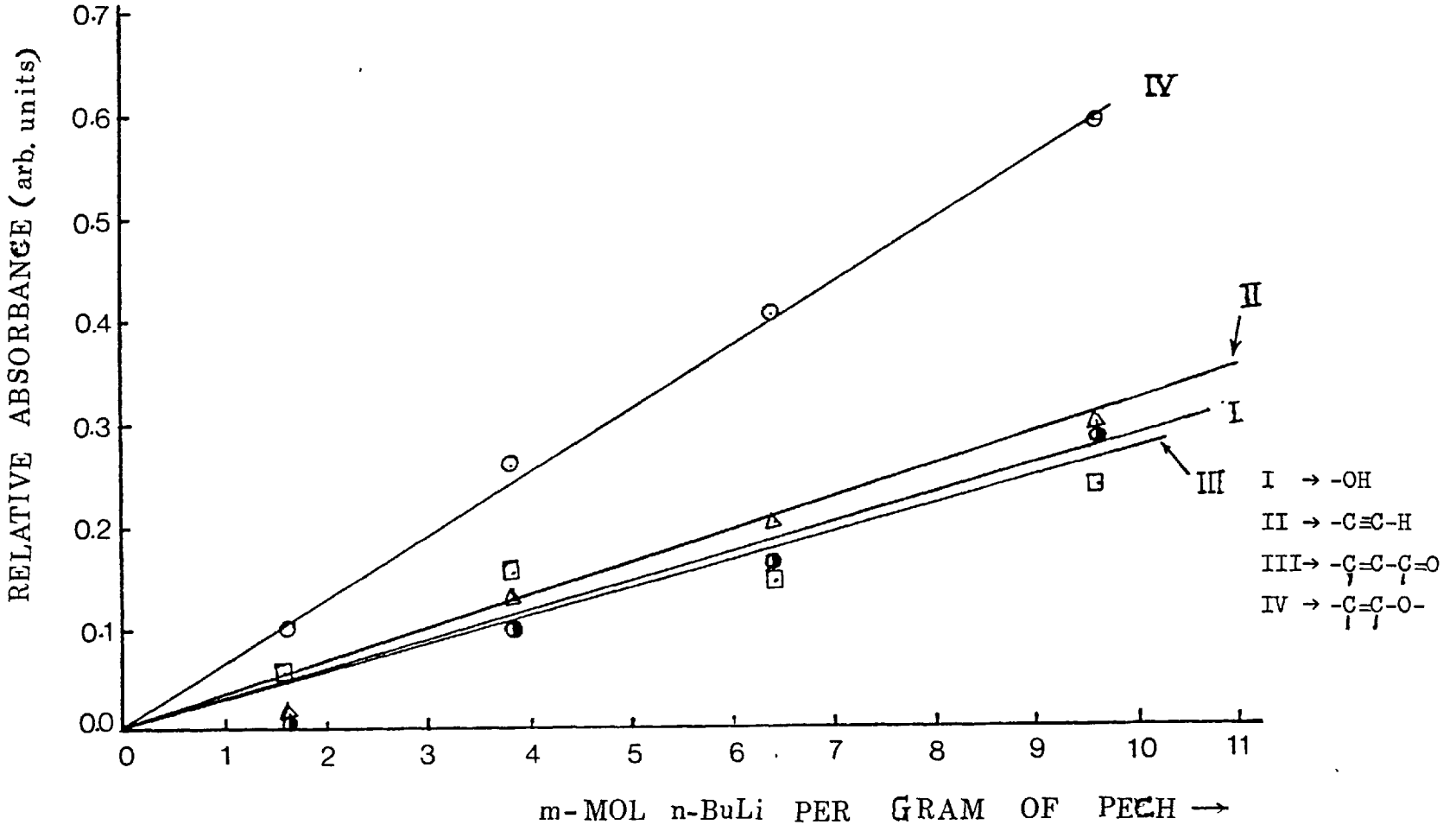


Figure 4.13. Drop in Molecular Weights in the BuLi-Cleavage Products of PECH as a Function of Molar Ratio R_1

$$R_1 = \left(\frac{\text{moles of n-BuLi used}}{\text{moles of Cl in initial PECH}} \right)$$

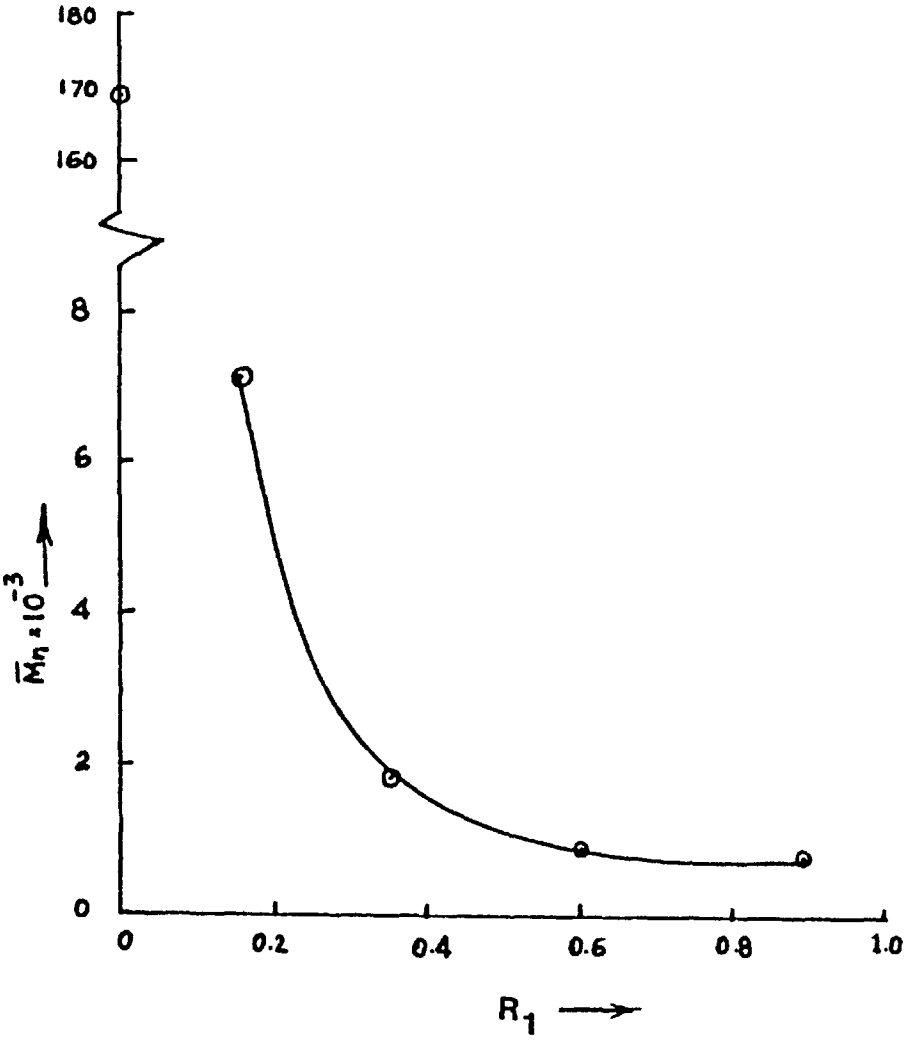


Figure 4.14. Viscometric results for PECH Sample E9
(in toluene at 30°C)

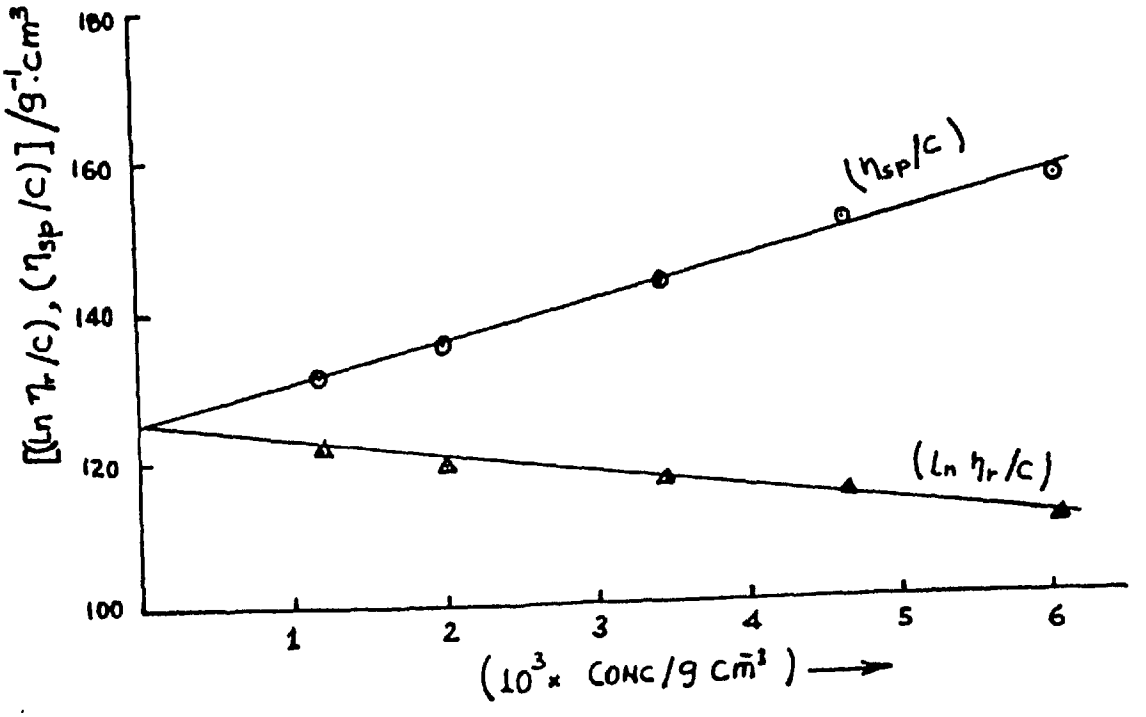


Figure 4.15. Drop in Limiting Viscosity Numbers in the BuLi-Cleavage Products of PECH as a Function of Molar Ratio R_1
(Limiting viscosity numbers measured in toluene at 30°C)

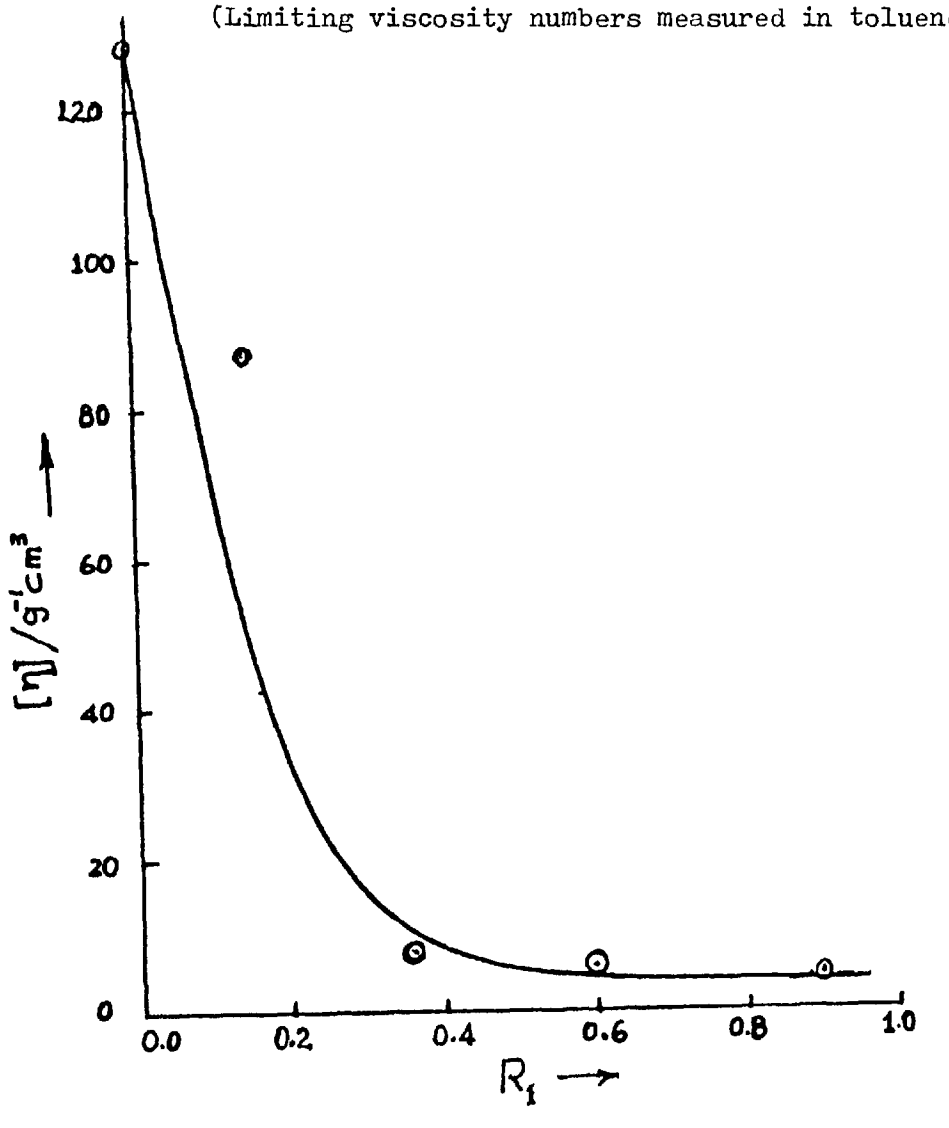
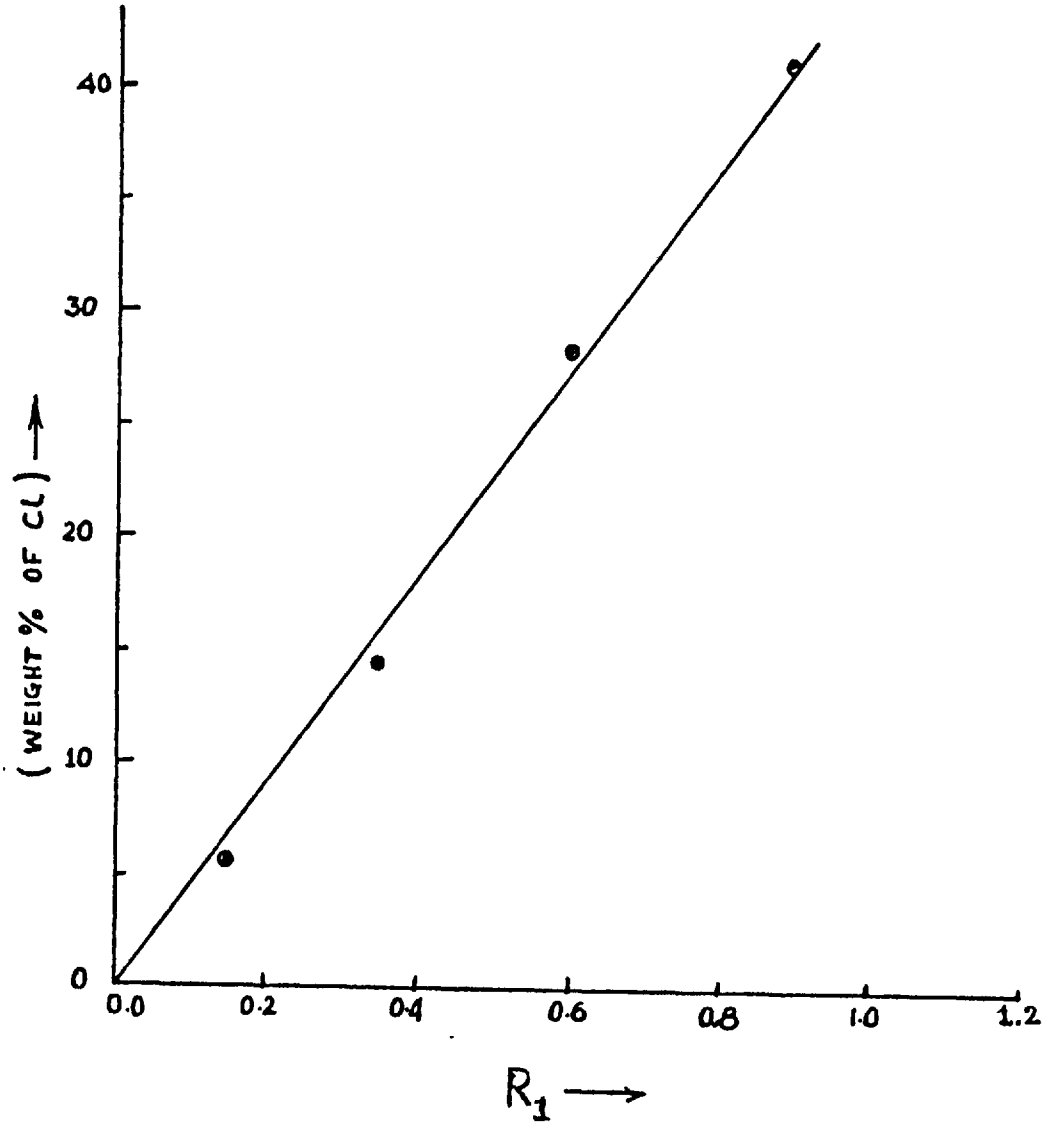


Figure 4.16. Weight Percent of Chlorine Displaced from PECH on Cleavage with n-BuLi against Molar Ratio R_1



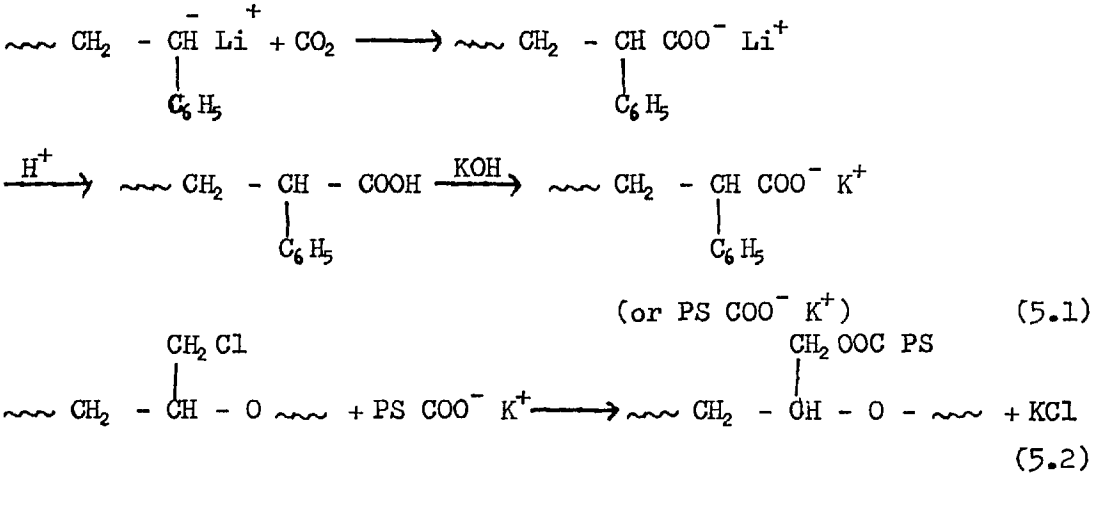
CHAPTER 5

CHEMICAL MODIFICATION OF POLYEPICHLOROHYDRIN AND SYNTHESIS OF POLY(EPICHLOROHYDRIN-g-STYRENE) USING POLYSTYRENE WITH A FUNCTIONAL END GROUP

5.1. Introduction

Various chemical modifications of epichlorohydrin polymers have been cited in the introductory chapter (Section 1.4). Some exploratory reactions were therefore carried out to find an easier method for grafting polystyrene onto polyepichlorohydrin. It was realized that a good nucleophile having a comparatively weak basic character would be a suitable reagent for coupling with epichlorohydrin polymers at the chloromethyl side chains. This combination of properties is difficult to achieve since strongly nucleophilic reagents are usually also strongly basic. A good solvent for both the polymer substrate and the modifying agent is also necessary. Some of the modification experiments are described in Section 5.3.

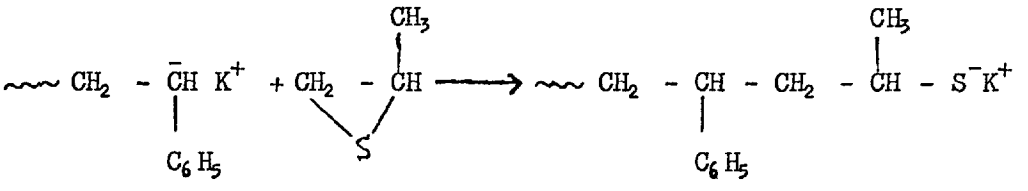
Following these modification experiments with smaller molecules, polyepichlorohydrin was later grafted with modified polystyrene by two methods. In the first method, living polystyrene was capped with -COOH end groups and then the K-salt was used for grafting onto polyepichlorohydrin.



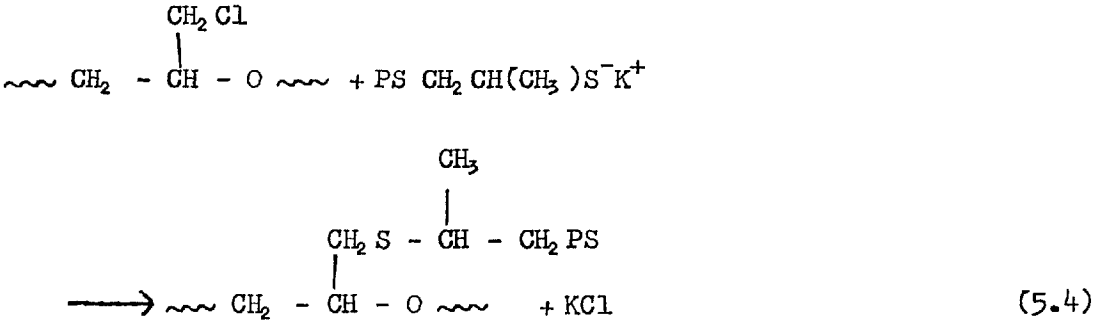
(5.1)

(5.2)

In the second method, $PS^- K^+$ was capped at the end with propylene sulphide and then the coupling of PECH with the polystyrene having mercapto end groups was carried out.



(or, PS^-K^+) [or, $PS\,CH_2\,CH(CH_3)S^-K^+$] (5.3)



(5.4)

The reaction (5.3) proceeds in a similar way to the capping of polystyryl sodium with ethylene oxide (138).

The introduction of functional end groups into living polymers has been described elsewhere (127,136-138).

5.2. Purification of Materials

(a) Benzene, THF, Styrene were purified and stored as described in Section 2.2.2.

(b) n-BuLi, Cumyl K were handled as described in Section 2.2.2. The concentration of cumyl K stored in the deep freeze was not estimated before use due to shortage of this chemical. So values of concentration obtained some time in the year previously were assumed.

(c) DMF (BDH) was dried over activated Linde 4A molecular sieve and then distilled under reduced pressure. The middle fraction was collected.

(d) Thiophenol (Aldrich Chemical Co.) used for the preparation of Na-thiophenoxide was used without further purification.

(e) Sodium thiophenoxide used for the exploratory chemical modification of PECH was prepared and purified as described elsewhere (189). It was stored in a vacuum desiccator in the dark before use.

(f) Phenyl acetic acid (Hopkin and Williams) 99% w/w pure, was used for modification of PECH without further purification.

(g) Propylene sulphide (Aldrich Chemical Co.) 98% w/w pure, was dried over powdered CaH_2 for 12 h and then distilled in the vacuum line immediately before use. This reagent was used for termination of living polystyryl potassium.

(h) Polyepichlorohydrin (Herchlor H) was purified as described in Section 4.2.1. All the PECH samples except E17 (Table 5.1) used in experiments described in this chapter were finally prpcipitated in MeOH containing 0.1% w/v antiocidant, Topanol CA.

5.3. Chemical Modifications of Polyepichlorohydrin

5.3.1. Experiments and Results

(a) Substitution of Cl atoms with thiophenoxide, C_6H_5S groups

1 g of PECH containing a trace of antioxidant (about 0.2% w/w) was dissolved in 100 cm^3 of distilled DMF and was mixed with 2.15 g PhSNa. The mixture was not completely homogeneous because of the incomplete solubility of PhSNa in DMF. The ratio (moles of C_6H_5 SNa/moles of Cl in PECH) used was 1.51. The well-mixed mixture was heated in a two-necked flask provided with a reflux condenser and a drying guard tube in a nitrogen atmosphere at 60°C for 10 h.with constant stirring. An insoluble polymer was formed. This polymer was thrice precipitated from a dispersion in DMF into MeOH and washed several times with fresh

MeOH to remove any unreacted PhSNa.

The dried polymer was an elastomeric solid insoluble in the common solvents for PECH. Microanalysis showed complete replacement of Cl by thiophenoxide groups.

