SYNTHESIS AND CHARACTERISATION OF NOVEL POLYURETHANE IONOMERS

A Thesis Submitted for
the Degree of Doctor of Philosophy

by

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March 1991

ABSTRACT

Polyurethane ionomers are a relatively new class of block copolymers, usually containing a small number of ionic groups in the polymer backbone or side chains. Only a limited number of methods of introducing ionic centres into the polymer have been reported in the literature.

This thesis discusses the synthesis of two new ionic diol chain extenders, potassium-S-1,2-dihydroxypropyl thiosulphate, TDOL and potassium-S-1,2-dihydroxypropyl sulphonate, SDOL, by nucleophilic substitution reactions. In addition, the synthesis of several series of polyurethane ionomers with various soft segments and ionic contents using these ionic chain extenders is described. Using the current method of ion incorporation, the ion composition in the polymers can be controlled accurately.

Also included in this thesis is the elucidation of the structure of these new ionic diols and ionomers by elemental analysis, infrared and ^{1}H nuclear magnetic resonance spectroscopy. The glass transition temperatures of the polymers and thermal stability assessed by differential scanning calorimetry and thermogravimetry are also considered. Furthermore, the physical and mechanical properties of the polymers are interpreted in terms of their structures. Properties include dynamic and

mechanical properties, surface morphology and equilibrium solvent uptake values.

Finally, the dilute solution properties of the ionomers obtained using solution viscometry and gel permeation chromatography in the absence and presence of lithium bromide are reported.

ACKNOWLEDGEMENTS

I wish to express my extreme gratefulness and appreciation to Dr. M. H. George and Dr. J. A. Barrie for their close supervision, helpful suggestions and constant guidance throughout the course of this research.

I am also deeply indebted to all the technicians in the Chemistry Department for their help on the use of the various equipments and useful discussions. The continuous support and encouragement of my wife, Yvonne, and my parents, cannot be more valuable.

Finally, I would like to acknowledge the financial support of this work by the London Borough of Barking and Dagenham.

ABBREVIATIONS

T_g	glass transition temperature
DSC	differential scanning calorimetry
DMTA	dynamic mechanical thermal analysis
TGA	thermogravimetric analysis
GPC	gel permeation chromatography
SEM	scanning electron microscopy
TEM	transmission electron microscopy
DMSO	dimethylsulphoxide
DMF	N,N'-dimethylformamide
MDI	diphenylmethane-4,4'-diisocyanate
TDI	toluene diisocyanate
THF	tetrahydrofuran
CPD	3-chloro-propane-1,2-diol
BD	butane-1,4-diol
PPG	polypropylene glycol
PEG	polyethylene glycol
PTMG	polytetramethylene glycol

TDOL	potassium-S-1,2-dihydroxypropyl thiosulphate
SDOL	potassium-S-1,2-dihydroxypropyl sulphonate
SDPS	sodium-S-1,2-dihydroxypropyl sulphonate
C_p	heat capacity
η	dynamic viscosity

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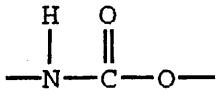
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CHAPTER ONE INTRODUCTION

1.1. Definitions

"Polyurethanes" are the generic names given to those polymers which contain the characteristic urethane linkage. These include not only the homopolymers, but copolymers both linear and crosslinked, in which the urethane linkage may constitute only a small portion of the total number of linkages in the polymer chain. The term "urethane" may also be regarded as an amide ester of a carbonic acid or an ester of an unstable carbamic acid.



The urethane link

This nomenclature may be somewhat confusing as polyurethanes cannot be obtained by simple polymerisation of urethane monomers nor can they be depolymerised to give the monomer, alkyl carbamate. Polyurethanes are usually prepared by the step-growth polymerisation of diisocyanates with polyesters or polyethers having hydroxyl end groups, simple low molecular weight diols, or mixtures of these hydroxy-terminated compounds. The functionality of the hydroxyl components as well as the isocyanate can be increased to form branched or crosslinked polymers. These polymers are thus sometimes called "isocyanate polymers" or simply "urethanes".