In another experiment using (moles of PhSNa/moles of Cl in PECH) = 0.50, carried out under identical conditions, the recovered polymer showed quantitative substitution of Cl by thiophenoxide groups. This modified polymer was partly soluble in DMF, THF, $CHCl_3$, C_6H_6 and other common solvents for PECH. The molecular weight of the polymer could not be accurately measured, because the GPC peak started two counts outside the range of the calibration curve. This suggested the presence of some very high molecular weight polymer, possibly due to cross-linking. However, the estimated $\bar{M}_n$ was 2.34×10^5 ignoring the high molecular weight GPC tail. With the number average molecular weight, $\bar{M}_n$ of the starting PECH as 1.98×10^5, the expected $\bar{M}_n$ of the substituted polymer would have been 2.77×10^5 for 50% substitution. The I.R. spectrum of the polymer film cast from CH_2Cl_2 solution showed the moderate aromatic C-H stretching peak at 3030 cm^{-1} and a sharp peak due to aromatic -C=C- stretching at 1580 cm^{-1}. This confirmed that substitution of Cl groups by C_6H_5S groups had occurred.

(b) Substitution of Cl atoms with phenyl acetate groups, $C_6H_5CH_2COO$-

1.002 g of PECH was dissolved in 50 cm^3 of distilled DMF. 1.08 g phenyl acetic acid dissolved in 40 cm^3 of DMF was titrated with a concentrated KOH solution in MeOH to the end point in the presence of phenolphthalein indicator. This potassium phenyl acetate solution and washings (vol. 50 cm^3) was mixed with the PECH solution. The mixed solution was then heated in a nitrogen atmosphere at 60°C for 10 h with constant stirring using a magnetic stirrer. The resulting polymer

was twice precipitated in MeOH from DMF solution and then dried in a vacuum oven at 45°C to constant weight.

Results: (moles of $C_6H_5CH_2COO^-$/moles of Cl in PECH) used was 0.73

Expected substitution of Cl = 73.0%

Observed substitution of Cl from microanalytical results = 29.6%. The I.R. spectrum showed characteristic aromatic C-H stretching peaks in the region 3000 - 3450 cm^{-1}, the aromatic -C=C- stretching peak at 1600 cm^{-1} and a very strong peak due to ester linkages at 1730 cm^{-1}

Number average molecular weights, $\bar{M}_n$

$\bar{M}_n$ of the starting PECH = 1.61×10^5

$\bar{M}_n$ (expected) of the partly substituted polymer with 29.6% substitution = 2.12×10^5

$\bar{M}_n$ measured = 1.89×10^5.

5.3.2. Discussion

The quantitative substitution of Cl in PECH by C_6H_5S groups is due to the greater nucleophilicity of the latter. The thiophenoxide group because of the polarizability of the electron cloud around each S atom is a very good nucleophile. An alkali metal salt of a thiol may be expected to have similar nucleophilicity to a thiophenoxide.

Substitution with phenyl acetate groups was shown to be incomplete in 10 h. However, quantitative substitution of Cl from PECH in DMF solution with acetate groups using excess of potassium acetate at 150°C has been achieved before (113). Acetic acid and phenyl acetic acid have similar acid strengths since their pK values in water are 4.75 and 4.28, respectively. Thus the acetate and phenyl acetate groups may be expected to have similar basicity and nucleophilicity in water and also in the polar solvent DMF. Hence complete substitution of Cl by phenyl acetate groups is expected to occur at higher temperatures.

On the basis of this assumption, it was anticipated that polystyryl carboxylate would graft onto PECH by substitution reactions.

5.4. Synthesis of Polystyrene with -COOH End-group (PS COOH)

5.4.1. Polymerization and Purification of Polymers

(a) Polymerization Polystyrene samples S22 and S23 were prepared in C_6H_6 in presence of a small amount of THF, initiated by n-BuLi and the sample S24 was prepared in THF initiated by cumyl potassium. The experimental conditions are given in Table 5.2. The procedure used was the same as described in Section 2.2.3. After the appropriate reaction time, the living polymer solution was forced out of the polymerization flask (Figure 2.6) into a slurry of solid CO_2 in purified THF contained in a beaker. The operation was done under a positive pressure of argon and by means of a length of steel tubing introduced through the breakseal 'S' in the side tube of the flask.

(b) Purification of polymers. Excess CO_2 was allowed to boil off from the terminated polymer. The polymer solution was diluted to a concentration of 4% w/v and filtered. The polymer was then precipitated into a ten-fold excess of methanol containing 0.1% v/v HCl and it was assumed that the excess of acid would convert all the PS $COO^- Li^+$ to the corresponding acid. The low molecular weight polystyrene, sample S23 (Table 4.2) was precipitated as a tacky mass adhering to the bottom of the precipitation beaker. This polymer was redissolved in THF and reprecipitated in ice-cold MeOH. Sample S22 was reprecipitated in a similar way.

The reprecipitated polymers were washed successively with methanol and distilled water on a sintered glass funnel to remove any unreacted HCl. The purified polymer samples were then dried to constant weight in a vacuum oven at 50°C.

(c) Fractionation of polystyrene sample S22. In anticipation that the PS COOH prepared in this work might have been contaminated with dipolystyryl ketone and tripolystyryl carbinol, as was observed before (137), the sample S22 was fractionated from a 2% w/v solution in C_6H_6 by dropwise addition of methanol. The solvent - non-solvent mixture was centrifuged to separate about one quarter of the total polymer in the form of a dispersion. This fraction was rejected. The solution containing the rest of the polymer was concentrated by rotary evaporation of some of the solvent at room temperature and the polymer was then precipitated and dried as before.

Surprisingly, the GPC profile of the fractionated sample S22-1 obtained from S22 contained a high molecular weight tail (footnote, Table 4.3), whereas the non-frationated sample S22 did not. The other polymer samples, S23 and S24, were therefore used without further purification. The GPC profile of the sample S23 also showed a high molecular weight tail.

5.4.2. Characterization : Determination of Number Average Molecular Weights.

(a) The end-group titration method

For the estimation of -COOH end-groups in the polymers and hence the molecular weights, a standard succinic acid solution in distilled water (1.5×10^{-2}M), a potassium hydroxide solution (about 2.5×10^{-2}M) in MeOH and freshly distilled DMF were used. The alcoholic KOH solution was filtered and used within two hours of preparation. It was standardized against the standard succinic acid solution using phenolphthalein as indicator.

PS COOH samples in DMF solution (about 0.5 g in 25 cm^3) were titrated against the KOH solution, again using phenolphthalein as indicator. Three titrations for each polystyrene sample were made. A blank titration was carried out using an equal volume of DMF for each titration.

The molecular weights calculated from the amounts of KOH used in the three titrations agreed within 0.5% for the sample S23 and within 3% for the sample S22-I but varied up to 10% for the sample S24 having a relatively high molecular weight. This shows the efficacy of the end-group titration method of determination of molecular weight for only low molecular weight polymers. The average of the molecular weights obtained from the titration results for each polystyrene sample was taken.

(b) Vapour pressure osmometry. Number average molecular weights for the samples S22-I and S23 were measured by vapour pressure osmometry using a Knauer Vapour Pressure Osmometer. The principle and method of operation were described in the instruction manual accompanying the instrument. Measurements were made at 37°C using toluene as solvent. The instrument was calibrated with benzil ($C_6H_5COCOC_6H_5$, MW = 210.2). A typical calibration curve is shown in Figure 5.1. The results obtained for the polystyrene sample S23 are plotted in Figure 5.2. The number-average molecular weight is given by

$$\bar{M}_n = \frac{K}{\lim_{c \to 0} \left(\frac{\Delta R}{c}\right)} \text{ g mol}^{-1} \qquad (5.5)$$

where ΔR is the decastat reading in ohm, c is the concentration of the polymer in g dm^{-3} and K is the calibration constant given by

$$K = \frac{\Delta R}{\lim_{c' \to 0} c'} \text{ ohm dm}^3 \text{ mol}^{-1} \qquad (5.6)$$

where c' is the concentration of the calibrant in mol dm^{-3}. Thus K and $\bar{M}_n$ were estimated from the intercepts of the plots of $\Delta R/c'$ against c' and $\Delta R/c$ against c, respectively.

(c) Gel permeation chromatography. The number and weight average molecular weights and the $\bar{M}_w/\bar{M}_n$ values as measured by GPC for the

polystyrene samples are given in Table 5.3, along with the number average molecular weights measured by the other methods.

5.4.3. Results and Discussion

The polystyrene samples S22-I and S23 (Table 5.3) had a high molecular weight tail amounting to about 3.3% w/w and 2.1% w/w of the total polymer respectively as calculated from the respective GPC chromatogram areas. Surprisingly, the GPC profile of the non-fractionated polystyrene sample S22 did not show any high molecular weight tail whereas the sample S22-I separated from S22 by fractionation showed such a tail.

These high molecular weight tails in the samples S22-I and S23 were not due to dipolystyryl ketone or tripolystyryl carbinol (137), because the molecular weights of the respective high molecular weight tails were about 81 and 39 times the molecular weights corresponding to the major peaks in the polymer samples, respectively. Probably the high molecular weight polystyrenes were formed by cross-linking of the PS COOH molecules during the purification of the polymers or less likely might be formed after injection into the GPC column.

The broad molecular weight distribution in the sample S24 as indicated by its high $\bar{M}_w/\bar{M}_n$ value (Table 5.3) was due to inefficient stirring during the preparation of this sample.

Amounts of inactive polystyrene (not ended with -COOH group) in the samples S22-I and S23.

When a PS COOH sample contains some inactive polystyrene molecules, the titration method will give a relatively high number average molecular weight. The number average molecular weight $\bar{M}_n'$ measured by the titration method can be related to the true number average molecular weight, $\bar{M}_n$, by the equation

$$\bar{M}'_n = \bar{M}_n/x \qquad (5.7)$$

when x is the weight fractions of active polystyrene molecules, assuming that both active and inactive polystyrene molecules have the same average molecular weight. The difference between the number-average molecular weights measured by vapour pressure osmomentry and titration methods (Table 5.3) suggests that there were more inactive polystyrene molecules in the sample S22-I than in S23. However, because of the presence of high molecular weight tails, the osmomentry also probably gave higher $\bar{M}_n$ values for the samples S22-I and S23. Hence, in all later calculations, the molecular weights of samples corresponding to the major peaks in their respective GPC profiles have been used.

5.5. Synthesis of Poly(epichlorohydrin-g-styrene) by Coupling the K-salt of PS COOH with PECH

5.5.1. Coupling Reaction and Purification of Graft Copolymers

(a) Coupling reaction. Usually 1 g of PECH containing a trace of antioxidant (about 0.2% w/w) was dissolved in 50 cm^3 of distilled DMF in a two-necked flask. A weighed amount of PS COOH dissolved in about 30 - 40 cm^3 of DMF, was separately titrated up to the end-point with KOH solution in MeOH in the presence of phenolphthalein as indicator. The KOH solution used was relatively concentrated and of unknown strength in the synthesis of series 4 graft copolymers and was approximately 0.1M for the synthesis of series 5 graft copolymers (Table 5.4).

The PS $COO^- K^+$ solution and its washings were mixed with the PECH solution so that the ultimate composition of PECH was 1% w/v. The mixed solution was then heated in a slow stream of nitrogen at the desired temperature for the requisite reaction time as mentioned in Table 5.4. A two-necked flask provided with reflux condenser and a drying guard tube served as a reaction vessel. The solution was vigorously stirred

during the reaction period using a magnetic stirrer. A liquid paraffin bath was used to maintain the temperature constant.

In some experiments, the weight of PECH used was either more or less than 1 g, but the final concentration of PECH in the mixed final solution was always maintained at 1% w/v.

After the measured reaction time, the solution was cooled, filtered and the polymer was precipitated in a Waring blender in a five-fold excess of MeOH containing 0.1% w/v antioxidant. The polymer was dried to constant weight in a vacuum oven at $45^{o}C$.

In the synthesis of graft copolymer samples G41 - G44, a fixed volume (25 cm^3) of the reaction mixture was pipetted out at different time intervals and the polymers were then precipitated and dried as before. A similar procedure was applied in the synthesis of graft copolymer samples G45 and G46.

(b) Purification of graft copolymers. All the graft copolymers of the two series were separated from homopolystyrene by fractional precipitation procedures based on turbidimetric titrations described in Section 4.2.3(c). A turbidimetric titration curve was drawn for one impure graft copolymer from a series and also for the homopolystyrene used in the synthesis of the graft copolymers in that series. The progressive separation of the graft copolymer was followed using a 1% w/v solution of the polymer mixture in C_6H_6 and methanol containing 0.1% antioxidant as the precipitant.

Attempts were made in all experiments to recover all of the graft copolymers. The solvent/non-solvent mixture, discarded after a precipitation was usually tested to check that no graft copolymer had been lost. This was achieved by evaporation of all of the liquid from a portion of the solvent/non-solvent mixture and recording the I.R. of the isolated

solid. This procedure ensured the complete recovery of the graft copolymer. All of the graft copolymers had to be twice purified by the fractional precipitation procedure, described above.

(c) Recovery of unreacted polystyrene. The homopolystyrene mixed with the graft copolymer sample G53 was recovered during the purification of the latter by fractional precipitation. The solid was precipitated from a 2% w/v solution in THF into MeOH containing 0.1% v/v HCl in order to convert any unreacted PS $COO^- K^+$ into PS COOH. The polymer was purified as before (Section 5.4.1 (b)). This polymer was however found to be dead polystyrene not containing -COOH groups.

(d) Purification of graft copolymers for composition determination. Some of the graft copolymers, especially those with PS contents less than 40% w/w in Series 5 (Table 5.4) were tough elastomeric solids. However, graft copolymers with PS contents of 40 - 60% w/w were in most cases tough leathery solids. It was difficult to isolate all of these copolymers in a suitable coagulated form, washed free of antioxidant, even by precipitation in ice-cold methanol.

For UV analysis, the polymers had to be free of antioxidant. This was ensured in all cases by extraction of the polymers with diethyl ether.

Previous experience showed that diethyl ether is a solvent for P(ECH-g-S) copolymers with short branches and a high extent of grafting. So washing with diethyl ether might have changed the overall composition of the graft copolymers. However, these graft copolymers were found to be very homogeneous in composition, as shown by the two following experiments.

In one experiment, graft copolymer sample G53, having overall PS content 46.1% w/w was roughly fractionated into two fractions G53-I and

G53-II. UV analysis showed that the reprecipitated dried polymer fractions G53-I and G53-II had PS contents of 47.6% w/w and 46.3% w/w respectively.

In another experiment, graft copolymer sample G51, freed from antioxidant, was extracted with boiling CCl_4 in a Soxhlet apparatus. CCl_4 is a swelling non-solvent for PECH. It was expected that any PS or antioxidant trapped in the polymer would be removed by this extraction. A porition of the graft copolymer was lost by this extraction, but the graft copolymer left unextracted was found, on reprecipitation and drying, to have almost the same composition as the starting graft copolymer sample G51.

5.5.2. Characterization

(a) Overall composition

(i) U.V. analysis was performed as described in Section 4.2.4 (c)(i). For the calculation of the PS content in a graft copolymer sample, the specific extinction coefficient value of the respective polystyrene used in the synthesis of the graft copolymer was used and the specific extinction coefficient value for PECH was taken as 0.06 $dm^3 g^{-1} cm^{-1}$ as measured for a freeze-dried antioxidant-free PECH sample.

(ii) Elemental microanalysis for carbon, hydrogen and chlorine was carried out. The percentage of polystyrene calculated from % Cl by Equations (4.2) and (4.3) agreed very well with the % PS w/w measured by UV analysis (Table 5.4).

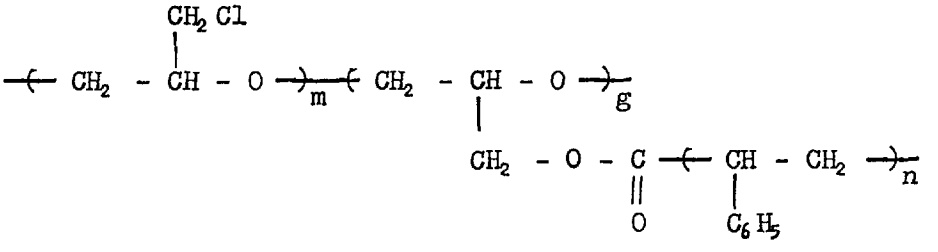
(b) Molecular weights, $\bar{M}_n$, $\bar{M}_w$ and the molecular weight distributions of the parent PECH samples and the purified graft copolymer samples (Table 5.5) were all obtained by GPC. All the samples showed single peaks in their respective GPC traces. A plot of the observed and calculated $\bar{M}_n$ for the series 5 graft copolymers against the y/x ratios is given in Figure 5.6, where y/x = (weight % PS/weight % PECH) in a graft copolymer.

(c) Limiting viscosity numbers, $[\eta]$, of the PECH samples and the purified graft copolymer samples were measured in toluene at 30°C, as described before (Section 4.5.3 (c)). A plot of the limiting viscosity numbers of the series 5 graft copolymers against the y/x ratios is given in Figure 5.8.

(d) I.R. spectra of the graft copolymers were recorded as before. The spectra of these graft copolymers were similar to those of the graft copolymers described in Chapter 4 except that a weak peak at 1735 cm^{-1} appeared in some cases. The appearance of this peak was probably due to ester linkages and may also be due to some carbonyl groups formed by the cleavage action of excess KOH used in some experiments on PECH.

(e) Calculation on the composition

Grafting efficiency of polystyrene, inverse graft frequency and predicted $\bar{M}_n$ values of the graft copolymers were calculated by similar equations as (4.6) - (4.9) in Section 4.2.4. For calculations of grafting efficiency and predicted $\bar{M}_n$, the weight % of PS and of PECH as measured by UV analysis were used. No corrections for the presence of ether units with chlorine atoms replaced by polystyrene branches was deemed necessary in the UV measurements. Inverse graft frequencies were calculated from the % chlorine contents obtained by microanalysis assuming the structure of the graft copolymer as



where m, g and n have the usual significance.

The Ratio y/x was calculated where x and y are weight % of PECH and PS in the graft copolymer as measured by UV analysis. Based on this ratio, predicted $\bar{M}_n$ values of the graft copolymers were calculated by equation (4.8). Figures 5.6 and 5.8 are plots of $\bar{M}_n$ and $[\eta]$, respectively, of the series 5 graft copolymers against $\frac{y}{x}$ values.

Composition of the initial PECH was slightly different from the theoretically expected composition of the polymer (Table 5.1). For all calculations, the theoretical composition of the polymer was used. No correction was made for the trace of antioxidant present in the polymers used for the grafting experiments.

The Symbol, R, used in places in the discussion is the ratio,

$$\frac{\text{number of moles of PS}}{\text{number of moles of Cl in PECH}}$$

used in a grafting experiment and $R' = \frac{1}{R}$. The number of moles of PS used was calculated from the amount of PS used and the $\bar{M}_n$ of the respective PS measured by GPC. The term "PS" in this discussion signifies polystyryl carboxylic acid, PS COOH which may be contaminated with some dead polystyrene, PSH.

5.5.3. Study of the Effect of KOH on the Graft Copolymers and PECH

(a) Effect of alkali on ester linkages of the graft copolymers

0.8 g of the graft copolymer sample G47 containing 53.3% PS (inverse graft frequency 44) dissolved in 50 cm^3 of DMF was stirred with 4.0 mmole of KOH in 5 cm^3 MeOH for $2\frac{1}{2}$ h. The recovered polymer was washed free of polystyrene with diethyl ether. The dried polymer did not show any PS content by UV analysis.

(b) Effect of KOH on PECH in DMF solution at 60°C

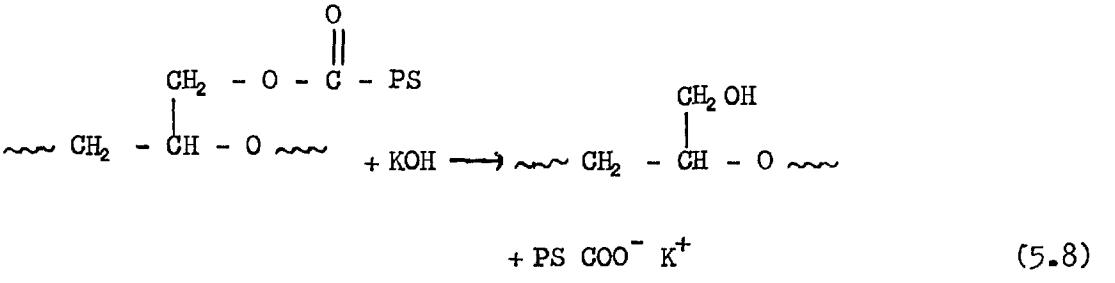
0.8 g of a PECH sample, ($[\eta]$ = 156 $g^{-1}cm^3$ in C_6H_6 at 25°C) dissolved in 50 cm^3 of DMF was heated with 4.0 mmole KOH in 5 cm^3 MeOH at 60°C

for 6 h. The polymer was recovered by precipitation in MeOH and dried as before. It had a limiting viscosity number of 158 $g^{-1}cm^3$ in C_6H_6 at 25°C. Since bases such as KOH usually exert a cleavage action on PECH (184), this increase in limiting viscosity number was surprising. The molecular weight $\bar{M}_n$ of the polymer treated with KOH, as measured by GPC, was 2.87×10^4 compared with a molecular weight of 5.85×10^5 for the starting PECH. The I.R. spectrum of the KOH-treated polymer showed a peak at 1665 cm^{-1} due to α,β-unsaturated aldehyde groups and a peak at 1630 cm^{-1} due to double bonds of a vinyl ether (Figure 5.9) but no peaks due to OH groups were observed.

5.5.4. Results and Discussion

(a) Grafting through ester linkage and stability

Grafting of PS COO^- onto PECH took place through the formation of ester linkages according to reaction (5.2). The resulting graft copolymers are likely to be unstable towards alkali in a medium where both the graft copolymers and the alkali are soluble. Thus, a graft copolymer underwent hydrolysis at the ester linkages (Section 5.5.3(a)) with the formation of pendant $-CH_2OH$ groups in the polymer



(5.8)

The grafting reaction was slow and dependent on temperature. However, these graft copolymers were found to be relatively homogeneous in composition (Section 5.5.1 (d)) and quite stable towards heat and light in the presence of antioxidant as was PECH itself.

(b) The grafting efficiency of PS COO^- onto PECH as a function of time, temperature and molar ratio R

(i) Grafting efficiency at 60°C as a function of time (Figure 5.3; PS COOH sample used, S22-I).

The grafting efficiency, that is the weight % of polystyrene grafted, increased with time for a weight ratio of PECH : PS equal to 25.2:74.8 and the molar ratio R' ($= \frac{1}{R}$, Section 5.5.2 (e)) equal to 16.4. The limiting grafting efficiency seemed not to have been attained even after a reaction time of 26 h. However, with a weight ratio of PECH:PS of 50:50 and the molar ratio R' equal 48.7 the limiting grafting efficiency seemed to have been reached before 26 h and remained almost constant up to 72 h. With a higher concentration of PECH in the reaction mixture, the grafting reaction reached completion earlier. The grafting efficiency did not increase beyond 74% probably because the ungrafted polystyrene was the inactive PSH rather than the active PS $COO^- K^+$.

(ii) Grafting efficiency with temperature for 26 h (PS COOH sample used S23)

A comparison of the grafting efficiencies of PS COO^- in the graft copolymer samples G53 and G56 (Table 5.4) prepared using the same molar ratio R in the two experiments indicated a lower grafting efficiency at a lower temperature. This shows that PS COO^- is a weak nucleophile and the grafting reaction is associated with a significant activation energy.