1.2. History

The basic work on polyurethanes was first started by Professor Otto Bayer in Germany in the late nineteen thirties(1,2). As the result of intense research into fibre-forming polymers, Bayer and his workers prepared a number of linear polyurethanes from diisocyanates and diols analogous to the polyamides. The urethane-formation systems have ever since been receiving continuous world-wide interest. The fact that these polymers can be synthesised in compositions that may contain not only the urethane links, but other groups in or pendant to the polymer chains to meet the required properties, makes them one of the most versatile class of polymers. A wide range of physical properties and morphologies can be obtained depending on the composition and chemical nature of the various constituents.

The availability of various isocyanates and a wide range of polyols of different molecular weights and functionalities enables the production of polyurethanes in an astonishing variety of forms from very flexible elastomers to rigid, hard plastics. Major uses include adhesives, binders, coatings, paints, fibres, foams, elastomers and there are applications in other areas such as the biomedical one.

1.3. Segmented Polyurethanes

Segmented polyurethanes are generally considered to be block copolymers of the $(A-B)_n$ type. These linear thermoplastic elastomers are characterised by their two-phase microstructure at service temperatures. The so-called soft segment usually consists of a polyester or polyether macrodiol and has a T_g well below room temperature, while the hard segment is formed by a diisocyanate, chain extended with a low molecular weight diol such as butane-1,4-diol and has a T_g above ambient temperature. The driving force for the phase separation in these systems is the thermodynamic incompatibility of the two segments. The elastomeric property of these polymers is mainly due to their two-phase morphology with the hard segment domains acting as physical crosslinks and/or as reinforcing fillers in the continuous soft segment matrix. These physical crosslinks break down at an elevated temperature or under the influence of suitable solvents and reappear with decreasing temperature or after removal of the solvent. In principle, no damage to the material results from the breakdown and restoration of crosslinking. Thus the size, shape and structure of the hard segment domains in segmented polyurethanes play a decisive role in the determination of their mechanical properties.

The extent of phase separation is directly related to the degree of interaction between the soft and hard segments. It has been reported that in polyester- and polyether-based polyurethanes, some of the urethane N-H groups could form hydrogen bonds with the oxygen of the ether or ester linkage causing partial phase mixing(3). To avoid the probability of hydrogen bonding between the two segments, Schneider et al(4) and Brunette et al(5) prepared polyurethanes based on hydroxy-terminated polybutadiene soft segment which possessed a high degree of phase separation.

1.4. Basic Chemistry

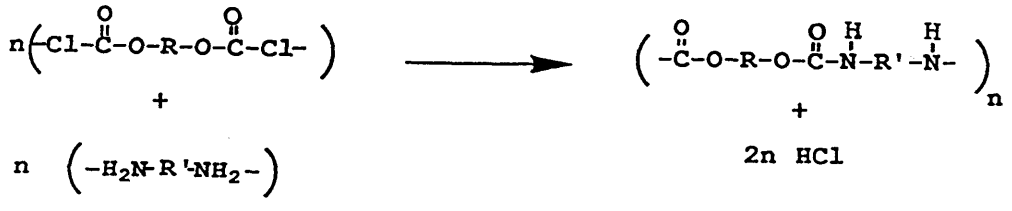
Although various synthetic routes for the preparation of polyurethanes have been studied in the past, the two most important ones are the condensation polymerisation between a bischloroformate and a diamine and the addition polymerisation between a diisocyanate and a diol. Both types of polymerisation proceed through a step-wise mechanism, hence the process is often named step-growth polymerisation.

1.4.1. Synthesis of Polyurethanes by Condensation Polymerisation

In this class of reaction, polymerisation usually takes place at the interface of an aqueous-organic solvent system. As the name implied, these reactions involve the

elimination of small molecules such as water, alcohol or hydrogen chloride at each step of the polymerisation. An important example of this class is the interfacial polycondensation between a bischloroformate and a diamine reported in 1945(6)(Fig.1.1).

Fig.1.1. Condensation Polymerisation between a Bischloroformate and a Diamine.

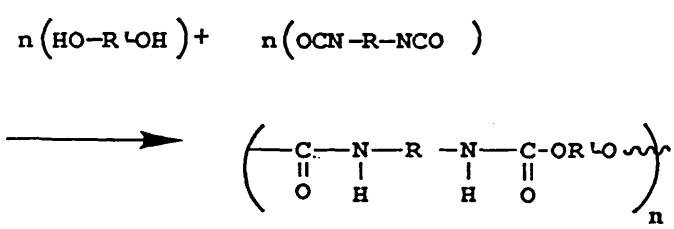


Before the development of this technique, conventional melt polymerisation methods were not suitable for the preparation of some polyurethanes due to the instability of these polymers at the polymerisation temperatures. Despite the successful application of interfacial condensation polymerisation methods to the synthesis of a number of polyurethanes, this route has been less significant commercially compared to the diisocyanate-diol route. The reaction conditions and other requirements for the production of high molecular weight polymers using this route were described by Lyman(7) and Morgan(8).

1.4.2. Synthesis of Polyurethanes by Addition Polymerisation

This is by far the most widely used method for the synthesis of polyurethanes and is the method employed in the present study. The most important reaction of this class is the polyaddition of a diisocyanate with a diol(Fig.1.2). This route has an added advantage over the condensation route, in that it involves mainly a simple addition reaction and proceeds without the formation of any by-products.

Fig.1.2. Addition Polymerisation of a Diisocyanate with a Diol.



The direct addition of diisocyanate to the glycol required elevated temperature in order to keep the reactants molten. This method was thus limited to the synthesis of the thermally stable polyurethanes in the early days. The development of polar aprotic solvents such as dimethyl sulphoxide (DMSO) and N,N'-dimethylformamide (DMF), however, enabled the polyaddition of a variety of diisocyanates and glycols to be carried out successfully in solution(9).

The usual method for the preparation of segmented polyurethanes is called the 'prepolymer route'. In this method, the diisocyanate and the polyol are reacted together to form a prepolymer which is normally a viscous liquid or low melting solid with little mechanical strength. This prepolymer is then further reacted with a diol chain extender to form the final high molecular weight polymer. This method is most suitable for the preparation of polyurethanes with a segmented structure.

Alternatively the polymer can be prepared by mixing all the reactants simultaneously, such system is often called the 'oneshot process'. As may be expected, the segmented polyurethanes obtained from this route will have a more random structure compared to those obtained by the prepolymer route.

1.5. Polyols

These soft segment polymers are hydroxy-terminated polymers with molecular weights usually in the range of 500 to 5000 and glass transition temperatures (T_g's) well below ambient temperature. The two most commonly used polyols for the preparation of segmented polyurethanes are the polyether and the polyester polyols. Both the molecular weight and the type of polyols are the prime factors in determining the elastomeric property of the final polyurethanes.

The polyester polyols are commonly produced by the classical esterification of diols or polyols with dicarboxylic acids according to the desired structure and molecular weight(Fig.1.3). The polyether polyols are usually prepared by the base-catalysed addition polymerisation of the monomeric epoxides(Fig.1.4).

Fig.1.3. Formation of Polyester Glycol by Esterification of a Diol and a Dicarboxylic Acid.