(iii) Grafting efficiency as a function of molar ratio, R, at 60°C for 26 h (Figure 5.5)

Grafting efficiencies involving the two polystyrene samples, S22-I and S23, decreased as the % of PS COO^- or the values of R used in the grafting reactions increased (Figures 5.4 and 5.5). This indicated an incomplete reaction at high values of R. However, at low values

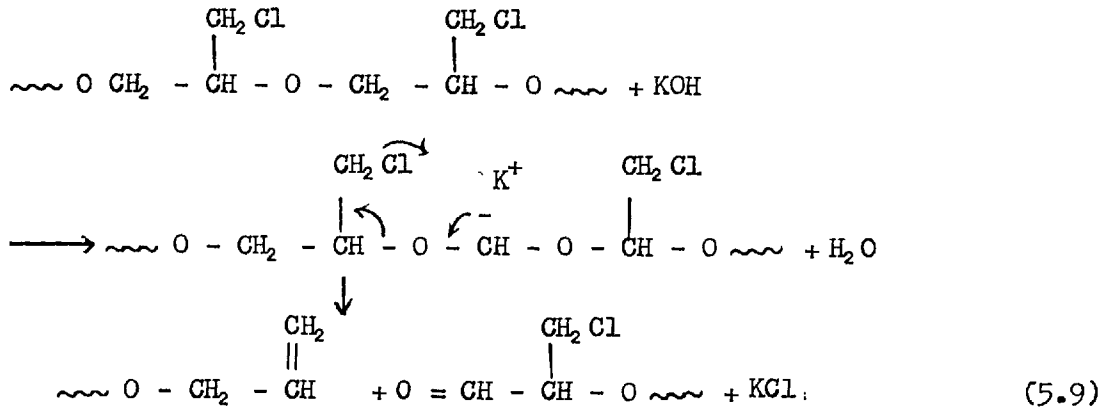
of R, the reaction seemed to be complete and maximum grafting was attained in 26 h at 60°C. The highest grafting efficiency achieved with the polystyrene sample S22-I (GPC $\bar{M}_n = 4.51 \times 10^3$) was about 10% less than the highest grafting efficiency with the polystyrene sample S23 (GPC $\bar{M}_n = 2.41 \times 10^3$). The lower grafting efficiency with sample S22-I was probably not due to any steric hindrance from the slightly longer branches of this already grafted sample. The effect was probably due to the different percentages of inactive polystyrene in the two samples. Thus the unreacted polystyrene recovered during the purification of the sample G53 was found to be PSH and not PS COOH. However, at higher values of R steric hindrance probably slowed down the grafting reaction and the grafting efficiency decreased.

(c) Effect of excess alkali on the molecular weights of graft copolymers and grafting efficiency of PS COO^-

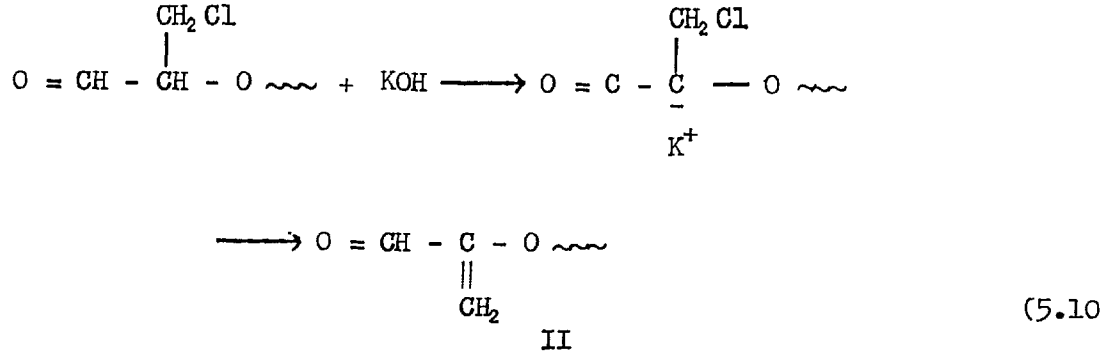
Excess of KOH could have two effects on the grafting experiments: (i) cleavage of PECH resulting in a decrease in the molecular weight of the graft copolymer, (ii) cleavage of polystyrene branches by the hydrolysis of ester-linkages.

(i) Backbone cleavage of PECH by alkali.

The cleavage action of NaOH on PECH in DMSO has been studied by Vandenberg (184). The author reported the formation of allyl ether and ordinary carbonyl end groups. The former product in his experiment formed hydroxyl end groups on later acid hydrolysis. An alkali cleavage product, untreated by later addition of acid, as described in Section 5.5.3 did not show any detectable OH groups in the I.R. spectrum. There were no ordinary carbonyl groups formed at 1730 - '35 cm^{-1} as observed by Vandenberg. The formation of the two peaks at 1665 cm^{-1} and 1630 cm^{-1} in the present case (Figure 5.9) may be ascribed to the following reactions:



(5.9)



(5.10)

The product II formed by the reaction (5.10) is probably responsible for both the I.R. peaks at 1630 cm^{-1} and 1665 cm^{-1}. Due to the electron-withdrawing effect of the carbonyl group, abstraction of tertiary hydrogen in the first step of this reaction becomes easier.

(ii) Cleavage of PS grafts by alkali and effect on grafting efficiency

The reaction (5.8) leading to the cleavage of the grafts by hydrolysis would not change the final grafting efficiency of the polystyrene if there was no unreacted KOH left at the end of the reaction. Thus any regenerated PS $COO^- K^+$ would be subsequently grafted to another $-CH_2Cl$ site. After 26 h, the slight excess of KOH used in most of the series 4 experiments would have been consumed by cleavage of PECH. Thus, the grafting efficiency of the most degraded graft copolymer samples, (for example G47, Table 5.4), when a relatively large excess of KOH had been used, were not markedly lower than those of other experiments.

(d) Molecular weights (GPC values) and limiting viscosity numbers (in toluene at 30°C) of the graft copolymers (Table 5.5 and Figures 5.6 - 5.8)

The above values for the graft copolymers were finally controlled by the extent of grafting and the amount of KOH used in the neutralization of the polystyryl carboxylic acid used in their preparation. Series 4 graft copolymers were prepared mainly in order to assess the efficiency of grafting as a function of time and R values. The KOH solutions used in the neutralization of corresponding polystyryl carboxylic acids were relatively concentrated (>> 0.1M) and the amounts were in most cases slightly greater than required for complete neutralization of the polymeric acid. Since the excess amounts of KOH used were not always the same, no correlation between molecular weights or limiting viscosity numbers and the extent of grafting was possible. However, except for samples G47 and G48, the purified graft copolymers generally had higher molecular weights and higher limiting viscosity numbers than the starting PECH. Graft copolymers G41 - G44 were recovered and purified from the same reaction mixture after different reaction times (Table 5.4). The limiting viscosity numbers of the graft copolymers showed an increase with increase of grafting reaction time (Figure 5.7). The molecular weights, $\bar{M}_n$ of samples G41 - G44 were higher than that of the starting PECH. But the expected increase in molecular weight with the increased extent of grafting of polystyrene was not achieved probably due to the slow cleavage action of KOH on the PECH backbone.

In the synthesis of series 5 graft copolymers, the polystyryl carboxylic acid was neutralized by a weaker alkali solution, approximately 0.1M KOH, to just beyond the end point. A gradual increase in

molecular weights (Figure 5.6) and limiting viscosity numbers (Figure 5.8) with an increase in the y/x ratios (Section 5.5.2.(e)) was attained. In particular, the limiting viscosity number of the sample G53 was much smaller than the general trend. The smaller value of limiting viscosity number in this case may be due to degradation of this graft copolymer at some stage of purification. A comparison of the calculated (expected) $\bar{M}_n$ and observed $\bar{M}_n$ (Figure 5.6) suggested that PS $COO^- K^+$ and a low concentration of OH^- had a very little degrading effect on PECH. However, since PS COO^- is a much weaker base than OH^- it should have a much less cleavage effect on PECH than OH^- under equivalent conditions.

Values of the Huggin's constant were calculated for the initial samples of PECH and the graft copolymers by analysis of the $[\eta]$-data in toluene at 30^oC. However, there was no general correlation between the values of the Huggin's constant, K, in the range 0.33 - 0.47 and the % PS grafted.

5.6. Synthesis of Poly(epichlorohydrin-g-styrene) by Coupling Polystyrene containing Propylene Sulphide End-group with PECH

5.6.1. Experimental : Coupling reaction and Isolation of Graft Copolymers

A sample of polystyrene (sample S-26, Table 5.2) was prepared anionically using cumyl K as the initiator and THF as solvent according to the procedure described before (Section 2.2.3). The living polymer was terminated by purified propylene sulphide, at room temperature up to the point of disappearance of the red colour of the former. The polymer was expected to have $-CH_2-CH(CH_3)S^-K^+$ end-groups, formed according to the reaction (5.3).

The polymer with propylene sulphide end-group in THF solution was added to a THF solution of PECH (previously freeze-dried). The reaction

conditions are given at the footnote of Table 5.6. The mixed THF solution was stirred under argon at 40°C for 1 hour and then terminated with degassed MeOH. The polymer mixture was precipitated in MeOH containing 0.1% w/v antioxidant, isolated and dried as before. Two graft copolymers, G71 and G72 (Table 5.6) were prepared.

Purification of the graft copolymers

On the assumption that the graft copolymers with long polystyrene branches of low frequency would be insoluble in boiling cyclohexane (b.p., 81°C) a non-solvent for PECH and a solvent for polystyrene, an attempt was made to separate any homopolystyrene mixed with the graft copolymer sample G72, in a Soxhlet apparatus. But along with the homopolystyrene, some of the graft copolymers were also extracted. Graft copolymer samples G71 and G72 were however, successfully purified by extraction with cyclohexane at 40°C. 1 g of the polymer mixture was extracted five times, taking 100 cm^3 of cyclohexane each time. The polymer insoluble in cyclohexane at 40°C was dissolved in C_6H_6 and precipitated in MeOH, as before.

5.6.2. Characterization

The graft copolymers were made free of antioxidant as before (Section 5.5.1 (d)). The polystyrene contents of the antioxidant-free graft copolymer samples were determined by UV analysis as before. The molecular weights were measured by GPC. The GPC traces for the purified graft copolymers consisted of a single peak. The different calculations based on the composition of the graft copolymers were made as before (Section 5.5.2 (e)) and the information is outlined in Table 5.6.

5.6.3. Results and Discussion

The purified graft copolymer samples G71 and G72 contained 59.6% w/w

and 79.3% w/w of polystyrene. The grafting efficiency of polystyrene in the two cases was 53.6% and 66.7% respectively. The calculated $\bar{M}_n$ of G71 and G72 on the basis of their PS contents and $\bar{M}_n$ of the starting PECH (2.20×10^5) should have been 5.45×10^5 and 10.63×10^5 respectively whereas the observed $\bar{M}_n$ values were 0.372×10^5 and 0.458×10^5 respectively. The graft copolymer samples were thus found to have undergone cleavage by a factor of about 14.7 and 23.1 respectively.

The grafting of polystyrene in these experiments were expected to have taken place according to the reaction (5.4). A hundred per cent efficiency of grafting of polystyrene was expected because of the higher nucleophilicity of the mercapto end-groups in the polystyrene molecules. However, $\sim\sim CH_2\text{-}CH(CH_3)S^-$ groups may react with PECH in a similar way to $PS^- Li^+$, as discussed before (Section 4.7.2).

5.7. Appendix to Section 5.5

Synthesis of Poly(epichlorohydrin-g-styrene) and Poly[(epichlorohydrin-co-ethylene oxide)-g-styrene] using PS COOH of long chain length

Two graft copolymers G61 and G62 (Table 5.5) were prepared according to the procedure described in Section 5.5.1 (a). The grafting reactions were carried out in DMF at 60°C for 26 h. The graft copolymer sample G61 had a PECH backbone and G62 had a P(ECH-co-EO) backbone. The PS COOH sample S24 (Table 5.3) had $\bar{M}_n = 3.69 \times 10^4$. A slight excess of KOH solution was used for the neutralization of PS COOH used in the coupling reaction with the epichlorohydrin polymers. There was therefore some cleavage of the backbone polymer by excess KOH, as discussed before.

The products of the grafting reactions in the two cases showed single broad peaks in their respective GPC traces. The polystyrene

used also had a broad distribution. In the GPC traces of the grafting reaction products, the peak due to the graft copolymer and that due to homopolystyrene were completely merged. It was therefore difficult to purify the graft copolymers free of homopolystyrene by fractional precipitation procedures. The graft copolymer samples were however freed of homopolystyrene, G61 by extraction with cyclohexane at 40°C as described before (Section 5.6.1) and G62 by extraction with boiling cyclohexane. Some graft copolymer molecules might also have been lost during the extraction procedure, because the solid recovered by extraction also showed weak ethereal peaks in the I.R. spectrum. The purified graft copolymers were later precipitated from C_6H_6 solution into MeOh containing 0.1% w/v antioxidant, and dried as before. A portion of the polymer from each sample used for composition determination was extracted with boiling MeOH and dried.

These two graft copolymers were characterized by UV, IR and GPC, as discussed before, and also used along with some other graft copolymers described in this chapter for the study of solutions and bulk properties, as discussed later in Chapter 6.

5.8. Attempted Grafting of Polystyrene onto PECH Induced by γ-Irradiation

5.8.1. Experiments and Results

(a) Mutual irradiation method. Purified PECH free from antioxidant (Section 4.2.1 (a)) was swollen in distilled styrene in an ampoule for 15 hours. Styrene was washed free of stabilizer according to the procedure described elsewhere (151) and then distilled as before (Section 2.2.2). The swollen polymer was degassed in the vacuum line at 10^{-5} Torr in three successive freeze-thaw cycles. The ampoule was sealed under vacuum at 10^{-5} Torr. The monomer-swollen polymer was then exposed to γ-radiation from a Co^{60} source at a dose rate of 1.44 Mrads/h for a definite period of time (Table 5.7). The polymer

was then precipitated from C_6H_6 solution into MeOH and dried to constant weight at 45°C in a vacuum oven.

In experiments 31 and 32 (Table 5.7) using a total dose of 1.44 Mrads and 4.32 Mrads (1.44 Mrads/h for 1 h and 3 h), respectively, the recovered polymers, G31 and G32, showed an increase in weight of 5.6% and 24.6%, respectively. This indicated that only about 1% and 4.4% of total styrene had been polymerized.

Sample G32 showed two overlapping peaks in its GPC trace. It was separated into three fractions by dropwise addition of cyclohexane into a fast-stirred 1% w/v solution of the polymer in C_6H_6. This procedure gave :

(I) a fraction, G32-I (major fraction) insoluble in benzene-cyclohexane, 1:3 v/v;

(II) a fraction G32-II held in colloidal suspension in the same benzene-cyclohexane mixture;

and (III) a fraction G32-III soluble in the C_6H_6-cyclohexane mixture. Benzene-cyclohexane mixture (1:3 v/v) was found to be a solvent for polystyrene of very high molecular weight ($\bar{M}_n \sim 10^5$).

The I.R. spectra of the fractions G31-I and G32-II showed peaks corresponding to PECH and PS. The peaks due to polystyrene were very weak in fraction G32-I. This fraction was washed several times with C_6H_6-cyclohexane (1:3 v/v) solvent mixture. The peaks due to polystyrene in the I.R. spectrum of the washed sample did not disappear nor become reduced in intensity. This fraction thus had very limited grafting.

The I.R. spectrum of fraction G32-II (Figure 5.10) showed a weak but broad peak in the region 3680 - 3500 cm^{-1} due to OH, and a sharp peak at 1670 cm^{-1} due to α,β-unsaturated aldehyde in addition to peaks

due to PECH and PS. The ether peak at 1170 - 1020 cm^{-1} was also very broad. Fraction G32-II was thus a degraded graft copolymer. The extent of grafting was higher in this fraction than in the fraction G32-I as evident from the relative peak heights due to polystyrene in I.R. spectra. However, G32-II comprised only about 10% w/w of the total polymer. Fraction G32-III was found to contain homopolystyrene only.

(b) Peroxide method. PECH free from antioxidant was cut into small pieces and exposed to γ-irradiation in the presence of air in an open ampoule at a dose rate of 1.44 Mrads/h. The objective was the formation of pendant hydroperoxide groups in the polymer. In the two experiments, 33 and 34, the polymer was irradiated at the above dose rate for 1 and 3 h respectively. The pre-irradiated polymers in the two experiments were then swollen in weighed amounts of distilled styrene for 7 and 4 h respectively. The swelling was not complete in these short periods of time. However, the partly swollen polymers were degassed in the vacuum line in three successive freeze-thaw cycles. The ampoules containing the swollen polymers were then sealed at a pressure of 10^{-5} Torr. The polymer-monomer mixtures were then heated in a thermostat at a temperature of 70°C for 13 h. The polymers were then precipitated and dried as in the previous experiments. The polymer samples G33 and G34 showed an increase in weight of 28% and 4.5%, respectively, indicating polymerization of only 5.5% and 0.8% of the total styrene used. Sample G33 showed a single peak in its GPC trace. It was separated into three fractions, like the sample G32 using benzene-cyclohexane mixture (1:3 v/v)

(I) fraction G33-I, insoluble in C_6H_6-cyclohexane did not show any peaks of polystyrene in the I.R. spectrum,

(II) fraction G33-II was held in colloidal suspension and on recovery again did not show the presence of polystyrene in the I.R.,

(III) the third fraction, G33-III, soluble in C_6H_6-cyclohexane was found from I.R. measurements to be completely homopolystyrene. Thus almost no grafting or undetectable grafting was achieved by the peroxide method.

The I.R. spectrum of the fraction G33-II showed a weak but broad peak at 3680 - 3500 cm^{-1} due to OH and a sharp peak at 1670 cm^{-1} due to α,β unsaturated aldehyde or ketone, indicating degradation of a part of the PECH used in pre-irradiation.

5.8.2. Discussion

The reason for the low extent of grafting in the mutual irradiation method may be due to low G value of the monomer. A polymer with a high G value and a monomer with a low G value is the most suitable combination for grafting with least contamination due to homopolymer formed from the monomer (190). In the present case, the G value of PECH is not known.

γ-irradiation also has some degrading affect on PECH but the molecular weights of G31 - G34 in comparison to that of the starting PECH (Table 5.7) suggest that there was no significant cleavage of the polymer backbones. Probably degradation was limited to the surface portion of the polymer directly exposed to γ-irradiation. That may be why peaks due to OH and carbonyl groups (conjugated to double bonds) appeared only in the small fraction G32-II. Grafting was also relatively high in that fraction. In high energy radiation-induced grafting by the mutual method, heterogeneous grafting is a common phenomenon (38,191).

In the peroxide method, no grafting could be detected. This may have been due to the termination of growing chains by traces of trapped oxygen within the partially swollen polymers. This suggestion is supported by the fact there was more homopolystyrene recovered from

experiment No.33 (7 h swelling, 1 h pre-irradiation) than in experiment 34 (4 h swelling, 3 h pre-irradiation). A commonly observed feature of both the mutual irradiation and the peroxide methods was the degradation of PECH on the surface of the irradiated polymer.

Table 5.1. Epichlorohydrin Polymer Samples [a] used for Grafting with Polystyrene containing a Functional End-group

Sample	Results from GPC			% Composition [c]			
	$\bar{M}_n \times 10^{-5}$	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$	C	H	Cl	O (from diff.)
E14 [b]	5.85	1.43	2.45	-	-	-	-
E15	1.98	1.11	5.62	-	-	-	-
E17	2.20	1.23	5.57	38.61	5.51	37.93	17.95
E18 [b]	4.10	9.13	2.23	42.40	6.33	28.68	22.59

[a] All the samples except E18 were PECH. Sample E18 was an ECH-EO copolymer; according to elemental composition, the molar ratio, ECH:EO in this sample was 3:2. Samples E14, E15 and E18 contained trace (about 0.2% w/w) of antioxidant.

[b] Roughly fractionated samples.

[c] Theoretical composition of PECH ; C = 38.94% H = 5.45%, Cl = 38.32%, O = 17.29%

Table 5.2. Synthesis of Polystyrene containing Molecules Ended with a Single Functional End-Group

Polymer Sample [a]	End-group on termination	Experimental Conditions						$\bar{M}_n$(cal) x 10^{-3}	GPC Results	
		Initiator	Solvent	Temp./ °C	Time/ h	[Monomer]/ mol dm^{-3}	10^2x[Initiator]/ mol dm^{-3}		$\bar{M}_n$ x 10^{-3}	$\bar{M}_w/\bar{M}_n$
S22	-COOH	n-BuLi	C_6H_6 [b]	20	6	1.498	3.226	4.84	4.43	1.46
S23	"	"	C_6H_6 [b]	20	6	1.185	4.961	2.49	2.41[c]	1.39
S24	"	cumyl-K	THF	-78,0	4	0.960	-	-	36.9	3.08
S26	$-CH_2-CH(CH_3)-SK$	cumyl-K	THF	-78,0	4	1.007	-	-	45.44	1.82

[a] Polymer Samples S22, S23 and S24 on termination with CO_2 and subsequent acidification were expected to form -COOH end-group. Polymer sample S26 on termination with propylene sulphide was expected to form $-CH_2-CH(CH_3)-\bar{S}K^+$ end group.

[b] 15 cm^3 THF in about 130 cm^3 C_6H_6 used

[c] The polymer sample S23 contained a high molecular weight 'tail' corresponding to an $\bar{M}_n$ value of 9.4×10^4 and 2.1% of the total polymer weight. The GPC values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ correspond to that of the major peak of the polymer.

Table 5.3. Molecular weights of PS COOH Samples used for Grafting Reactions

Polymer	$\bar{M}_n \times 10^{-3}$ (Osmometry)	$\bar{M}_n \times 10^{-3}$ (Titration method)	GPC Results [a]		
			$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
S22-I	5.95	7.49	4.51	6.23	1.38
S23	3.12	3.31	2.41	3.34	1.39
S24	-	41.85	36.90	114.0	3.08

[a] Polymer Samples S22-I and S23 contained a high molecular weight 'tail' corresponding to $\bar{M}_n$ values of 3.65×10^5 and 9.4×10^4, respectively, and to 3.3% and 2.1% of the respective total polymer weight, as calculated from the GPC peak areas. The GPC values of $\bar{M}_n$ and $\bar{M}_w$ correspond to those of the major peak of the polymer.

Table 5.4. Poly(epichlorohydrin-g-styrene) Samples Prepared by Coupling PECH with the K-salt of PS COOH and their Composition (by weight)

Graft copolymer series	Purified graft copolymer	Experimental conditions for preparation[a]					Composition of the Graft copolymers			Grafting efficiency of PS(%) d
		PECH sample used b	PS COOH sample used c	% PS w/w used	Temp./ °C	Time/h	% Cl (micro-analysis)	% PS (cal. from % Cl)	% PS (UV analysis)	
4	G41	E14	S22-I	74.8	60	4.5	20.83	45.6	47.2	30.2
	G42	E14	S22-I	74.8	60	10	15.62	59.2	60.0	50.6
	G43	E14	S22-I	74.8	60	21.5	13.03	66.0	66.5	67.0
	G44	E14	S22-I	74.8	60	26	12.37	67.7	68.0	71.7
	G45	E14	S22-I	50.0	60	26	-	-	42.1	72.7
	G46	E14	S22-I	50.0	60	72	-	-	42.5	73.9
	G47	E14	S22-I	60.0	60	26	-	-	53.3	76.1
	G48	E14	S22-I	88.9	60	26	-	-	82.3	58.1

Table 5.4 (continued)

Graft copolymer series	Purified graft copolymer	Experimental conditions for preparation[a]					Composition of the Graft copolymers			Grafting efficiency of PS [d] (%)
		PECH sample used [b]	PS COOH sample used [c]	% PS w/w used	Temp./ °C	Time/h	% Cl (micro-analysis)	% PS (cal. from % Cl)	% PS (UV analysis)	
5	G51	E15	S23	20.0	60	26	31.06	18.9	17.9	87.2
	G52	E15	S23	35.1	60	26	26.14	31.8	31.4	84.6
	G53	E15	S23	50.0	60	26	20.57	46.3	46.1	85.2
	G54	E15	S23	65.0	60	26	15.12	60.5	59.5	78.9
	G55	E15	S23	80.0	60	26	11.54	69.9	70.7	60.3
	G56	E15	S23	50.0	30	26	-	-	21.1	26.7

[a] All reactions were carried out in DMF solution under a nitrogen atmosphere.

Initial concentration of PECH was 1 g per 100 cm^3 of solvent.

[b] PECH samples used were those listed in Table 4.1

[c] PS COOH samples used were those listed in Table 4.3

[d] The grafting efficiency was calculated from the % PS w/w obtained by UV analysis.