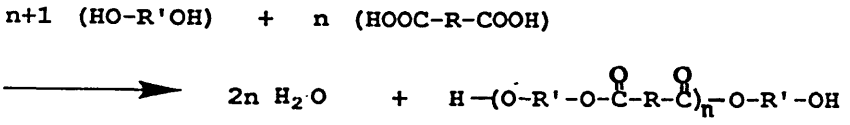
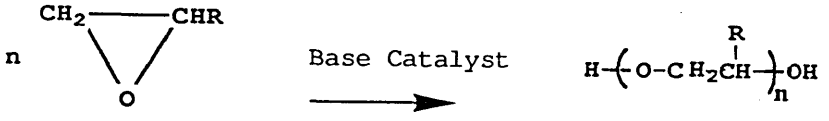


Fig.1.4. Formation of Polyether Glycol by Addition Polymerisation of an Epoxide.



Sometimes when special properties of the final products are required, as in the case of polyester polyurethane foams, several polyesters can be employed. Because of the different ester linkages contained in the polymers, their tendency to crystallise is reduced, which in term imparts good physical properties to the polyurethanes at low temperatures.

In applications requiring good environmental stability, polyurethanes based on polybutadiene or polyisobutylene soft segments may be used. Both hydroxy-terminated polybutadiene and polyisobutylene exhibit good hydrolytic stability and low moisture permeability(10,11). Polyisobutylene, in particular, is superior in this area for it has better oxidative stability compared with polybutadiene as a soft segment material(12). The main difficulty encountered when using these hydrocarbon based macroglycols is the difference in the solubility between the soft segments and the urethane hard segments which imparts difficulty in finding a suitable common solvent. Therefore, synthesis of polyurethanes based on polybutadiene or polyisobutylene is often carried out using bulk polymerisation techniques.

1.6. Diisocyanates

Aromatic diisocyanates are more widely used as compared to aliphatic diisocyanates mainly due to their relatively higher reactivities. Currently about 95% of all polyurethanes manufactured are based on diphenylmethane-4,4'-diisocyanate, (MDI), and toluene diisocyanate, (TDI). Both diisocyanates are harmful if inhaled. TDI in particular is designated as highly toxic and is so volatile that it often causes problems during handling.

Isocyanates can be produced in a variety of ways. In practice, however, only the phosgenation of an amine or its salt is commercially important(Fig.1.5). This reaction was first reported by Hentschel (13) and later extended by Gattermann to aliphatic amine hydrochloride(14). Other methods which have been used with some success in the laboratory include the Curtius, Hoffman and Lossen rearrangements(Fig.1.6).

Fig.1.5. Formation of Isocyanate by Phosgenation of an Amine.

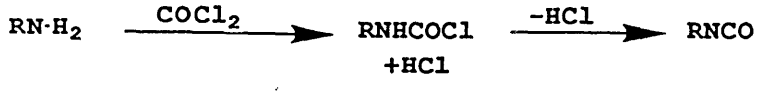
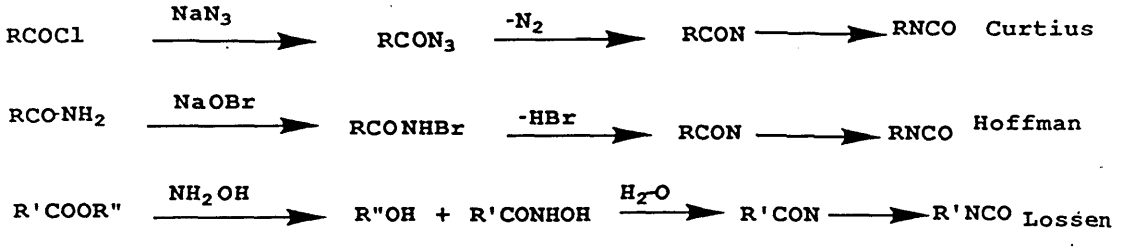


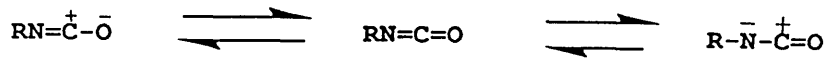
Fig.1.6. The Curtius, Hoffman and Lossen Rearrangements.



1.7. Reactions of Isocyanates

The reactivity of the isocyanate molecule is best assessed by studying the structure and the distribution of the electron density in the -NCO group. The isocyanate molecule can be considered as resonance hybrides with the following canonical forms(Fig.1.7).

Fig.1.7. Resonance Hybrides of the Isocyanate Molecule.

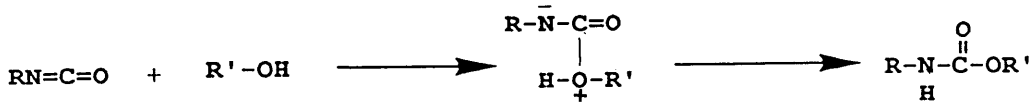


It can be seen that the isocyanate molecule consists of an electron deficient carbon atom with a negative charge delocalised on both the nitrogen and oxygen atoms. Bond rotation energies and dipole moment data suggest that there is no appreciable conjugation between the R and NCO groups at least in alkyl isocyanates and that the nitrogen atom is more negative than the oxygen atom(15).

Therefore, if steric factors are neglected, any electron withdrawing groups attached to the -NCO moiety will increase its reactivity and any electron donating groups will reduce its reactivity towards nucleophilic attack. This also explains the higher reactivity of aromatic isocyanates compared to their aliphatic counterparts. Thus the isocyanate molecule reacts readily with compounds containing active hydrogens.

The reaction between an isocyanate molecule and an alcohol molecule in the absence of any catalyst is mainly a nucleophilic attack of the alcohol on the carbon atom of the isocyanate group followed by a 1,3 shift of the hydrogen atom to the nitrogen(Fig.1.8).

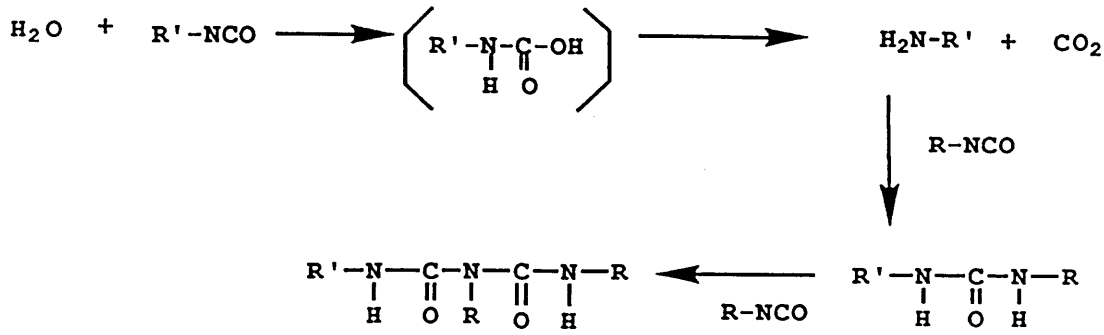
Fig.1.8. Reaction between an Isocyanate and an Alcohol.



There are potential side reactions which may be encountered using the polyaddition route. In order to obtain linear high molecular weight polymers, special precautions must be taken to control or eliminate these undesirable side reactions which include:

(1) The diisocyanate molecule reacts readily with any trace of water present in the system to give an amine, which reacts further with another molecule of diisocyanate to form a urea. If there is an excess of diisocyanate present, this will lead to chemical crosslinking of the polymer through the formation of the biuret linkage(Fig.1.9).

Fig.1.9. Formation of Urea and Biuret.



(2) As in all linear step-growth polymerisations, the balance of reactants is critical in order to achieve high molecular weight polymers. In the polyaddition route for the synthesis of polyurethanes, any excess of diisocyanate present will react with the active hydrogen of the urethane group to form the allophanate linkage(Fig.1.10). This will again cause chemical crosslinking of the polymer.