Table 5.5. Molecular Weights and Limiting Viscosity Numbers [a] of the Graft Copolymers prepared by Coupling PECH with PS COO^-K^+

Series	Graft copolymer sample	Initial PECH				%PS w/w (UV analysis)	$\bar{M}_n$(cal) x 10^{-5}	Results from GPC			$[\eta]$/ $cm^3 g^{-1}$	K	λ	$\bar{M}_n$(PS branch) x 10^{-3} (GPC)
		$\bar{M}_n$(GPC) x 10^{-5}	$\bar{M}_w/\bar{M}_n$ (GPC)	$[\eta]$/ $cm^3 g^{-1}$	K			$\bar{M}_n$ x 10^{-5}	$\bar{M}_w$ x 10^{-5}	$\bar{M}_w/\bar{M}_n$				
5	G51	1.98	5.62	111.0	0.34	17.9	2.41	2.42	8.85	3.66	115.0	0.40	115.2	2.41
	G52	"	"	"	"	31.4	2.89	3.05	11.31	3.71	133.5	0.33	58.3	"
	G53	"	"	"	"	46.1	3.67	2.89	9.41	3.26	96.0	0.40	31.9	"
	G54	"	"	"	"	59.5	4.89	3.89	17.47	4.49	143.0	0.47	18.4	"
	G55	"	"	"	"	70.7	6.76	5.25	24.30	4.63	161.5	0.38	12.5	"
4	G41	5.85	2.45	134.0	0.39	47.2	11.08	6.48	23.29	3.60	156.0	0.47	50.4	4.51
	G42	"	"	"	"	60.0	14.63	5.98	21.99	3.68	158.0	0.39	35.0	"
	G43	"	"	"	"	66.5	17.46	7.17	22.19	3.10	161.0	0.38	26.4	"
	G44	"	"	"	"	68.0	18.28	6.26	22.53	3.60	163.0	0.36	24.5	"
	G45	"	"	"	"	42.1	10.10	-	-	-	151.0	-	-	"
	G46	"	"	"	"	42.5	10.17	-	-	-	151.0	-	-	"
	G47	"	"	"	"	53.3	12.53	-	-	-	132.5	-	44.0	"
	G48	"	"	"	"	82.3	33.05	-	-	-	62.0	-	-	"
	G61	1.98	5.62	111.0	0.34	69.6	6.51	2.05	11.82	5.78	-	-	175.3	36.90
	G62 [b]	4.10	2.23	-	-	74.5	16.08	2.03	5.89	2.90	-	-	-	"

a Limiting viscosity numbers of PECH and graft copolymer samples were measured in toluene at 30°C

b Graft copolymer sample G62 had P(ECH-co-EO) backbone

K, Huggin's constant, calculated from η-data in toluene at 30°C

λ, inverse graft frequency.

Table 5.6. Molecular Weights and Composition of Poly(epichlorohydrin-g-styrene) copolymers prepared by Coupling Polystyrene containing Propylene Sulphide End-Groups with Polyepichlorohydrin [a]

Purified graft copolymer	Composition used in the reaction mixture			Composition and $\bar{M}_n$ of the purified graft copolymers				Grafting efficiency of PS (%)
	(PS used per g PECH)/g	% PS w/w	10^3R	% PS w/w	$\bar{M}_n$ (cal) $\times 10^{-5}$	$\bar{M}_n$ (obs) $\times 10^{-4}$	f	
G71	2.751	73.3	5.61	59.6	5.45	3.72	14.7	53.6
G72	5.740	85.2	11.70	79.3	10.63	4.58	23.2	66.7

[a] Reaction conditions : temp., 40°C; time, 1 h; solv., THF.

$\bar{M}_n$ (GPC) of PS (separately terminated) = 4.54×10^4

$\bar{M}_n$ (GPC) of PECH used = 2.20×10^5

Conc. of PECH before coupling = 1 g in 50 cm^3 THF

Conc. of PS before coupling (cal. from $\bar{M}_n$, GPC) = 2.31×10^{-3} mol dm^{-3}

$$R = \frac{\text{number of moles of PS added}}{\text{number of moles of Cl in PECH}}$$

$$f = \bar{M}_n(\text{cal})/\bar{M}_n(\text{obs})$$

Table 5.7. Grafting of Polystyrene onto PECH Induced by γ-Irradiation : Experimental Conditions

Experiment No.	Technique [a]	PECH used/g	Styrene used/g	Total dose/Mrads [b]	Total polymer recovered/g	% styrene w/w polymerized	Molecular weights of recovered polymers [c]		
							Sample No.	$\bar{M}_n$ (GPC) x 10^{-4}	$\bar{M}_w/\bar{M}_n$
31	Mutual irradiation	1	5.515	1.44	1.056	1.0	G31	8.80	8.86
32	"	1	5.594	4.32	1.246	4.4	G32	4.09 [d]	16.80
33	Peroxide method	1	5.109	1.44	1.280	5.5	G33	8.29	3.16
34	"	1	5.409	4.32	1.045	0.8	G34	3.39	3.45

a In mutual irradiation technique, PECH swollen by styrene was directly exposed to γ-irradiation in absence of air at ambient temperature. In the peroxide method, polymer pre-irradiated in presence of air at ambient temperature was later heated with styrene in absence of air at 70°C for 13 h.

b Dose rate, 1.44 Mrads/h

c Starting PECH had $\bar{M}_n = 1.30 \times 10^5$, $\bar{M}_w/\bar{M}_n = 10.09$. The recovered polymer samples were mixtures of homopolymers and graft copolymers.

d The polymer sample G32 had two overlapping peaks in the GPC trace; $\bar{M}_n$ corresponding to the two peaks were separately 2.19×10^5 and 1.83×10^4 respectively.

Figure 5.1. Calibration of Vapour Pressure Osmometer

(Benzil in toluene at 37°C)

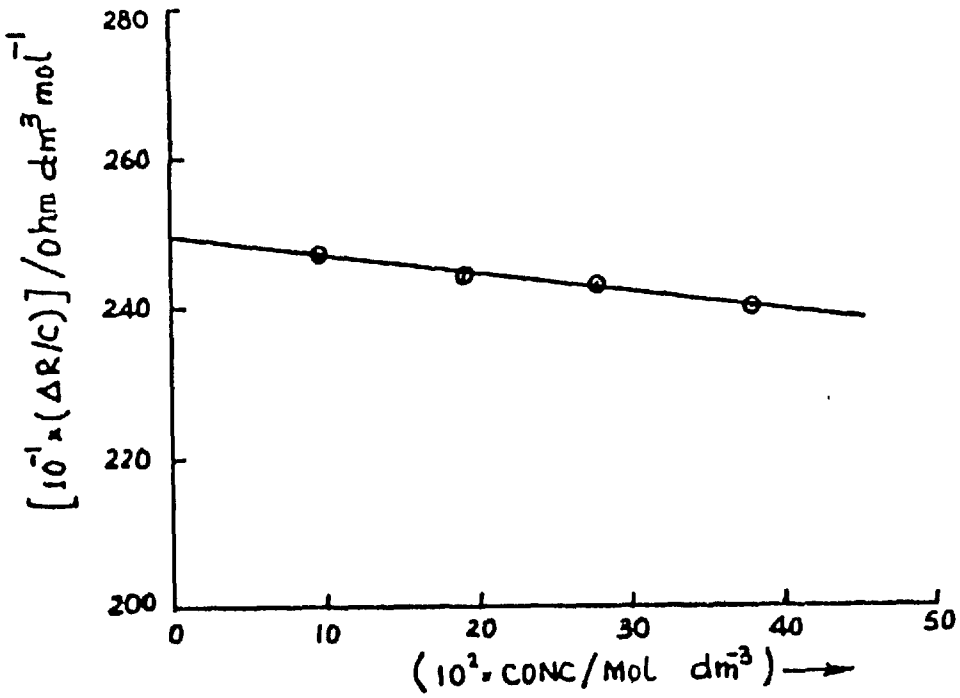


Figure 5.2. Results of Vapour Pressure Osmometry on Polystyrene (PS COOH) Sample S23

(in toluene at 37°C)

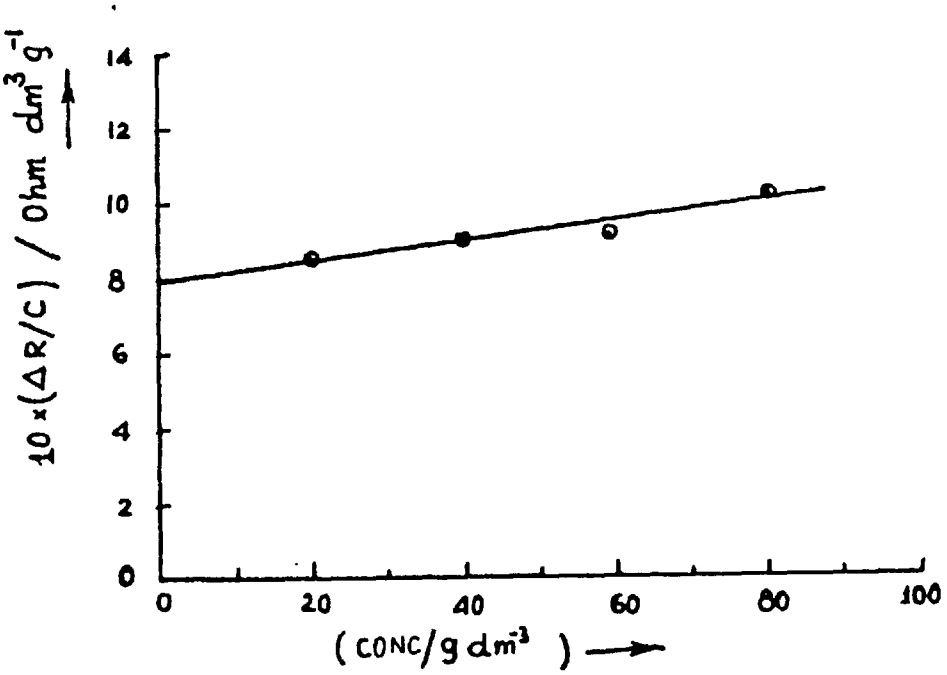


Figure 5.3. Grafting Efficiency of PS COO^- (from K-salt of PS COOH) onto PECH at 60°C as a Function of Time

PS COOH sample used, S22-I

⊙ PECH : PS used = 25.2:74.8 w/w

Δ PECH : PS used = 50:50 w/w

(PS stands for PS COOH mixed with any polystyrene not containing -COOH end-group)

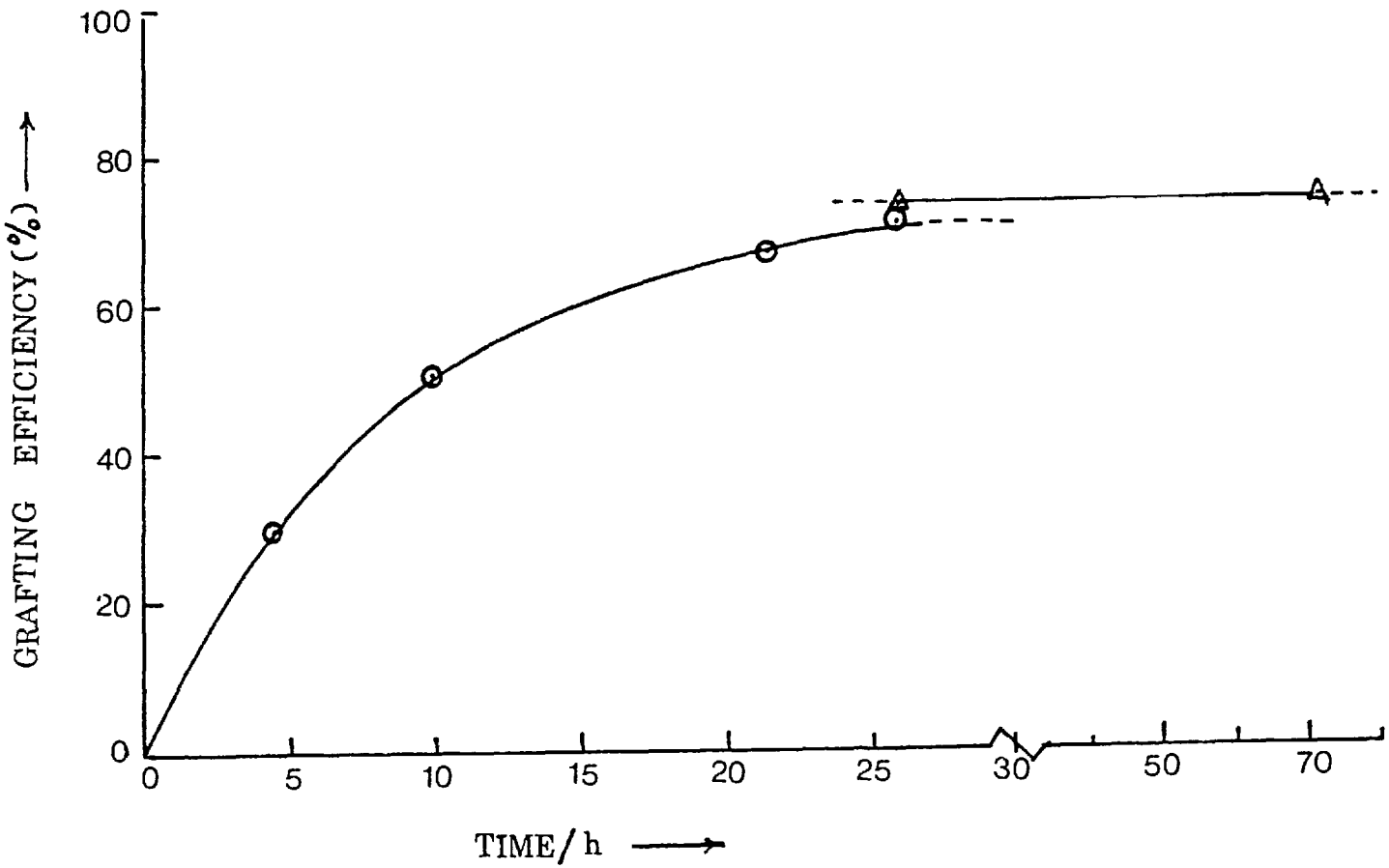


Figure 5.4. Grafting Efficiency of PS COO^- (from K-salt of PS COOH) onto PECH against % PS w/w used

⊙ PS COOH sample S23 Time of reaction, 26 h

Δ PS COOH sample S22-I Temp., 60°C

(PS stands for PS COOH mixed with any polystyrene not containing -COOH end-group)

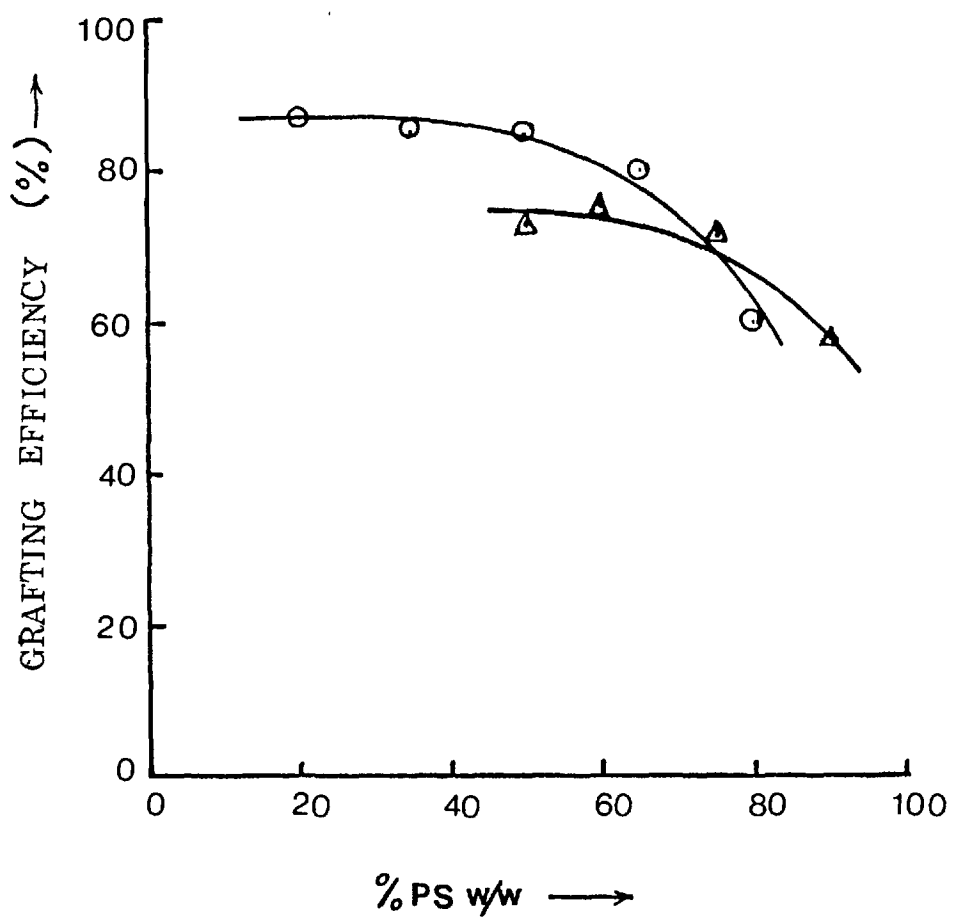


Figure 5.5. Grafting Efficiency of PS COO^- onto PECH as a Function of R

$R = \left(\frac{\text{moles of PS}}{\text{moles of Cl in PECH}}\right)$ used in a grafting experiment

O PS COOH sample S23 Time of reaction, 26 h

Δ PS COOH sample S22-I Temp., 60°C

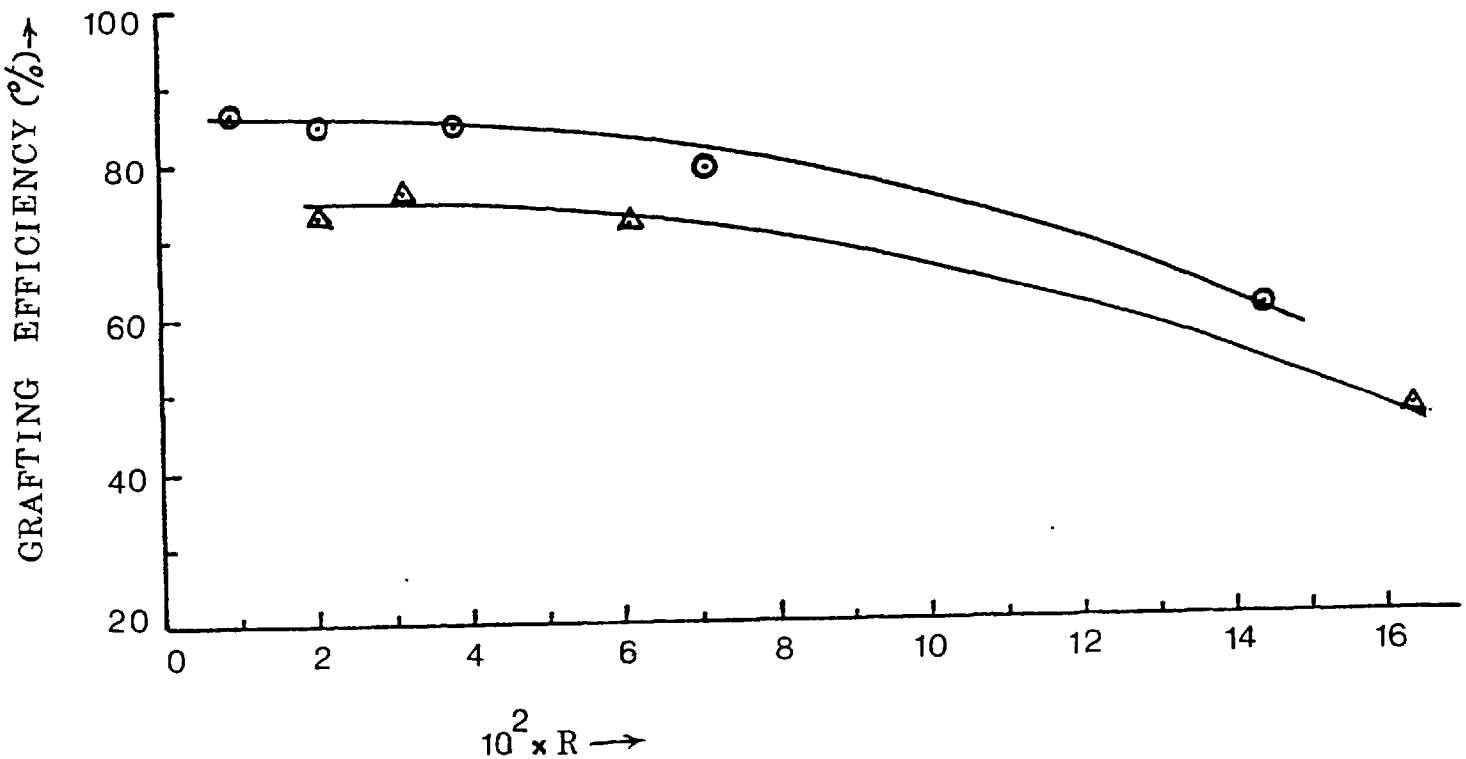


Figure 5.6. Relationship between Number Average Molecular Weights of the Graft Copolymers (Series 5, Table 5.5) and the Ratios Y/X

$\frac{Y}{X} = \left(\frac{\text{Weight \% PS}}{\text{Weight \% PECH}}\right)$ in a graft copolymer (Section 5.5.2(e))

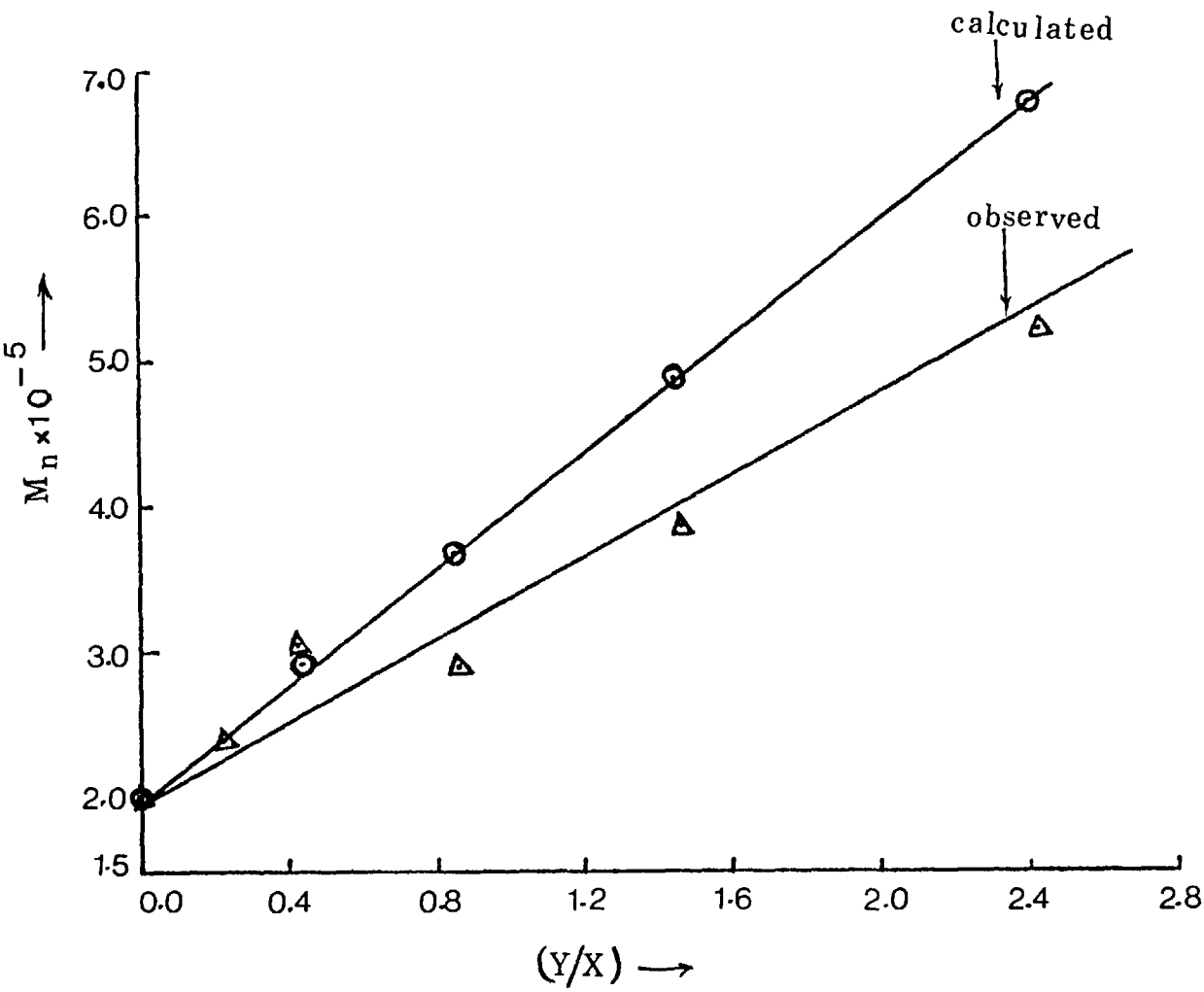


Figure 5.7. Relationship between Limiting Viscosity Numbers and Grafting Reaction Time for Graft Copolymer Samples, G41-G45 (Tables 5.4 and 5.5)

(Limiting viscosity numbers measured in toluene at 30°C)