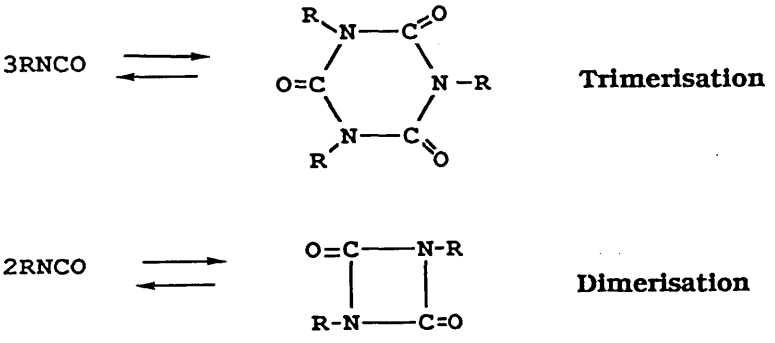
Fig.1.10. Formation of the Allophanate Linkage.



(3) Diisocyanates are capable of undergoing self-addition reactions, especially in the presence of basic catalysts to give uretidinediones (dimers) and isocyanurates (trimers)(Fig.1.11). The formation of dimer

occurs mainly with aromatic diisocyanates. The uretidinediones are not thermally stable and only formed at low temperatures(16). The main use of uretidinediones is to block isocyanates which can be regenerated at elevated temperatures. Most aryl isocyanates will slowly dimerise at room temperature even in the absence of catalysts. This reaction, however, is an equilibrium process and is easily reversed by heat.

Fig.1.11. Oligomerisation of the Isocyanate Groups.



Trimerisation of diisocyanates, on the other hand, appears in either aromatic or aliphatic diisocyanates. A number of basic compounds such as lithium oxide, sodium and potassium alkoxides, tertiary amines and N,N'-dimethylformamide are known to be effective catalysts for this reaction. Trialkylphosphines have been found to catalyse the trimerisation of aliphatic isocyanates as well as the dimerisation of aromatic isocyanates(17).

The isocyanate trimers are extremely stable to heat and not easily reversed. Isocyanurates formed from both MDI and TDI show little degradation at temperatures of about 300°C. The presence of isocyanurates hinders the formation of high molecular weight polymers by upsetting the reactant balance.

Another less common reaction of the isocyanates is their self-condensation reaction to form carbodiimides with the elimination of carbon dioxide(Fig.1.12). Special catalysts such as various types of phospholene oxide are required for this reaction(18). However, in the absence of such catalysts, the reaction only proceeds at high temperatures. Special carbodiimides are used as stabilisers against hydrolysis of polyurethanes.

Fig.1.12. Self-condensation of Isocyanate to give Carbodiimide.

$$RNCO + OCNR \xrightarrow{\text{Catalyst}} R\text{-}N{=}C{=}N\text{-}R + CO_2$$

1.8. Chain Extenders

The most commonly used chain extenders for polyurethane synthesis are the low molecular weight diols such as butane-1,4-diol. Other diols containing functional groups such as 3-chloro-1,2-propane diol or butene-1,4-diol are

used mainly for the modification of the polyurethane structure, such as the preparation of ionomers or potential grafting sites(19,20).

The reactivity of the chain extenders is strongly dependent upon their structures and nucleophilicity. The reactivity of some common active hydrogen compounds usually varies in the following order: amines> alcohols> water> phenols> thiols> ureas>> acids> amides> urethanes. However, other factors such as steric effects, catalyst and reaction medium have to be considered when choosing polymerisation conditions. For a series of alcohols with varying chain lengths and structures, both the steric effects and polarity of the alcohols play an important role in determining their reactivities(21).

Low molecular weight diamines such as ethylene diamine can also be employed for chain extension of isocyanate-terminated prepolymers to give poly(ureaurethanes). Due to their stronger nucleophilic character, the diamine-isocyanate reaction is generally much faster than the diol-isocyanate reaction.

1.9. Catalysts

Although the diisocyanate-diol addition reaction proceeds readily without the use of any catalysts particularly in the case of aromatic diisocyanates, the application of catalysts to these systems are very

popular especially in the manufacture of polyurethane foams. In such systems the catalyst must be selective towards the isocyanate-hydroxyl (polymerisation) and the isocyanate-water (blowing) reactions. Furthermore the choice of catalysts can affect the morphology and ultimate properties of the resulting polyurethanes.