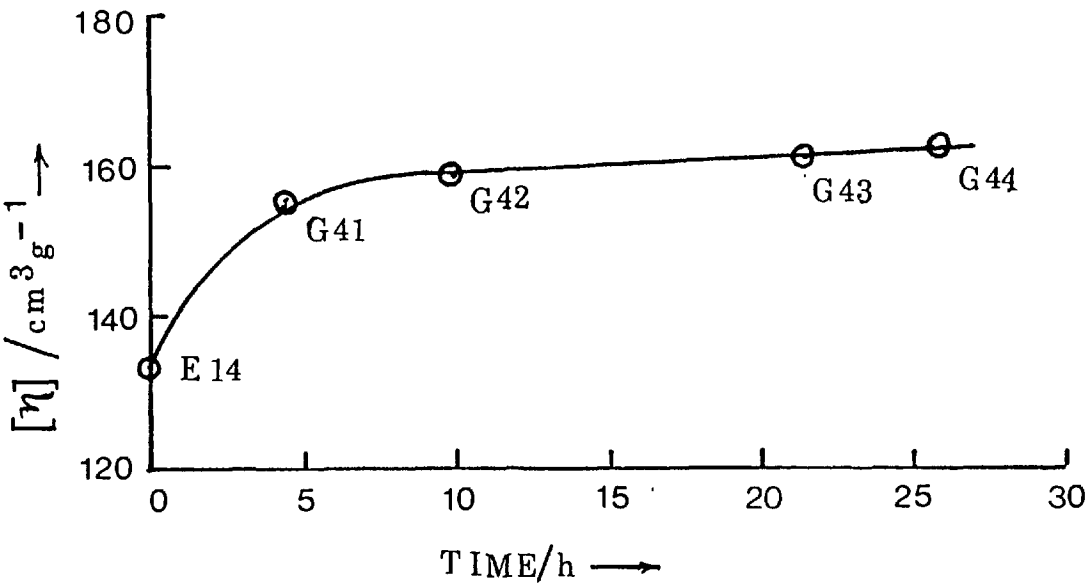


Figure 5.8. Relationship between Limiting Viscosity Numbers of the Graft Copolymers (Series 5, Table 5.5) and the Ratios Y/X

$\frac{Y}{X} = \left(\frac{\text{weight \% PS}}{\text{weight \% PECH}}\right)$ in a graft copolymer

(Limiting viscosity numbers measured in toluene at 30°C)

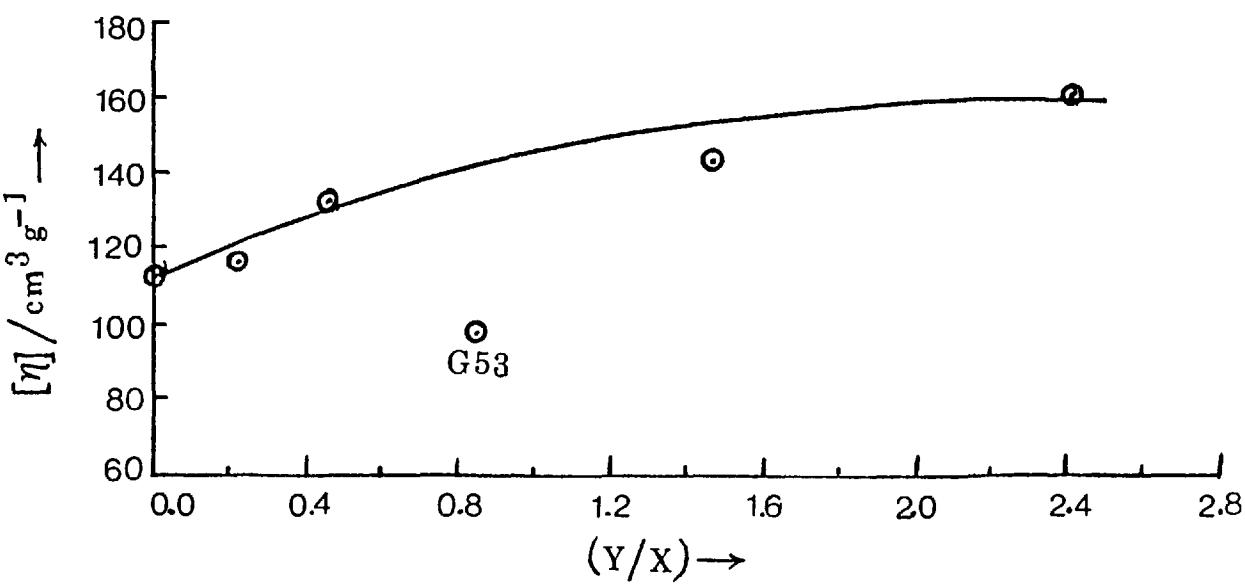


Figure 5.9. Infra-red Spectrum of PECH Partially Degraded by KOH

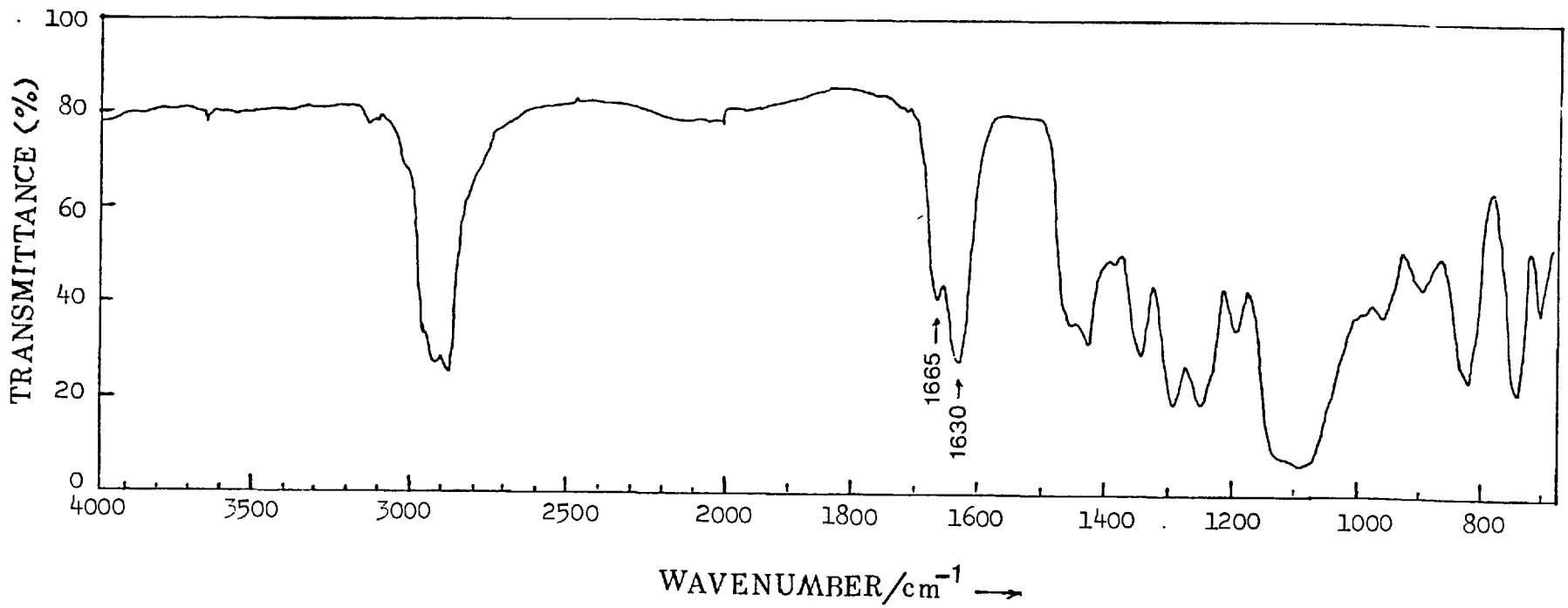
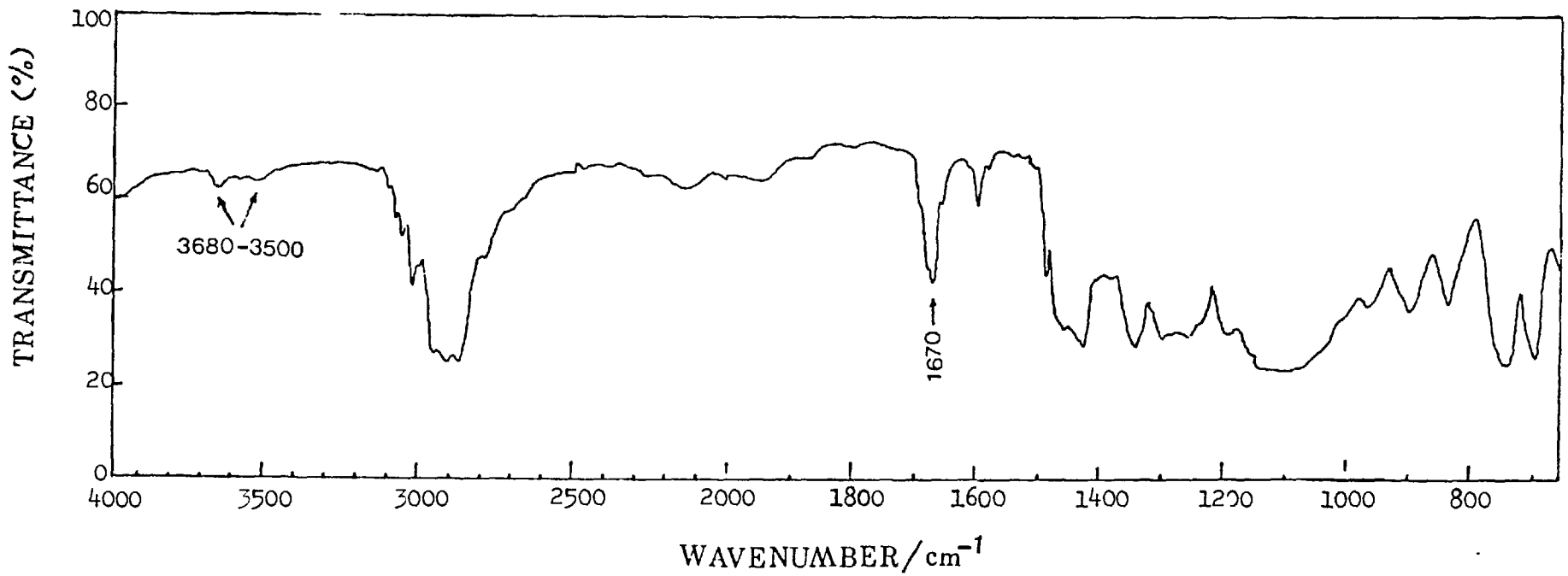


Figure 5.10. Infra-red Spectrum of P(ECH-g-S) Sample G32-II Prepared by Mutual γ-Irradiation Technique



CHAPTER 6

SOLUTION AND BULK PROPERTIES OF POLY(EPICHLOROHYDRIN-g-STYRENE) COPOLYMERS

6.1. Introduction

The repulsive interaction between the chemically different sequences in a block or graft copolymer and the microphase separation that results from this interaction has been discussed briefly in Chapter 1 (Section 1.1.5). This phenomenon is the basis of the distinct and interesting properties of block and gract copolymers in the bulk state and also to a great extent in solution. Due to microphase separation, block and graft copolymers in some cases exhibit properties characteristic of component homopolymers. There are of course some block and graft copolymers which do not undergo phase separation. In such cases, the block or graft copolymer behaves like a random copolymer which has properties intermediate between those of the component homopolymers.

The glass transition temperature is a bulk property which indicates whether or not microphase separation is occurring in a block or graft copolymer. The morphological studies by electron microscopy also give valuable information about microphase separation in a block or graft copolymer. The behaviour of block and graft copolymers in solution is also of considerable interest. The dilute solution properties and bulk properties of some of the polymers, prepared as described in Chapters 4 and 5 have been studied and are presented in the following sections.

6.2. Solution Properties

6.2.1. Experimental

The solution behaviour of the graft copolymers and the component homopolymers mentioned in Table 6.1. were studied. The limiting viscosity

numbers of PECH sample E14, P(ECH-g-S) samples G44 and G61 were measured in benzene-carbon tetrachloride solvent mixtures at 25° as a function of solvent composition (Figure 6.1). Similarly, limiting viscosity numbers of PECH sample E15, PS sample S23, P(ECH-g-S) samples G53 and G55 were measured in toluene-cyclohexane solvent mixtures at 40°C as a function of solvent composition (Figure 6.2). As the backbone of the graft copolymers underwent varying extents of degradation (cleavage), the molecular weight of the backbone in a graft copolymer is not the same as the molecular weight of the starting PECH.

The solvents used for viscosity measurement, benzene and toluene, (A.R. grade), carbon tetrachloride and cyclohexane, (G.P.R. grade), were used without further purification. The experimental procedure of viscosity measurements has been described before (section 4.5.3(b)). Benzene and toluene were good solvents for both the PECH backbone and polystyrene branches, whereas CCl_4 and cyclohexane (at 40°C) were good solvents for the polystyrene branches but poor solvents for the PECH backbones. The solutions were made up in the pre-mixed solvents. For experiments carried out at 40°C, a temperature correction for the concentration of the solutions was made using the density plots of the solvents against temperature (192). The temperature control of the viscosometry bath was better than $\pm$ 0.02°C, as measured by a Beckmann thermometer.

6.2.2. Results and Discussion

The limiting viscosity number $[\eta]$, is a measure of the size of a polymer molecule in solution. For a linear homopolymer of molecular weight greater than 10^4 (193),

$$[\eta] = \Phi \, (\langle r^2 \rangle)^{\frac{3}{2}} \, M^{-1} \qquad (6.1)$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the polymer and ϕ is a constant. For a branched polymer (193),

$$[\eta] = \phi' (\langle s^2 \rangle)^{\frac{3}{2}} M^{-1} \qquad (6.2)$$

where $\langle s^2 \rangle$ is mean square radius of gyration. Thus an increase in the dimension of a polymer molecule in solution is manifested in an increase of $[\eta]$.

Solution properties of block (24, 194-195) and graft copolymers (24, 196-200) have been investigated from measurements of $[\eta]$ in pure and mixed solvents previously. It has been established that the solution properties are affected by interaction between unlike sequences in the polymer (polymer-polymer interaction) in solution and also by the polymer-solvent interaction. The effect of solvent-solvent interaction parameter on the limiting viscosity behaviour of graft copolymers in mixed solvents has also been studied (200). Polymer-solvent interaction plays a dominant role in the solution properties of graft copolymers and is dependent on the selectiveness of the solvent. Thus if a non-solvent for the main-chain of a graft copolymer is added to a solution of the latter in a good solvent, there is observed a decrease in the limiting viscosity number. At low concentration, it is believed that 'monomolecular micelles' are formed in which unsolvated backbone is protected by solvated grafts which prevent the graft copolymer from being precipitated out of solution (24, 196-198). Association of the 'monomolecular micelles' into 'polymolecular micelles', especially at higher concentration and with graft copolymers containing relatively fewer grafts may lead to precipitation of the graft copolymers (198,199). Polymer-polymer interaction sometimes leads to an increase in the limiting viscosity number in a mixed solvent. For example, in the study of the solution behaviour of poly(diphenyl propene-g-styrene) in dioxane-cyclohexane mixed solvents,

it was observed that as the proportion of cyclohexane, a non-solvent for the backbone, poly(diphenyl propene), was increased, the graft copolymer first showed an increase in $[\eta]$. This was followed by a sharp decrease in $[\eta]$ on further increase in the proportion of non-solvent (198). The increase in $[\eta]$ was explained on the basis of increased repulsion between the unlike sequences in the polymer. The polymer was said to have undergone a transformation from a 'random conformation' to a 'segregated conformation' in passing through the maxima in the limiting viscosity curve. A block or graft copolymer may have a 'random conformation' when there are a large number of 'heterocontacts' which cause larger interaction between unlike units and hence a large expansion of the molecule, specially in a good solvent. In a selective solvent, that is when the solvent is good for one type of sequence but poor for the other, the number of heterocontacts is usually reduced and the polymer assumes a 'segregated conformation'. The decrease in $[\eta]$ actually takes place when a polymer in solution has a 'segregated conformation'.

In the present studies of the solution behaviour of the graft copolymers, in mixed solvents (Figures 6.1 and 6.2), no transformation from a 'random' to a 'segregated' conformation was observed. The graft copolymers may have segregated conformations in the mixed solvents. The selectiveness of the solvent for the backbone played an important part in deciding the solution behaviour of the graft copolymers. This behaviour was in agreement with some previous studies (24, 196-197). The limiting viscosity numbers of the graft copolymer samples G44 and G61 and PECH sample E14 in C_6H_6/CCl_4 solvent mixtures as a function of composition of the solvent at 25°C (Figure 6.1) indicate that as the solvent became richer in CCl_4, a non-solvent for PECH but a good solvent for PS grafts, the backbone

homopolymer and the graft copolymers all underwent a shrinkage. The shrinkage was greater in the PECH sample than in the graft copolymers. With the PECH sample E14, precipitation occurred at a solvent composition containing 58% v/v CCl_4. The two graft copolymers, were however held in solution throughout the solvent composition range, although in pure CCl_4, the solution of the graft copolymer sample G61 with long PS branches was a little colloidal. The relatively unsolvated PECH backbones in the graft copolymers were protected by the solvated polystyrene branches from becoming precipitated from the solution. Monomolecular micelles probably were formed. The two graft copolymers G44 and G61, having similar composition but different inverse graft frequencies and graft lengths, behaved almost similarly except that the graft copolymer sample G61 gave a colloidal solution in pure CCl_4. Probably polymolecular micelles were formed with this sample at higher % v/v of CCl_4 in the solvent mixture.

The behaviour of the graft copolymers G53 and G55 in toluene-cyclohexane solvent mixtures (Figure 6.2) was almost similar to the behaviour of P(ECH-g-S) copolymers in C_6H_6/CCl_4 solvent mixtures, as discussed before. The decrease in the limiting viscosity numbers of both PECH and the graft copolymers was, however, steeper in this solvent mixture in comparison to that in C_6H_6/CCl_4. This indicates that C_6H_6/CCl_4 mixtures at 25°C is a thermodynamically better solvent than toluene/cyclohexane mixtures at 40°C. A 0.8% w/v solution of PECH sample E15 in toluene solution, when titrated with cyclohexane at 40°C showed precipitation at a solvent composition containing 28% v/v cyclohexane. The graft copolymer samples were however held in solution in the solvent composition range studied. Both the graft copolymers in dilute cyclohexane

solution formed colloidal solutions. The actual precipitation points for neither of the graft copolymers could be detected on titration of a 1% w/v solution in toluene with cyclohexane even at room temperature. Cyclohexane is a good solvent for polystyrene (above 34°C). The low molecular weight polystyrene sample S23 apparently remained unaffected as regards chain dimensions, by the solvent composition. Hence it was mainly the selectiveness of the solvent for the backbone which decided the solution behaviour of the graft copolymers. As in C_6H_6/CCl_4 solvent mixtures, the graft copolymers in toluene-cyclohexane solvent mixtures were retained in solution by the solvated polystyrene grafts.

6.3. Thermal Analysis

6.3.1. Experimental

Thermal analysis of some of the graft copolymer samples and the component polyepichlorohydrin and polystyrene samples described in Chapters 4 and 5 were carried out according to the procedure described before (section 3.2.3 (d)). All the graft copolymer samples had relatively high molecular weights ($\tilde{M}_n > 10^5$). PECH and the graft copolymer specimens used for thermal analysis, were prepared by evaporation of the solvent from the samples in C_6H_6 solution. Several aliquots of solution were dried in the DSC pan until the pan was almost half-filled with polymer. The polymer samples were finally dried in a vacuum oven at 60°C for 72 h. This procedure of sample preparation was expected to give better thermal contact than the freeze-dried samples placed directly in the pan. Polystyrene samples were, however, used directly as fine dry powders. Some of the copolymer samples previously dried in the DSC pan were further dried by heating at 105°C in a vacuum oven. In the discussion, these samples with heat treatment at 105°C will be regarded as annealed samples. The T_g referred to in the discussion will usually mean that of a non-annealed

sample unless the term 'annealed' is mentioned. The results of thermal analysis on the graft copolymers are listed in Table 6.4 and those of the component homopolymers in Tables 6.2 and 6.3. DSC traces of PECH sample E14, polystyrene sample S23 and some graft copolymer samples are given in Figures 6.3 - 6.6.

6.3.2. Results and Discussion

Block and graft copolymers studied by other workers have been found to exhibit different kinds of thermal behaviour.

(i) When complete microphase separation occurs two distinct glass transition temperatures each close to the value of T_g for the homopolymers have been observed. This happens in systems when the segmental motion of one type of sequence is not affected by the other sequence. Such behaviour has been observed, for example, in 'ideal' styrene-butadiene block copolymers (201,202).

(ii) In the absence of any microphase separation, a T_g similar to that of a random copolymer of similar composition is expected (203). For a random copolymer, a single T_g occurs between those of the separate component homopolymers, defined by the equation (204):

$$\frac{1}{T_g} = \frac{1}{W_A + BW_B}\left(\frac{W_A}{T_{g_A}} + \frac{BW_B}{T_{g_B}}\right) \qquad (6.3)$$

where W_A and W_B are the weight fractions of the two constituents in the copolymer, T_{g_A} and T_{g_B} are the glass transition temperatures for the homopolymers and B is a constant for the pair of monomers. When B = 1 the equation reduces to

$$\frac{1}{T_g} = \frac{W_A}{T_{g_A}} + \frac{W_B}{T_{g_B}} \qquad (6.4)$$

Data for many random copolymers of vinyl monomers obey this equation (204).

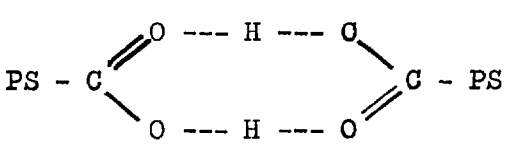
(iii) In intermediate cases, when the only partial microphase separation occurs, two ill-defined T_g's may be observed. In such cases the T_g of each kind of sequence sometimes moves towards that of the random copolymer with a similar overall composition. Such behaviour has been observed with styrene-isoprene block copolymers (205), and also with isoprene-styrene graft copolymers (206), for example.

In the present study, the PECH and the P(ECH-co-EO) samples showed a sharp and distinct glass transition with a T_g value of -27°C and -41°C, respectively. These values agreed reasonably well with the literature values of T_g for 'Herchlor' elastomers (Table 6.2).

All the polystyrene samples showed distinct glass transitions but the observed T_g values for the samples containing -COOH end-groups, especially the samples S22-I ($\bar{M}_n = 4.51 \times 10^3$) and S23 ($\bar{M}_n = 2.41 \times 10^3$) were much higher than their respective calculated T_g values (Table 6.3). The calculated values were obtained from the Fox-Flory equation (207)

$$T_g = T_g^{\infty} - K/M \qquad (6.5)$$

assuming $T_g^{\infty} = 100°C$, $K = 1.2 \times 10^5$. If dimeric association of the polystyrene molecules occurred due to the hydrogen bonding of the -COOH ends, the calculated values of T_g are closer to the observed values. The dimeric form may be represented, by analogy to $(CH_3COOH)_2$, as :



This type of association of PS COOH molecules such as in sample S23 ($\bar{M}_n = 2.41 \times 10^3$) and other low molecular weight samples was likely to occur when the precipitated polymer samples were dried at 50°C, a temperature close to the calculated T_g values of non-associated samples. Thus the calculated value of T_g for the sample S23 was 50.2°C and for S22-I was 73.4°C. In practice, much lower glass transition temperatures

would be expected due to the presence of trapped solvent. Since the drying temperature was thus possibly higher than the T_g of the monomeric PS COOH molecules, diffusion could occur relatively easily in this rubbery state and association to form dimers or higher associated species occurred. This would explain why the T_g values observed were higher than otherwise expected. Hydrogen bonding probably also occurred for sample S24, but now the effect of association on T_g is expected to be small. Values of T_g assuming that the associated dimeric species, $(PS\ COOH)_2$ were formed exclusively are also shown in Table 6.3.

The thermal behaviour of the graft copolymers was difficult to interpret. In most cases, two glass transition temperatures were observed (Table 6.4) indicating that some phase separation occurred. However, except in a few cases, both the upper glass transition temperature, T_{g_A}, and the lower glass transition temperature, T_{g_B}, were diffuse (ill-defined) and difficult to determine accurately. Even annealing the samples above 100°C did not improve the sharpness of the T_g values significantly.

Graft copolymer samples G51, G53, G55 all contained polystyrene grafts of $\bar{M}_n = 2.41 \times 10^3$. As the % PS w/w in these graft copolymers increased, T_{g_A}, the lower glass transition temperature became more diffuse, as expected (Figure 6.5). For this series, the increase in % PS w/w and graft frequency, with the same graft molecular weight increased the T_{g_A} values (Figure 6.7). However, this trend was not observed in other samples. T_{g_A} for these and other P(ECH-g-S) copolymers were close to the T_g of PECH. When some of the graft copolymers were annealed, the lower glass transition became slightly sharper but appeared at the same temperature as before.

Usually (except for G51) as the percentage of polystyrene in the graft copolymer increased, the upper glass transition became sharper. The values of T_{g_B} in all graft copolymers with short PS branches, except G51, were lower than the T_g values of the component homopolystyrenes. The relationship between the % PS w/w content and the glass transition temperatures T_{g_A} and T_{g_B} in some graft copolymers with short PS grafts is shown in Figure 6.7. A decrease in T_{g_B} was observed experimentally for all the samples on annealing (Figures 6.6 and 6.7). T_{g_B} values for the annealed samples were also sharper than for the non-annealed samples. The decrease in T_{g_B} on annealing may be due to some sort of phase re-arrangement.

The graft copolymer sample, G61 containing long polystyrene branches ($\bar{M}_n$(PS) = 3.69 x 10^4) showed a diffuse T_{g_A} at -26°C but no T_{g_B}. The annealed sample however, showed T_{g_A} at -28°C and T_{g_B} at 36°C. The non-annealed graft copolymer sample G62 with a P(ECH-co-EO) backbone and long PS branches showed a diffuse T_{g_A} at -44°C and another diffuse T_{g_B} at 93°C. The ill-defined T_g's for G61 and G62, both containing long PS branches, may indicate incomplete microphase separation.

6.4. Dynamic Mechanical Testing

6.4.1. Introduction

The viscoelastic nature of polymers is unique in the field of material properties. The time-dependent changes in polymers subjected to constant stress (creep) or constant strain (stress relaxation) give information on their viscoelastic properties. Considerable information about the viscoelastic properties of a polymer can be obtained by the study of dynamic mechanical properties. Here, the response (stress) in a polymer subjected to a small amplitude cyclic deformation (strain) is measured. The molecules perturbed this way store a portion of the

imparted energy elastically and dissipate a portion in the form of heat. The applied deformation and the resulting stress, both vary sinusoidally with time but are out of phase because of energy dissipation or damping in the polymer. The ratio of the dissipation to the storage energy depends on the temperature and the frequency of measurements. The relation between the alternating stress, σ and strain, ϵ in such a case is expressed by the relation

$$\sigma = \epsilon G \tag{6.6}$$

where G is a frequency dependent complex dynamic modulus defined by

$$G = G' + iG'' \tag{6.7}$$

G is composed of two frequency dependent components; G', called storage modulus, is the real part in phase with the strain and G'' is the loss modulus defined as the ratio of the component 90° out of phase with the stress to the stress itself. G' measures the amount of stored energy and G'', sometimes called the imaginary part, is actually a real quantity, measuring the amount of energy dissipated by the material. The quantities G' and G'' may be measured as functions of frequency at a constant temperature and more easily as functions of temperature at constant frequency.

The damping in the system or the energy loss per cycle can be measured from the "loss tangent" tan δ given by the relation

$$\tan \delta = G''/G' \tag{6.8}$$

where δ is the phase angle between the applied strain and the resulting stress.

The mechanical response of a polymer depends upon temperature, time-scale of the experiment, molecular structure, morphology and composition. The variation in molecular motion in a polymer is reflected

in the behaviour of G', G'' and hence tan δ. At the T_g of an amorphous or semi-crystalline polymer significant segmental motion (coordinated translational and rotational) involving a relatively large number of carbon atoms, 10 to 50, occurs. In this region, the storage modulus G' shows a decrease over a relatively small temperature range at a constant frequency. The loss modulus G'' and the dissipation factor, tan δ go through a maximum, the latter at a slightly higher temperature than the former. At very low frequencies and very slow rate of heating, the maximum in the loss tangent, tan δ, corresponds to a temperature close to the T_g of the polymer, for example, as determined by dilatometry. This transition is sometimes termed the mechanical transition temperature, T_t. Similar behaviour in G', G'', tan δ as discussed above are also observed at the melting point of a crystalline polymer and sometimes at minor transitions due to increased motion of certain pendant groups as in polypropylene. In the latter case, however, the maxima in G'' or tan δ are not as sharp as in T_g or T_m.

The effect of copolymerization on mechanical damping is similar to the effect on T_g (208). Hence information about phase separation in a block or graft copolymer can be obtained from a study of tan δ and related properties. Plasticizer lowers the temperature of loss modulus and the tan δ maximum in the same way as it does for the glass transition (208). The molecular weight of a polymer strongly affects the dynamic mechanical properties at temperatures exceeding T_g but at temperatures below this point the effect of molecular weight is much smaller (209).

6.4.2. Experimental

The dynamic mechanical testing of some graft copolymer samples (Table 6.4) was performed using a direct-reading dynamic viscoelastomer,

the Rheovibron (Model DDV-II-C, Toyo Baldwin Co.Ltd). A small strip of the polymer film, prepared as described below, was fitted between two clamps and subjected to forced sinusoidal oscillation (strain) of fixed frequency (11 Hertz) applied at one end; the response (stress) was measured electrically by a transducer at the other end of the sample. A second transducer monitors the strain. The two signals are processed to provide a direct reading of tan δ and the data required to calculate G' and G". The measurements were recorded at 2°C interval per minute. During the test, the sample tension was continuously adjusted to the minimum value which just prevented the sinusoidal wave from being distorted. Plots of tan δ as a function of temperature for the graft copolymer samples G51, G54 and G62 (Table 6.4) are given in Figures 6.8 - 6.10.

Preparation of test specimens

Polymer films about 0.5 mm thick were prepared by casting from benzene solutions onto a mercury surface. The solvent was allowed to evaporate slowly from the mercury surface in a Petri dish covered by a glass dish in a fume cupboard. The films were finally dried to constant weight at 50°C in a vacuum oven. Very transparent and tough films of graft copolymers were produced this way. However, films prepared from homopolystyrene by the casting method were brittle and unsuitable for testing on the Rheovibron. Films prepared from homo-polyepichlorohydrin or poly(epichlorohydrin-co-ethylene oxide) on taking out from the mercury surface contracted and became coiled and could not be used.

6.4.3. Results and Discussion

The graft copolymer sample G51 containing 17.9% w/w PS of short chain length showed a sharp mechanical transition at -5°C, the temperature

of tan δ maximum (Figure 6.8). The trend in the tan δ vs temperature plot shows that there may be another very weak but broad transition between 75° to 85°C. However, the dynamic mechanical measurements could not be continued beyond 73°C because of the great increase in the softness of the polymer film. This polymer sample showed two relatively sharp T_g's at -26°C and 90°C as measured by DSC.

The graft copolymer sample G54 containing 59.5% w/w PS grafts of the same chain length as G51 showed a sharp transition at 62.5°C (Figure 6.9). The loss modulus-temperature plot for the sample also showed a maximum at 0°C, and a weak transition occurred at about +5°C as indicated by the tan δ-temperature curve. Apart from the weak transition, the single sharp transition in the graft copolymer samples G51 and G54 suggest that they behaved as random copolymers. The temperature of sharp transition in these two graft copolymer samples is obviously dependent on the PS content in the copolymers, increasing with an increase of % PS w/w. The weak upper transition in G51 and the weak lower transition in G54 along with the observed sharp transition points however, suggest the existence of two T_g's in these graft copolymers. This is in agreement with the DSC measurements which showed that with an increase in the % PS w/w content of short chain length in the graft copolymers, the lower transition became gradually more diffuse whereas the upper transition became more pronounced. The behaviour of these graft copolymers can be explained by assuming that they partially phase separate into a polyepichlorohydrin rich phase and a polystyrene-rich phase. At lower PS contents, the polyepichlorohydrin-rich phase is dominant whereas at higher PS contents, the polystyrene-rich phase is dominant. This type of phase separation may be responsible for two

transitions in the graft copolymers and also the variation of the T_g and T_t values with the PS content.

The graft copolymer sample, G62, P[(ECH-co-EO)-g-S] containing long PS branches showed two sharp mechanical transitions - the lower transition at -32°C and the upper transition at 68°C (Figure 6.10), thus indicating microphase separation. This sample also showed two ill-defined T_g's in the DSC trace - the lower T_g at -44°C and the upper T_g at 93°C (Table 6.4).

The difference in the transition temperatures of a graft copolymer, as observed in the DSC and Rheovibron instruments may be due to :

(1) the different time-temperature scales used in the two techniques,

(2) the underlying principles in the two techniques are different since the DSC measures the change in specific heat in a polymer as a function of temperature, while the Rheovibron measures the dynamic mechanical response;

(3) the different methods of specimen preparation.

6.5. Transmission Electron Microscopy

6.5.1. Introduction

Transmission electron microscopy is widely used for the study of phase separation and morphology of polymers in the bulk state. The technique may be used to detect any discontinuity in the structure of a polymer, provided such discontinuities can be contrasted and are large enough to be resolved by the microscope. In order to create contrast between different phases, the polymer samples are often preferentially stained with a heavy atom which selectively attaches itself to one of the components to give the stained area a dark appearance in the electron microscope micrograph. For example, osmium tetroxide has been used successfully with styrene-butadiene and styrene-isoprene block copolymers (15,28,210-211). In these systems, the double bond of the butadiene and

isoprene units is readily oxidized by osmium tetroxide. Transmission electron microscopic studies are restricted to samples thin enough to transmit electrons. Samples are prepared by two techniques :

(i) as thin films cast from dilute solutions

(ii) as thin sections cut from a bulk specimen by an ultramicrotome.

In the present studies, no staining procedure was applied. It was assumed that the chlorine atoms in the polyepichlorohydrin sequences, having higher electron densities than the other atoms in poly(epichlorohydrin-g-styrene) molecules will offer the necessary contrast when any phase separation occurs.

Microphase separation in block and graft copolymers lead to ordered arrays of domains. Polymers studied in this context are mostly the styrene-butadiene and styrene-isoprene di-block and tri-block copolymers. The types of domain structure and the factors governing the nature and regularity of domains have been discussed before briefly (section 1.1.5.(b)(ii)). In comparison to block copolymers, morphological studies on graft copolymers have been rather limited. Only a few reports on graft copolymers, relating to the formation of micelles in solution and domain structures in the solid state have appeared in the literature (19,29,212-213). A graft copolymer with several junction points between unlike sequences represents a situation intermediate between a block copolymer and a random copolymer of similar composition. Microphase separation in a graft copolymer is less distinct and the resulting morphology less regular than that observed for the block copolymers, specially when the grafts are short and numerous.

6.5.2. Experimental

Samples and specimen preparation

The graft copolymer samples, G51 and G54 and a blend of PECH and PS, designated as B50 (Table 5.5) were studied by electron microscopy.

Specimens were prepared according to the following techniques :

(i) Polymer sample G51 on precipitation from C_6H_6 solution in MeOH and drying at 50°C formed a tough elastomeric solid lump. Thin sections (900 - 1000 Å thick) were cut from this polymer sample using a LKB Ultra Microtome. The sample was cooled to -160°C with the cryokit attachment of the ultra microtome, before sectioning.

(ii) Thin films (500 - 600 Å thick) of all of the polymers were cast on deionized water surfaces from a 0.02% w/v solution of the polymers in toluene. This method was recommended by Hall (214). A calculated volume of the polymer solution was pipetted on the water surface in a petri dish so as to form a film of the desired thickness on evaporation of the solvent. The solvent was allowed to evaporate slowly. The film was eventually caught on a number of small 400 mesh copper grids placed previously on top of another larger supporting copper grid at the bottom of the dish. The 400 mesh grids with the film on top were then cut free and air-dried at room temperature. Extreme care was to be taken to ensure that the films on the grid were not broken.

Electron microscopic study

A JEM 100 B (supplied by JEOL) transmission electron microscope was used to examine the specimens. Micrographs of the samples studied are given in Figures 6.11 and 6.12.

Electron micrograph of the graft copolymer sample G51 with the specimen prepared by the first technique showed distinct black spots scattered irregularly (Figure 6.11 (a)). Some sort of phase separation was believed to have taken place. A scanning of the chlorine content through some of the black spots in a micrograph was therefore made using a JEOL-JEM 100 CX TEM Scan Electron Microscope. The result is given in Figure 6.11 (b).

6.5.3. Results and Discussion

In the present studies, the graft copolymers used had grafts of short length ($\bar{M}_n \sim 3,000$). With such graft copolymers, complete phase separation and hence distinct domain formation is unlikely. The results of the electron microscopic investigations on the graft copolymer samples G51 and G54 and the polymer blend 1350 are discussed below individually.

Figure 6.11(a) shows the electron micrograph of an ultra thin section of the precipitated polymer sample G51 containing 17.9% PS. For phase separation in this sample, polystyrene domains were expected to be dispersed in a polyepichlorohydrin matrix. The micrograph indicates some phase separation with irregularly dispersed domains (black spots) of unequal sizes. Scanning of chlorine (Figure 6.11(b)) indicated a higher chlorine content in the domains than in the matrix which means some polyepichlorohydrin domains were segregated and the matrix constituted the phase relatively poorer in PECH, probably PS mixed with PECH. Such behaviour was unexpected considering the composition of the graft copolymer.

Figure 6.11(c) is a micrograph of a film of the P(ECH-g-S) sample, G51 cast on a water surface. This also indicates some incomplete phase separation. The micrograph shows that a phase poorer in chlorine content (white diffused spots) formed the approximately spherical domains dispersed in a phase richer in chlorine content. The difference in Figures 6.11(a) and 6.11(c) may be due to the different solvent-nonsolvents used in the polymer-specimen preparation. In a single experiment, when the circular black spot indicated by 'S' in Figure 6.11(c) was viewed through the electron microscope with higher magnification, one part of the black area was found to be moving (Figure 6.12(a)). This may be

due to the electron beam causing some degradation of the PECH segments in the domains.

Figure 6.12(b) is a micrograph of a film cast on a water surface from a toluene solution of the polymer sample G54 containing 59.5% w/w PS. Some chlorine-rich phase seemed again to have segregated forming irregular domains.

Figure 6.12(c) is a micrograph of a blend of PECH and low molecular weight polystyrene (composition, PECH:PS = 40:60 w/w) indicating phase separation on much larger scale than for the graft copolymer samples.

The electron microscopic investigation of the graft copolymer samples is incomplete and the results are difficult to interpret. However, some phase separation was observed in the graft copolymers studied. Further work is clearly necessary.

Table 6.1. Graft Copolymers and Component Homopolymers used for Measurement of Limiting Viscosity Numbers in Mixed Solvents (Section 6.2)

Sample No.	Polymer	$\bar{M}_w$ (GPC) x 10^{-5}	% PS w/w	λ	ℓ
G44	P(ECH-g-S)	22.53	68.0	24.5	43.2
G61	"	11.82	69.6	175.3	354.3
G53	"	9.41	46.1	31.9	23.1
G55	"	24.30	70.7	12.5	23.1
E14	PECH	14.30	0	-	-
E15	"	11.10	"	-	-
S23	PS	.0334[a]	100%	-	-

λ, inverse graft frequency

ℓ, graft length (average number of styrene repeat units in a graft)

a $\bar{M}_w = 3.34 \times 10^3$.

Table 6.2. Glass Transition Temperatures of Epichlorohydrin Polymer Samples (measured by DSC)

Sample No.	Polymer	$M_n \times 10^{-5}$	T_g(Obs.)/°C	T_g/°C [a] (Literature value)	Ref.
E14	PECH	5.85	-27	-28.5 (DTA) -27 (Dilatometry)	178
E15	"	1.98	-27	"	
E18	P(ECH-co-EO)	4.10	-41	-40 (DTA)	178

a T_g's for 'Herchlor' elastomers measured by the techniques mentioned. T_g for P(ECH-co-EO) was obtained from the plot of T_g's for 'Herchlor' elastomers as a function of ethylene oxide % w/w content. Sample E18 contained ECH and EO in a 3:2 molar ratio.

Table 6.3. Glass Transition Temperatures of Polystyrene Samples

Sample [a]	$\bar{M}_n \times 10^{-3}$	T_g(obs.)/°C	T_g(cal.)/°C [b]	
			monomeric form	dimeric form
S23	2.41	82	50.2	75.1
S22-I	4.51	91	73.4	86.7
S24	36.90	102	96.8	98.4
S28	5.45	82	78	-

a Samples S23, S22-I and S24 contained -COOH end-group.

b T_g values calculated from the Fox Flory equation (207).

Table 6.4. Glass Transition Temperatures (T_g) and Mechanical Transition Temperatures (T_t) of Poly(epichlorohydrin-g-styrene) Copolymers

Sample No.	$\bar{M}_n \times 10^{-5}$	% PS w/w	$\bar{M}_n$(PS graft) $\times 10^{-3}$	Inverse graft frequency, λ	T_g of component homopolymers/°C (measured)		T_g measured				T_t measured	
							Sample non-annealed		Sample annealed			
					PECH	PS	T_{gA}/°C	T_{gB}/°C	T_{gA}/°C	T_{gB}/°C	T_{tA}/°C	T_{tB}/°C
G51	2.42	17.9	2.41	115.2	-27	82	-26(s)	90(s)	-26(s)	26(d)?	-5	75-85 [a]
G53	2.89	46.1	"	31.9	"	"	-22(m)	76(d)	-	-	-	-
G54	3.89	59.5	"	18.4	"	"	-	-	-	-	5 [a] (approx.)	62.5
G55	5.25	70.7	"	12.5	"	"	-14(d)	46(s)	-14(d)	39(s)	-	-
G41	6.48	47.2	4.51	50.4	"	91	-24(m)	not observed	-25(s)	40(d)	-	-
G44	6.26	68.0	4.51	24.5	"	"	-29(d)	52(d)	-29(d)	43(d)	-	-
G141G	6.19	46.6	5.45	67.8	"	82	-	-	-27(s)	26(d)	-	-
G61	2.05	69.6	36.90	175.3	"	102	-26(d)	not observed	-28(m)	36(m)	-	-
G62 [b]	2.03	74.5	36.90	-	-41	102	-44(d)	93(d)	-	-	-32	68

T_{gA} indicates lower and T_{gB}, upper glass transition temperature measured by DSC

T_{tA} indicates lower and T_{tB}, upper mechanical transition temperature measured by Rheovibron

(s), sharp; (d) diffuse, very ill-defined; (m) moderately defined

a very weak and broad mechanical transition observed

b Graft copolymer sample G62 had P(ECH-co-EO) backbone.

Table 6.5. Polymer Samples used for Electron Microscopy

Sample	Polymer	$\bar{M}_n \times 10^{-5}$	$\bar{M}_n$(backbone)[a] $\times 10^{-5}$	$\bar{M}_n$(graft) $\times 10^{-3}$	% PS w/w	λ
G51	P(ECH-g-S)	2.41	1.98	2.41	17.9	115.2
G54	"	3.89	1.58	"	59.50	18.4
B50	PECH + PS blend	-	1.98	2.41	60.0	-

[a] $\bar{M}_n$ of the backbones in the graft copolymers are calculated values.

Figure 6.1. Dependence of Limiting Viscosity Number of P(ECH-g-S) Copolymers and PECH on Solvent Composition in Benzene-Carbon Tetrachloride Solvent Mixtures at 25°C.

G44, G61, graft copolymers
E14, PECH

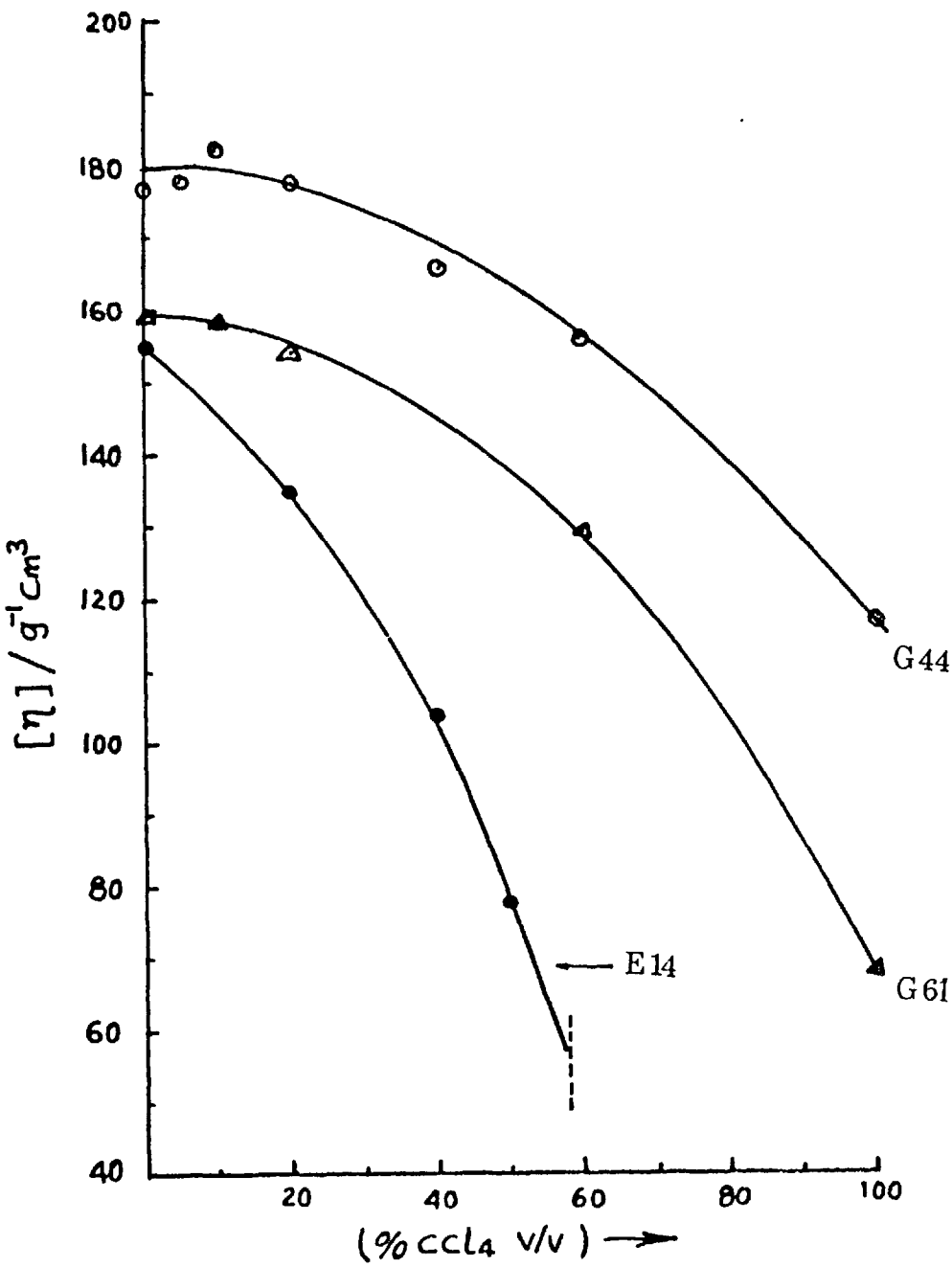


Figure 6.2. Dependence of Limiting Viscosity Number of P(ECH-g-S) Copolymers and Component Homopolymers on Solvent Composition in Toluene-Cyclohexane Solvent Mixtures at 40°C.

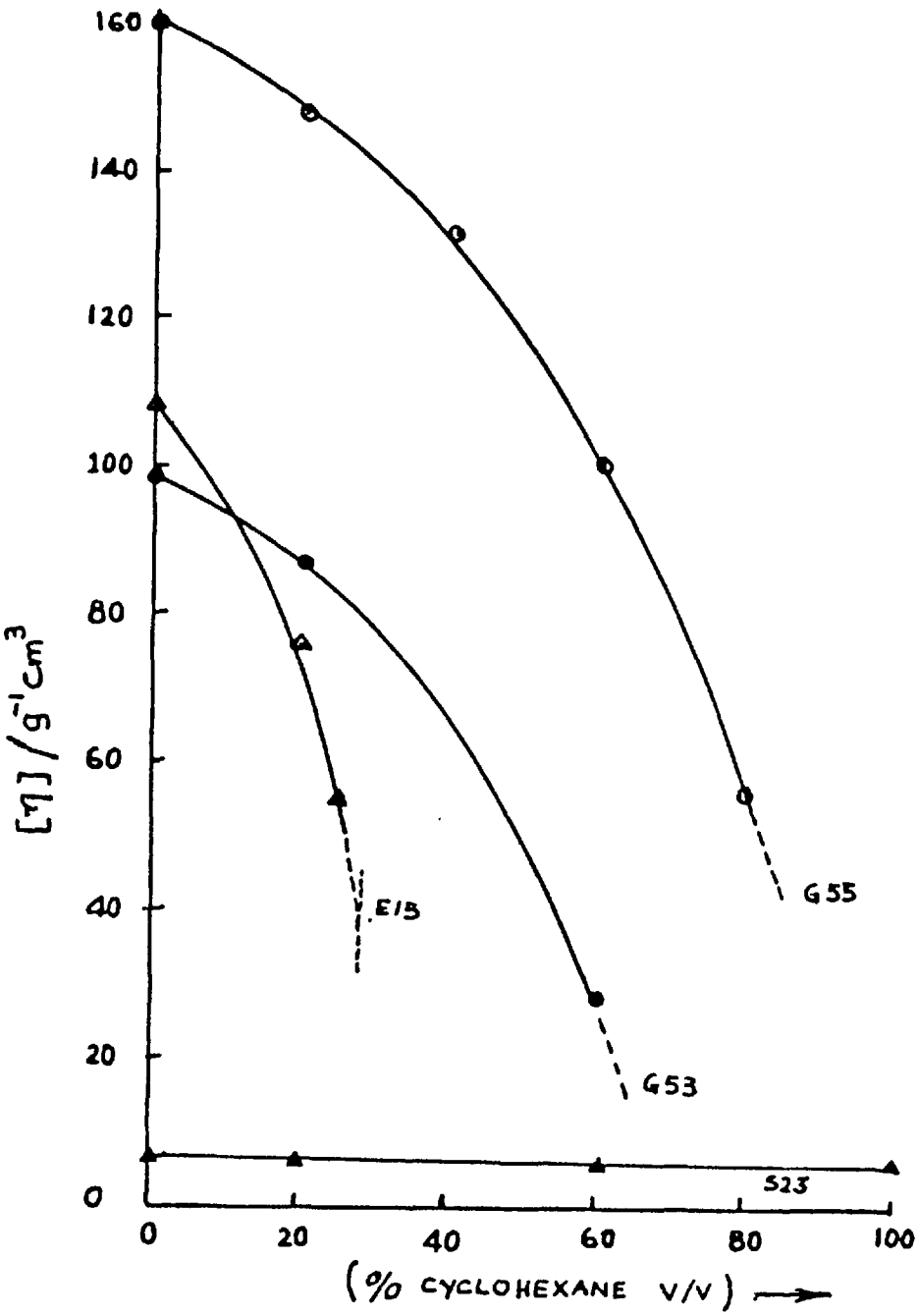


Figure 6.3. DSC Thermogram of Polyepichlorohydrin Sample E14

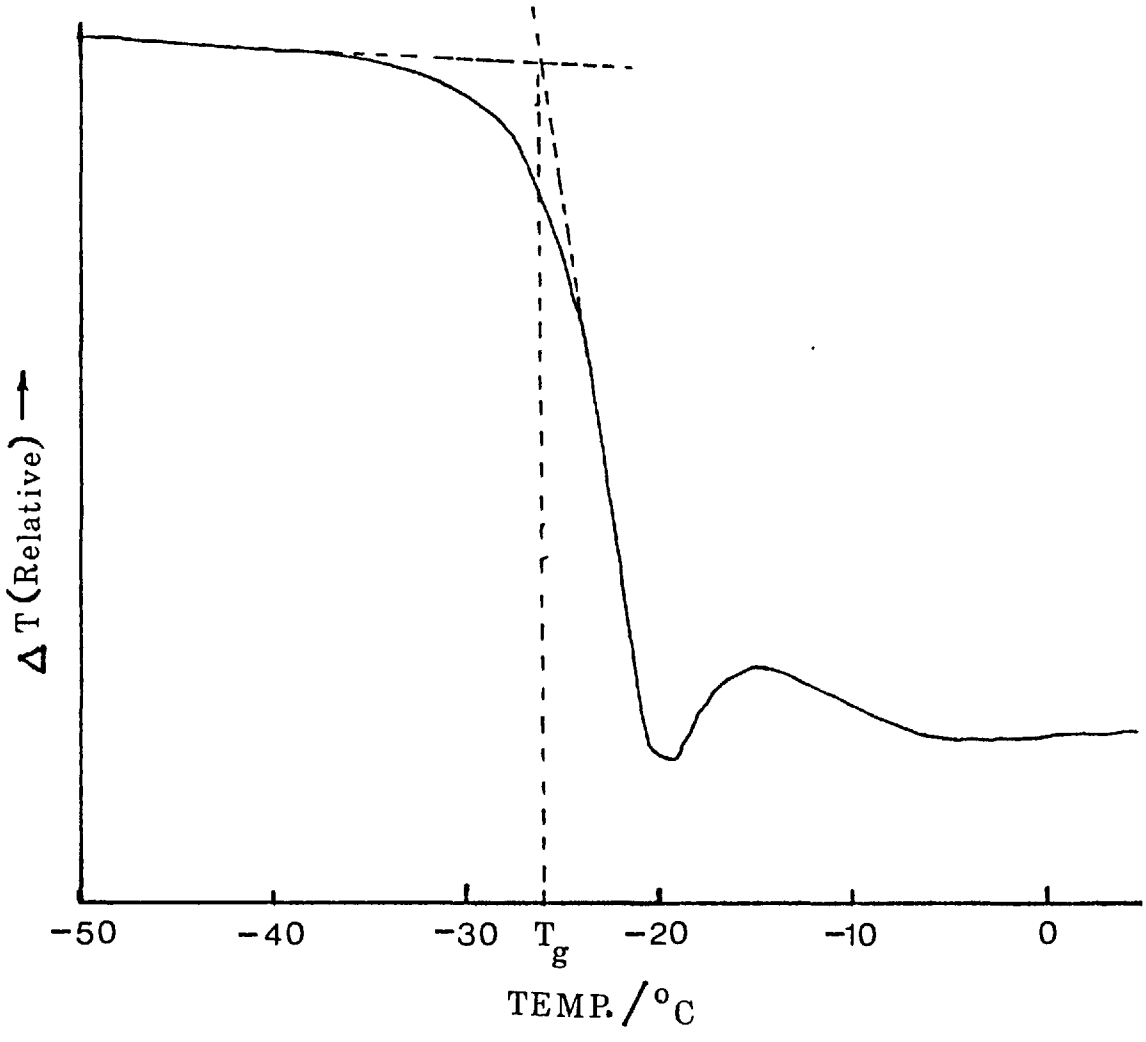


Figure 6.4. DSC Thermogram of Polystyrene (PS COOH), Sample S23

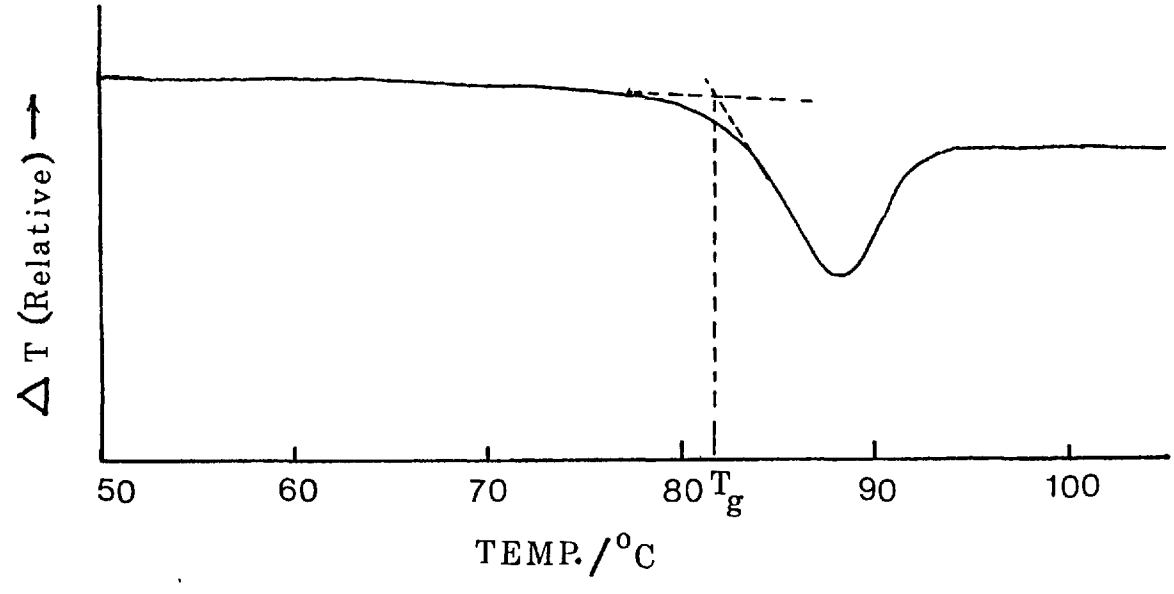


Figure 6.5. DSC Thermograms of Poly(epichlorohydrin-g-styrene) Samples, G51, G53 and G55 (non-annealed) showing Glass Transition Temperatures

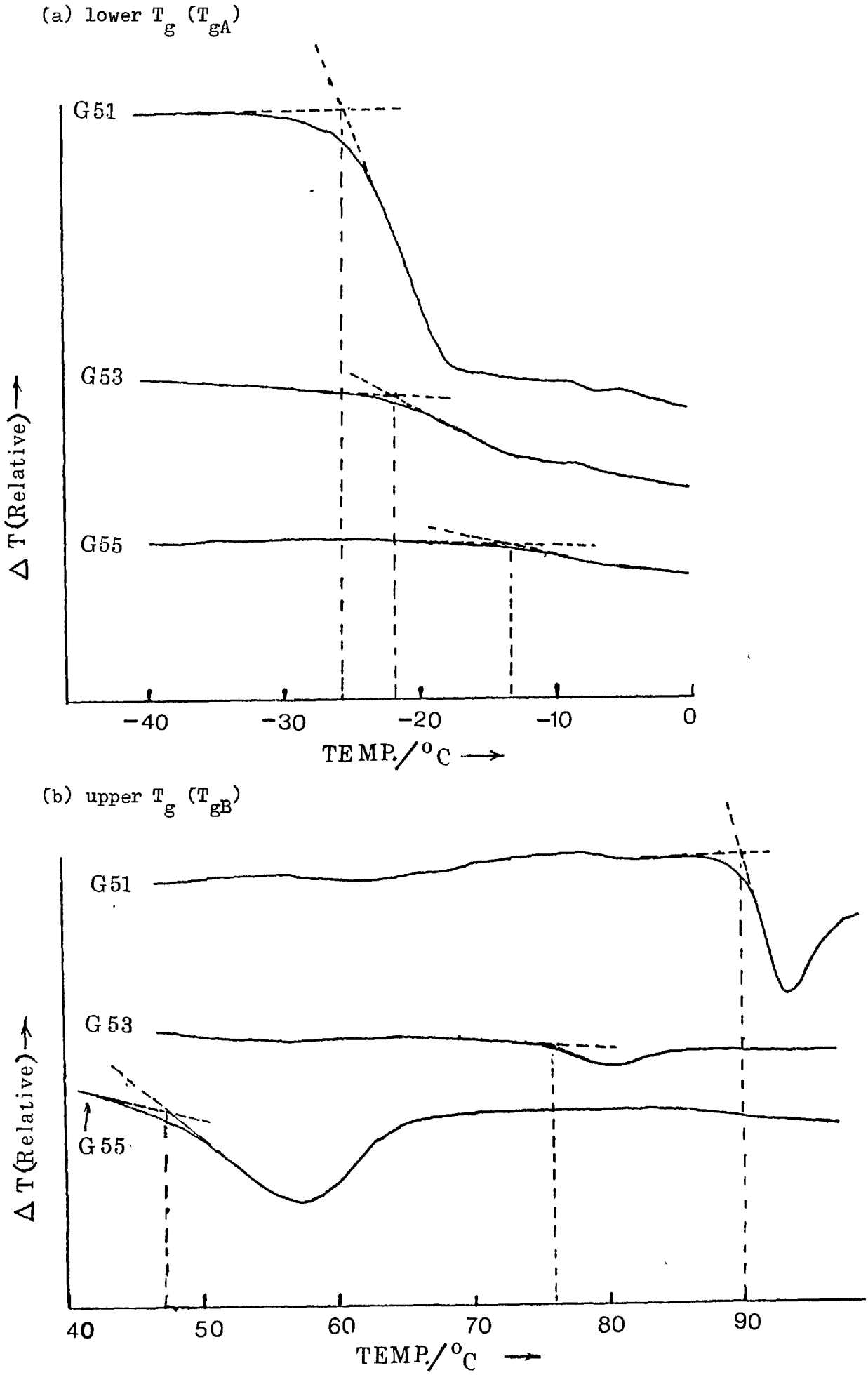
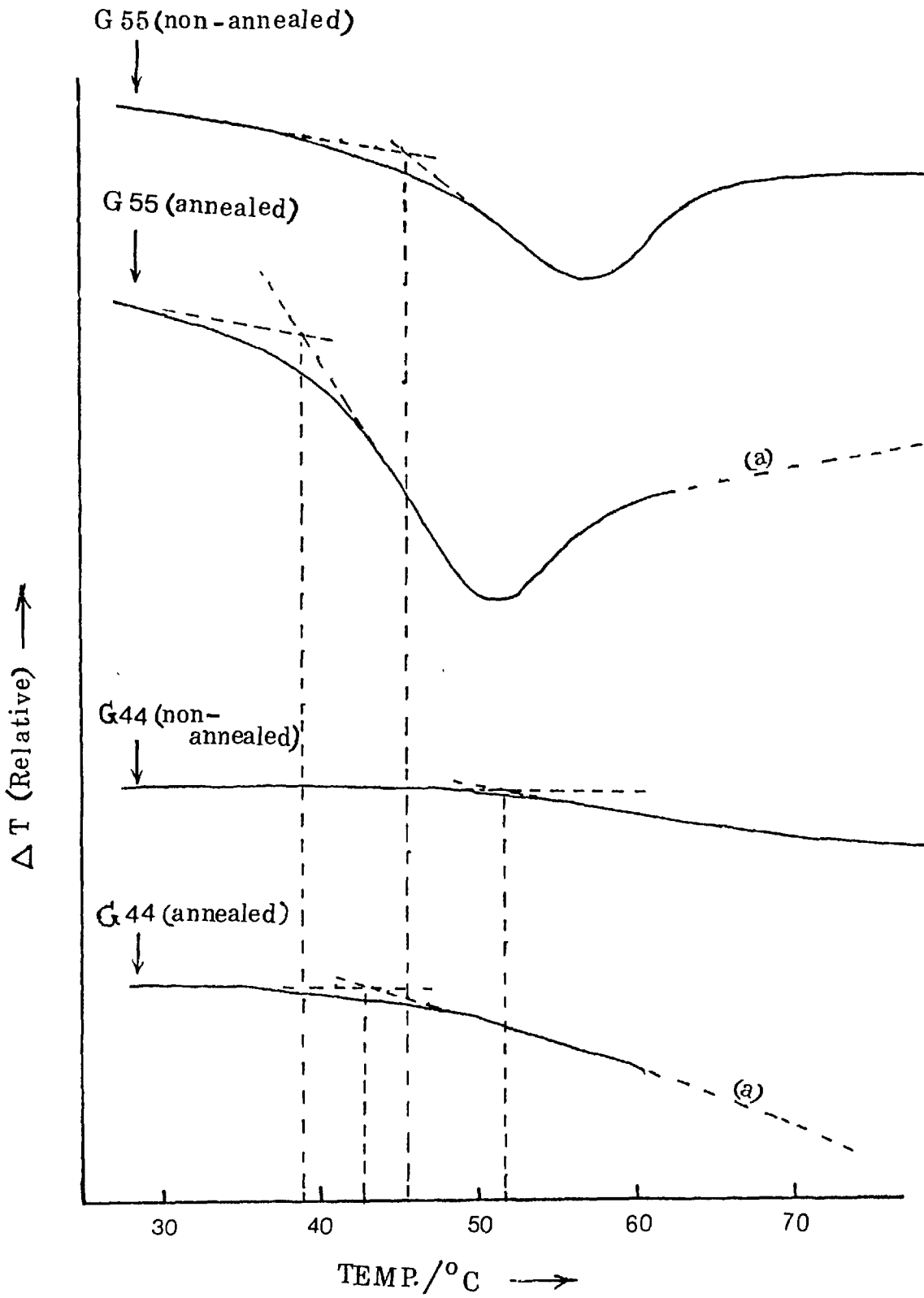


Figure 6.6. DSC Thermograms showing Upper Glass Transition Temperatures (T_{gB}) for Poly(epichlorohydrin-g-styrene) Samples G55 and G44 (non-annealed and annealed)



(a) instrumental instability possibly due to degradation, was observed for all the annealed samples at temperatures above about 60°C.

Figure 6.7. Glass Transition Temperatures of Poly(epichlorohydrin-g-styrene) Copolymers with Short Polystyrene Grafts as a Function of % PS w/w.

T_{gA}, lower T_g in non-annealed and annealed samples

T_{gB} (non-annealed), upper T_g in non-annealed samples

T_{gB} (annealed), upper T_g in annealed samples

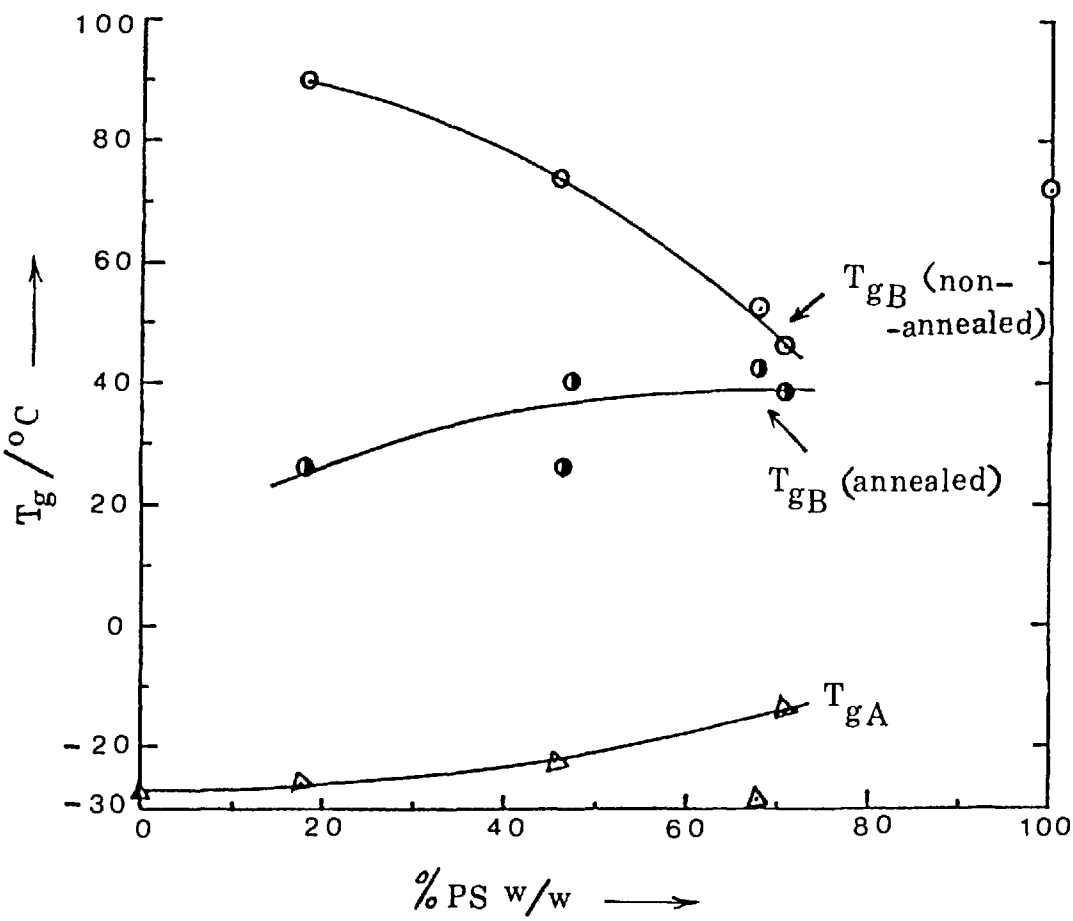


Figure 6.8. Result of Dynamic Mechanical Testing on Poly(epichlorohydrin-g-styrene) Sample G51

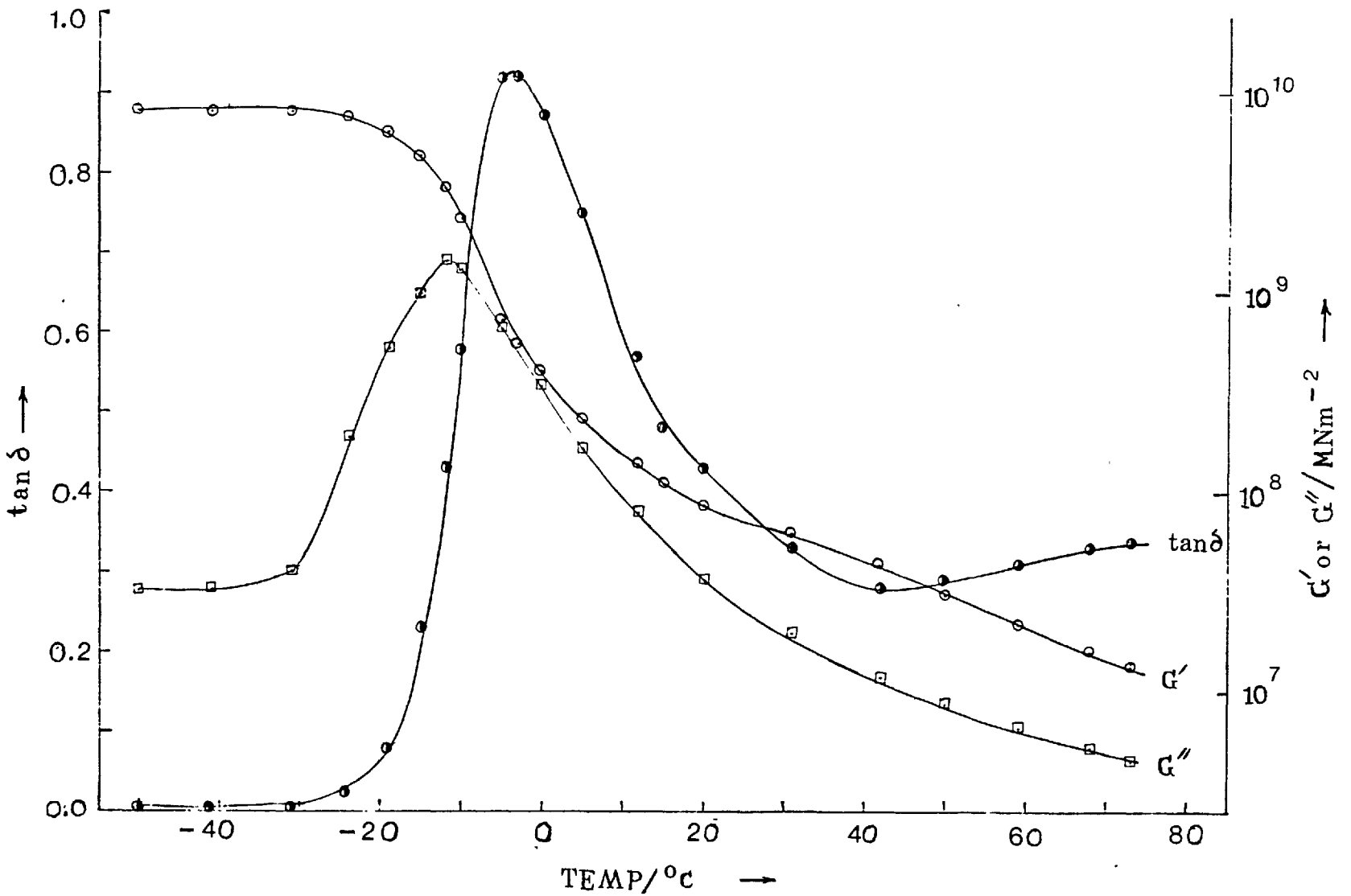


Figure 6.9. Result of Dynamic Mechanical Testing on Poly(epichlorohydrin-g-styrene) Sample G54

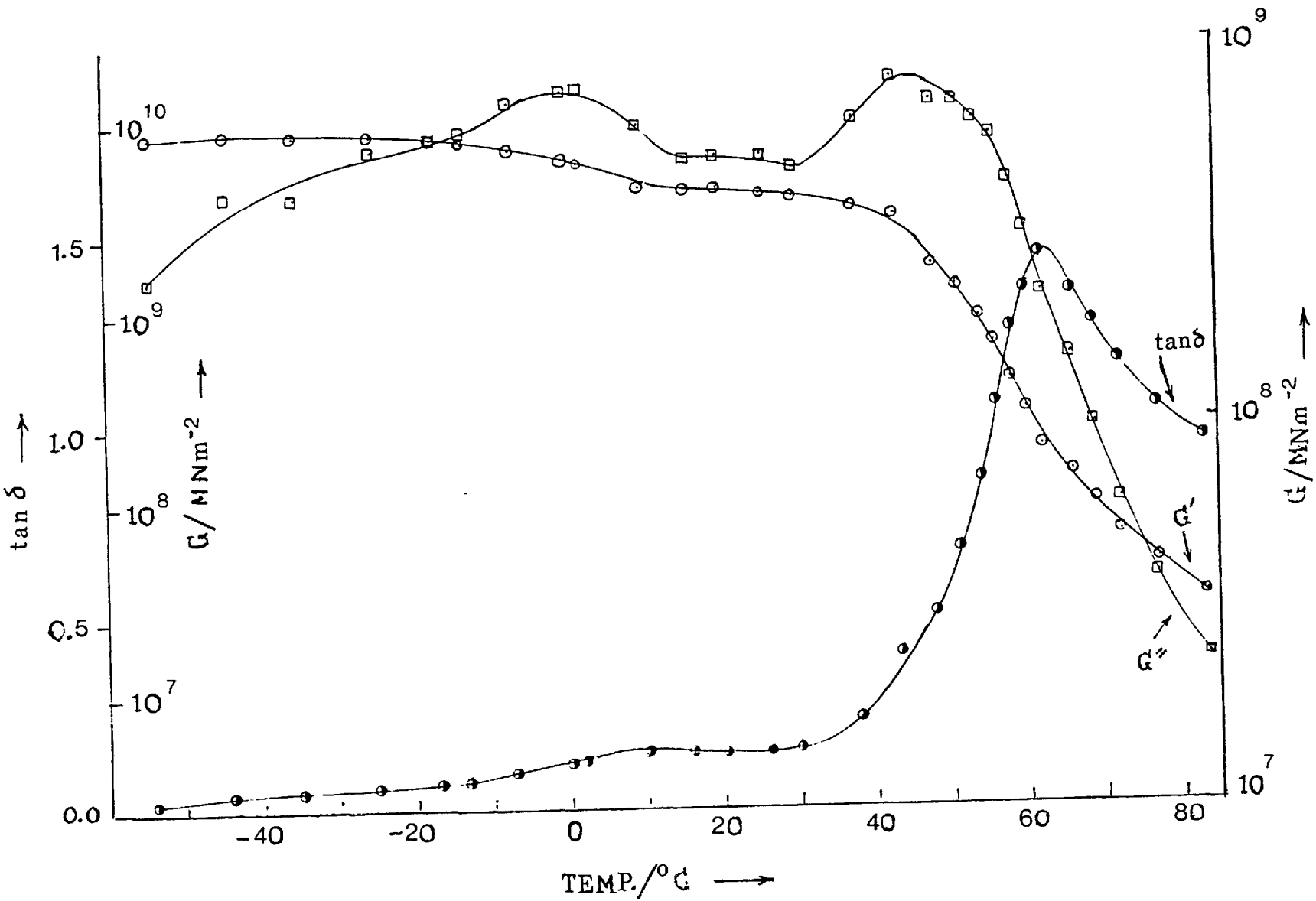
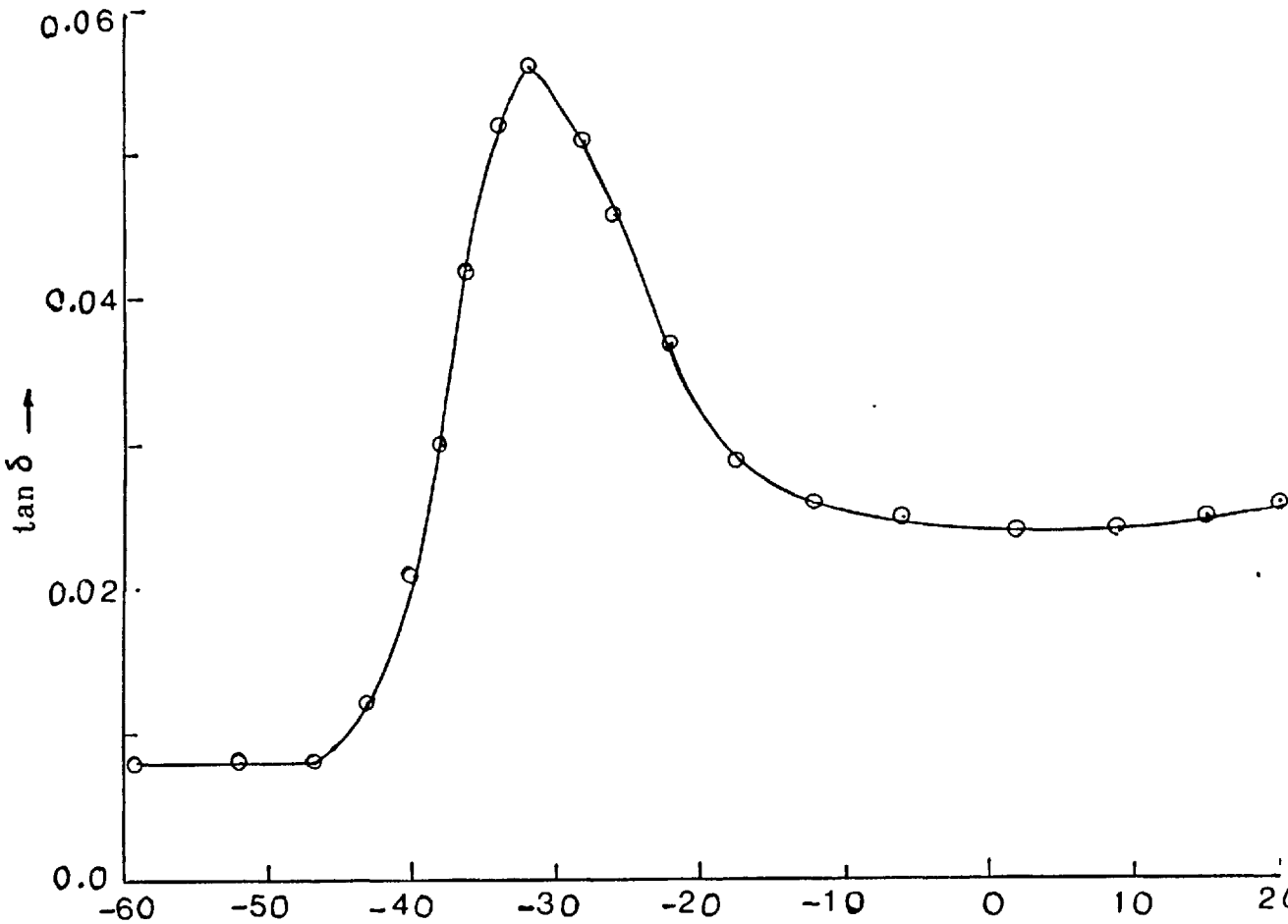


Figure 6.10. Results of Dynamic Mechanical Testing on Poly[(epichlorohydrin-co-ethylene oxide)-g-styrene] Sample, G62, showing Mechanical Transition Temperatures

(a) lower mechanical transition



(b) upper mechanical transition

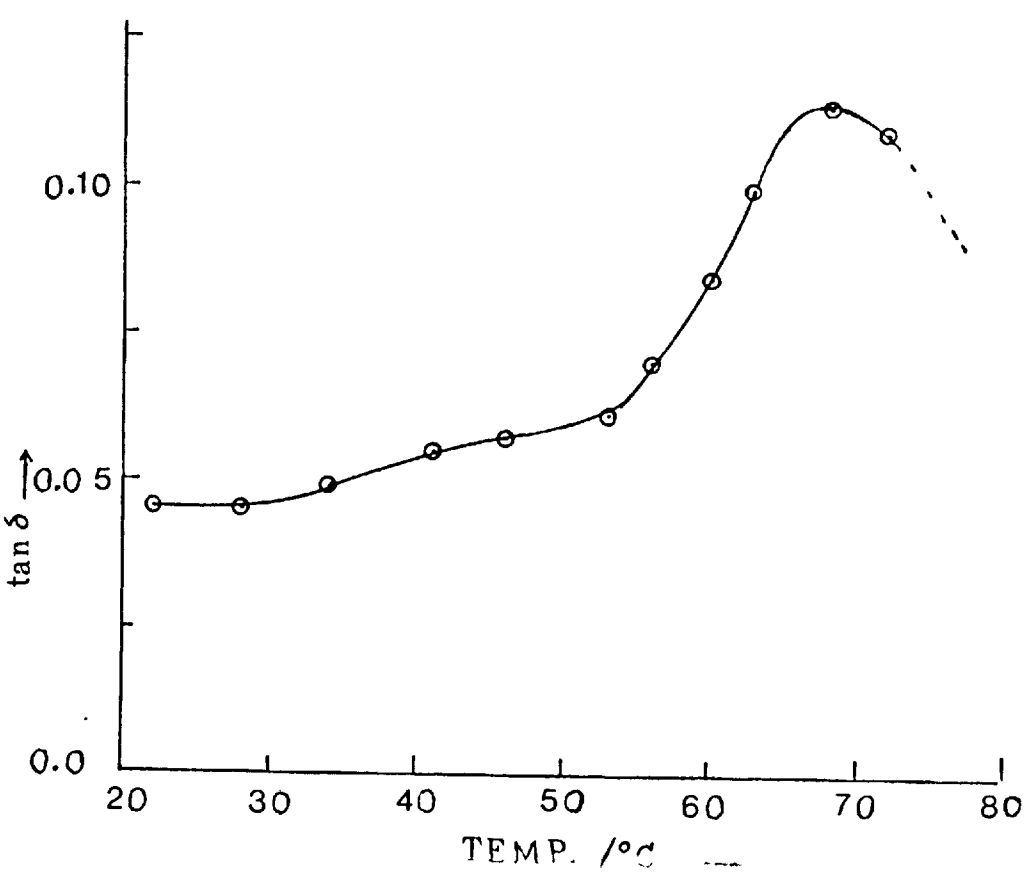
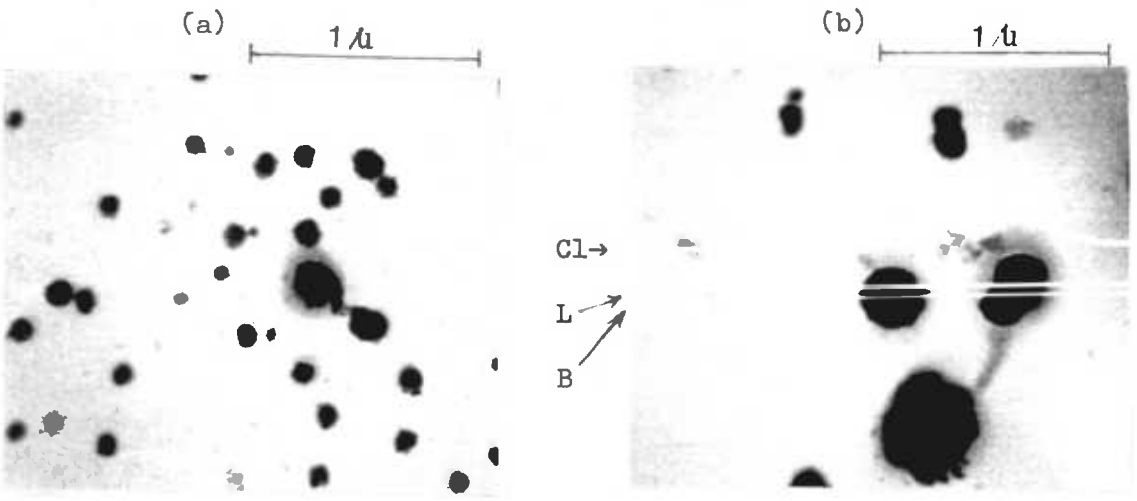


Figure 6.11. Transmission Electron Micrographs of Poly(epichlorohydrin-g-styrene) Sample G51

(a) an ultra-thin section prepared by technique (i) (Section 6.5.2);
(b) scanning of chlorine through an ultra-thin section prepared by technique (i);
(c) a film prepared by technique (ii) (Section 6.5.2).



L → line for scanning Cl
B → base line
Cl→ relative measure of Cl content along the line 'L'

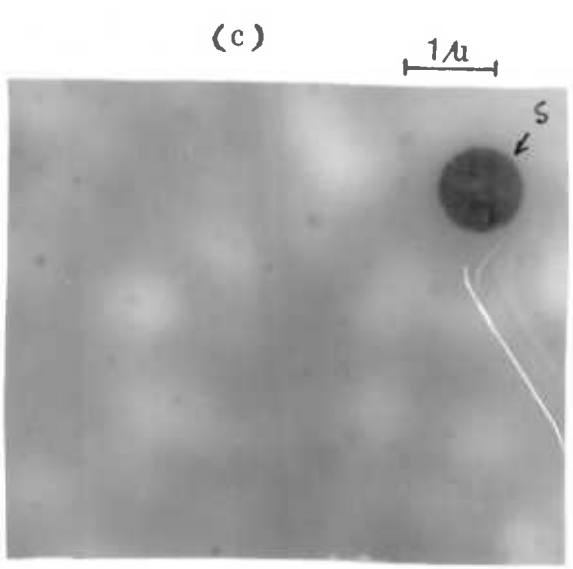
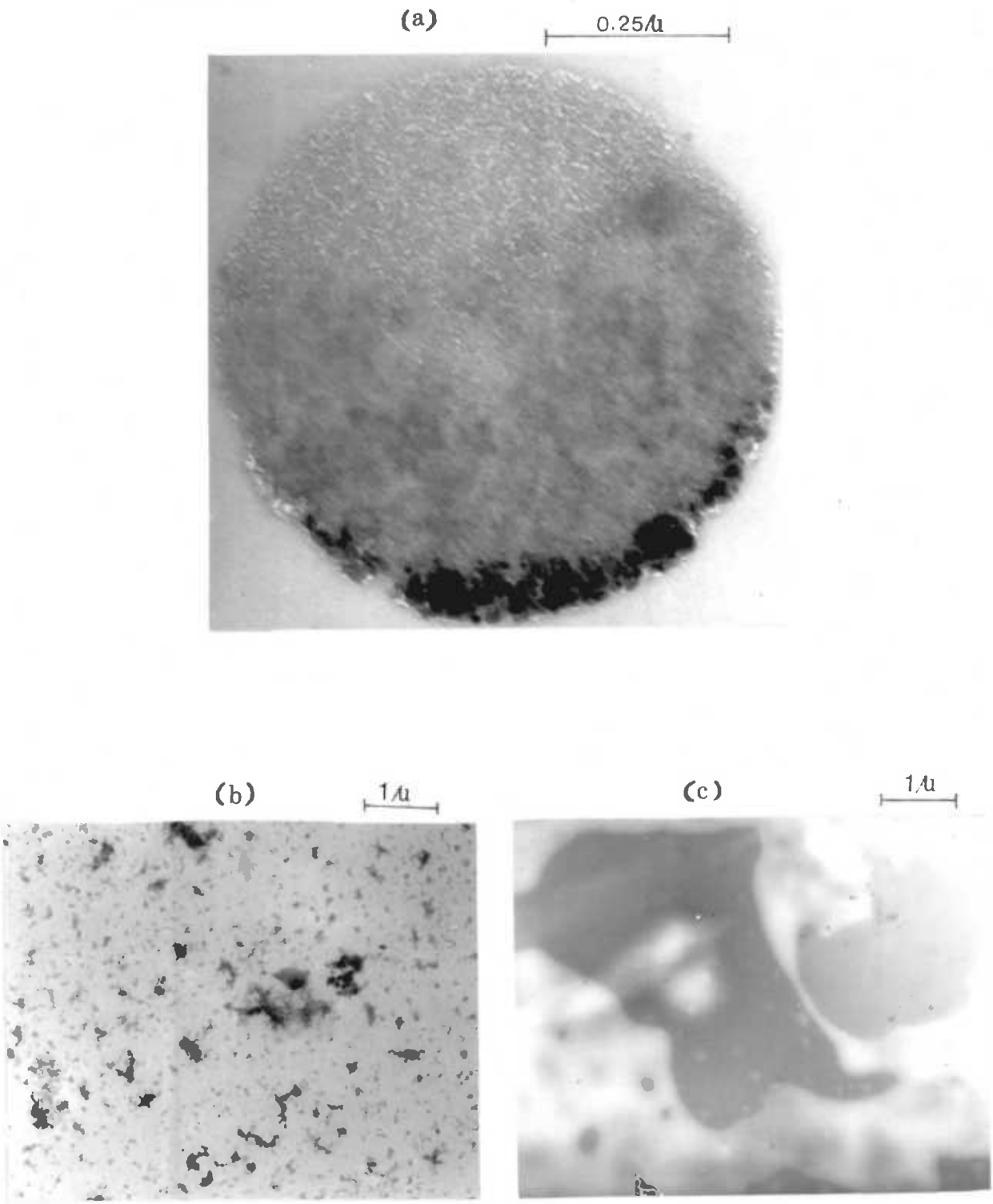


Figure 6.12. Transmission Electron Micrographs

(a) a domain-like circular black spot 'S' (Figure 6.11(c) in the micrograph of Sample G51 when viewed under high magnification in the microscope;
(b) P(ECH-g-S) Sample G54 (a film prepared by technique (ii), Section 6.5.2);
(c) a blend of PECH and PS (Sample B50, a film prepared by technique (ii))



CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Poly(epichlorohydrin-g-styrene) copolymers have been prepared by three different methods of coupling reaction:

(1) by anionic coupling or carbanionic deactivation of living polymer with the chloromethyl groups of polyepichlorohydrin in different solvent media, such as benzene, toluene, benzene-THF mixtures and THF usually at 20°C,

(2) by coupling of the potassium salt of polystyryl carboxylic acid with polyepichlorohydrin in DMF solution, usually at 60°C,

and (3) by coupling of the potassium salt of polystyryl propylene sulphide with polyepichlorohydrin in THF at 40°C.

Grafting by the first method was complicated by various side reactions such as cross-linking and colloidal phase separation in non-polar solvent media, some degradation of the backbone polymer in all solvents and some non-degradative termination of the living polymer. The cross-linking in pure hydrocarbon solvent media was due to lithium-halogen interchange reactions and was observed even at -78°C in toluene. The degradation reaction was less prominent in polar solvent media such as THF and THF/C_6H_6 solvent mixtures than in non-polar solvents. In spite of the greater extent of degradation in non-polar solvents (C_6H_6 and toluene), the extent of grafting was also found to be higher in these solvents than in THF and THF/C_6H_6 mixtures (67:ss v/v). Whether contact ion-pairs or solvated ion-pairs in the living anion-counter ion system were more efficient in the coupling reactions with polyepichlorohydrin was not investigated. Thus, this aspect of the coupling reaction needs further investigation. Further investigations are also necessary

to ascertain the relative degree of grafting and degradation in solvents of different dielectric constant.

One of the major problems faced in the grafting of polystyrene onto polyepichlorohydrin by carbanionic deactivation is the proper purification of the backbone polymer. Reprecipitation of the commercial polyepichlorohydrin twice in pure MeOH and subsequent freeze-drying of the purified samples did not completely remove all of the volatile and non-volatile impurities. Hence a fraction of the added living polymer was terminated by these impurities as evidenced by the low grafting efficiency, for example, in THF/C_6H_6 mixtures, even in the absence of much degradation of the backbone polymer. However, previous workers have observed that the synthesis of graft copolymers by the carbanionic deactivation technique is always accompanied by the termination of some living polymer either by side reactions or impurities. Thus it is not possible to prepare graft copolymers free from homopolymers by this technique. Pure graft copolymers in the previous and the present studies could only be obtained by post-synthetic purification.

The second method of grafting was comparatively easier. Once a polymer ended with a -COOH functional group is prepared, it can be used for grafting onto polyepichlorohydrin without maintaining the stringent experimental conditions required for grafting by carbanionic deactivation. Commercial polyepichlorohydrin, containing traces of antioxidant and solvents without rigorous purification can be used directly. In this method of grafting, a hundred per cent grafting efficiency of polystyrene can be achieved, provided the polymer chains to be used as grafts all contain -COOH functional end-groups and the proper molar ratio R' (Section 5.5.2(e)) is maintained in the reaction mixture. The problem here concerns the synthesis of polymer molecules

all having -COOH end-groups. Polystyrene molescules each having a -COOH end-group, free from dipolystyryl ketone and tripolystyryl Carbinol, (137), have been prepared before, using polystyryl potassium and purified gaseous carbon dioxide (136). In the present study, polystyryl carboxylic acid was prepared by termination of polystyryl lithium or polystyryl potassium in an excess of dry ice/THF slurry and subsequent acidification. There was no evidence of the formation of dipolystyryl ketone or tripolystyryl Carbinol. However a portion of the polymer was probably terminated by moisture contained in the dry ice. Hence purification of dry ice is ideally necessary to prepare polystyryl carboxylic acid with all molecules possessing -COOH end-groups. Another aspect of the research work needs further investigation. The low molecular weight PS COOH samples (S22-I and S23, Table 5.3) prepared from polystyryl lithium were found to contain about 2 - 3% w/w of very high molecular weight polymer. It is desirable to discover the reason for the formation of such high molecular weight polymer and to develop experimental methods which eliminate its formation.

The grafting of PS COO^- onto polyepichlorohydrin is a relatively slow reaction. Because of this, all the polyepichlorohydrin molecules have an equal chance of becoming grafted by PS COO^-. Hence the graft copolymers prepared by this method were very homogeneous which is clearly an advantage. Moreover, since the poly(epichlorohydrin-g-styrene) copolymers have a greater solubility than polyepichlorohydrin itself in DMF, the grafted molecules are presumably more extended in solution than the ungrafted molecules. The effect of possible sterric hindrance to further grafting on the already grafted chains is thus minimised. Because of the relatively low basic character of PS COO^-,

side reactions such as the degradation of the polyepichlorohydrin backbone are limited. To summarize, allowing sufficient time, polyepichlorohydrin can be satisfactorily grafted homogeneously by this method, without pronounced degradation of the backbone polymer.

The third method of grafting, that is grafting through thioether linkages using PS $CH_2CH(CH_3)S^-K^+$, resulted in a high grafting efficiency of polystyrene. However, the simultaneous cleavage of the backbone polymer was also quite marked. The nature of the cleavage reaction in this method of grafting needs further systematic investigation. Probably the cleavage reaction could be minimized by conducting the coupling reaction at ambient or lower temperatures. Epichlorohydrin polymers have been modified previously (Section 1.4.2) using the sodium and potassium salts of different alkanols, thiols and thiophenols, at 60^oC and higher temperatures. However, no mention was made about any side reactions or even the molecular weights of the modified polymers.

In the present study, polyepichlorohydrin has been modified by substitution of chlorine atoms with thiophenoxide and phenyl acetate groups. Esterified polymers prepared by substitution of chlorine atoms with carboxylate groups, for example acetate or phenyl acetate groups, can be converted into epichlorohydrin-glycidol copolymer containing a large number of pendant-CH_2OH groups. This conversion occurs by simple alkali hydrolysis at ambient or even low temperatures. This technique of introducing pendant -OH groups into polyepichlorohydrin causes negligible degradation to the backbone. Degradation of polyepichlorohydrin on reaction with alkali was found in this study to take place at relatively high temperatures. Polymer containing pendant $-CH_2OH$ groups might later be grafted with polyurethane molecules containing -NCO end-groups and network polymers of controlled

structure could be prepared. Graft copolymers could be synthesized by reaction of the $-CH_2OH$ groups with polymers containing a single -NCO end-group. Similarly, by reacting calculated amounts of bi-functional polystyryl carboxylate, $-OOCPS\ COO^-$ with polyepichlorohydrin, network polymers with controlled structures could be prepared.

Butyl-lithium cleavage of polyepichlorohydrin forms polymer with -OH, $> C = O$ and acetylene end-groups. These polymers could possibly be used for the synthesis of block copolymers of polyepichlorohydrin involving condensation reactions with other polymers containing suitable functional end-groups. Thus the carbonyl groups could be reduced with $LiAlH_4$ to form hydroxyl-ended polymers prior to further reactions.

Epichlorohydrin homo and copolymers, used as speciality rubbers are very stable polymers which are resistant to ozone, heat, and flames (100,111). However, polymers without antioxidant or containing only very small amounts of antioxidant were found to be unstable, undergoing oxidative degradation in the presence of sunlight. This aspect of the chemistry of epichlorohydrin polymers needs further investigation to elucidate the mechanisms of degradation.

The solution behaviour of poly(epichlorohydrin-g-styrene) copolymers, as measured by dilute solution viscometry, was interesting. Graft co-polymers of similar composition but having different graft length and inverse graft frequency behaved almost similarly in solvent-non solvent mixtures. There was clear evidence of micelle formation in solvent-non solvent mixtures. However, the interaction between the polyepichloro-hydrin backbone and the shorter polystyrene branches was not marked enough to be readily detected. Graft copolymers with very much longer polystyrene branches ($\bar{M}_n \sim 10^6$) need to be synthesized and their solution properties investigated.

Differential scanning calorimetry and dynamic mechanical testing by the Rheovibran gave some evidence of incomplete phase separation. Further systematic work including electron microscopy is necessary to investigate the precise extent of such phase separation and its effect on mechanical properties needs to be studied. The synthesis of further series of graft copolymers with the same length of backbone but with grafts of varying lengths and frequencies, seems desirable.

Poly(epichlorohydrin-g-styrene) copolymers were found to form very transparent, tough films when the polystyrene content was relatively high. The films were elastic however when the polystyrene content was relatively low. Commercially some of these graft copolymers might be used for homogenizing the component homopolymers and also might be profitably used for preparation of impact modified polystyrene.

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