A variety of catalysts such as organic base, metal salts and organometallic compounds as well as their mechanisms have been proposed by different workers (15,22). It is generally believed that the catalysis of urethane reactions involves the formation of complexes between catalysts and reactants. Recently Wongkamolsesh reported that the catalytic activity of amines was associated with the induced polarisation of the hydroxyl group in the urethane formation reaction whereas organotin compounds participated in the polarisation of the isocyanate group during the catalysis (23). Furthermore the activity of the organotin compounds was said to be much greater compared to that of the amines in the catalysis of urethane reactions (24).

1.10. Polyurethane Ionomers

Polyurethane ionomers are a relatively new class of block copolymers usually containing a relatively small number of ionic groups in the polymer backbone or side chains. Ion-containing polymers have received considerable interest in the past decades particularly in

the coating and adhesive industries(25,26). The major reason for the enormous attention paid to these materials lies in the large influence in the physical and mechanical properties which can be obtained by introducing ions(27). In general their mechanical properties are enhanced and the normally hydrophobic character of the polyurethanes could become hydrophilic at high levels of ionic contents. The various aspects of these ionic polymers have been reviewed in a number of recent articles(28-31).

The advance in ion-containing polyurethanes began in the early 1940's, Schlack(32) reported the reaction between diisocyanates and diols containing tertiary amino groups to form basic polyurethanes which dissolved in aqueous acids to form polyurethane polyammonium salts. These polyelectrolytes contained large number of ionic centres and were only soluble in water, but not in organic solvents. They were of no important use in the field of plastics. Dieterich et.al.(25,33) synthesised segmented polyurethane ionomers by reaction of isocyanate-terminated prepolymers with bifunctional anionic chain extenders such as dihydroxy- and diamino-carboxylic acids in the form of sodium or potassium salt. The polyurethane urea ionomers obtained had high tensile strength and were resistant to solvents.

Most of the recent developments in these novel polyurethane ionomers were carried out by Cooper et.al.(34-37). Different ionic groups were introduced into the hard segments of polyurethane block copolymers using various routes. The improved mechanical properties observed in all cases were attributed to the changes in morphology and microstructure upon ionisation. Introducing ionic species was thought to increase the polarity difference between the hard and soft segments and to improve the hard segment domain cohesion through coulombic interaction of the ionic groups. Both these effects may have contributed to the increase in the degree of phase separation and to the improvement in the ability of hard segment domains to act as physical crosslinks and/or fillers which resulted in the increase in tensile strength and elasticity of these predominantly linear polymers.

1.11. Synthetic Pathways to Polyurethane Ionomers

The recent upsurge of interest in polyurethane ionomers has seen a corresponding activity in the preparation of these novel polymers, especially within the Polymer Group at Imperial College. Since their first appearance few decades ago, the synthesis of polyurethane ionomers have been reported by many workers using a number of methods(32-37). While most of these techniques have been applied successfully, many of them have drawbacks or

limited applications. Therefore there is a strong need for the development of new synthetic routes to polyurethane ionomers.

Generally, ionic groups can be incorporated into polyurethanes in two ways: (1) Straight ionisation of polyurethanes carrying reactive functional groups. (2) Introduction of ionic centres into the corresponding monomers prior to polymerisation. Direct introduction of ions into the polymers, however, are usually not quantitative due to various steric reasons. In addition, factors such as the difference in solubility between the various substrates can sometimes limit the method of ion incorporation. In many cases ionisation is best effected before polymerisation. This section describes most of the recognised synthetic methods employed by various workers, including some of the new methods recently developed in this laboratory.

1.11.1. Polyurethane Ionomers via Quaternisation of Chain Extenders containing Tertiary Nitrogen Atoms

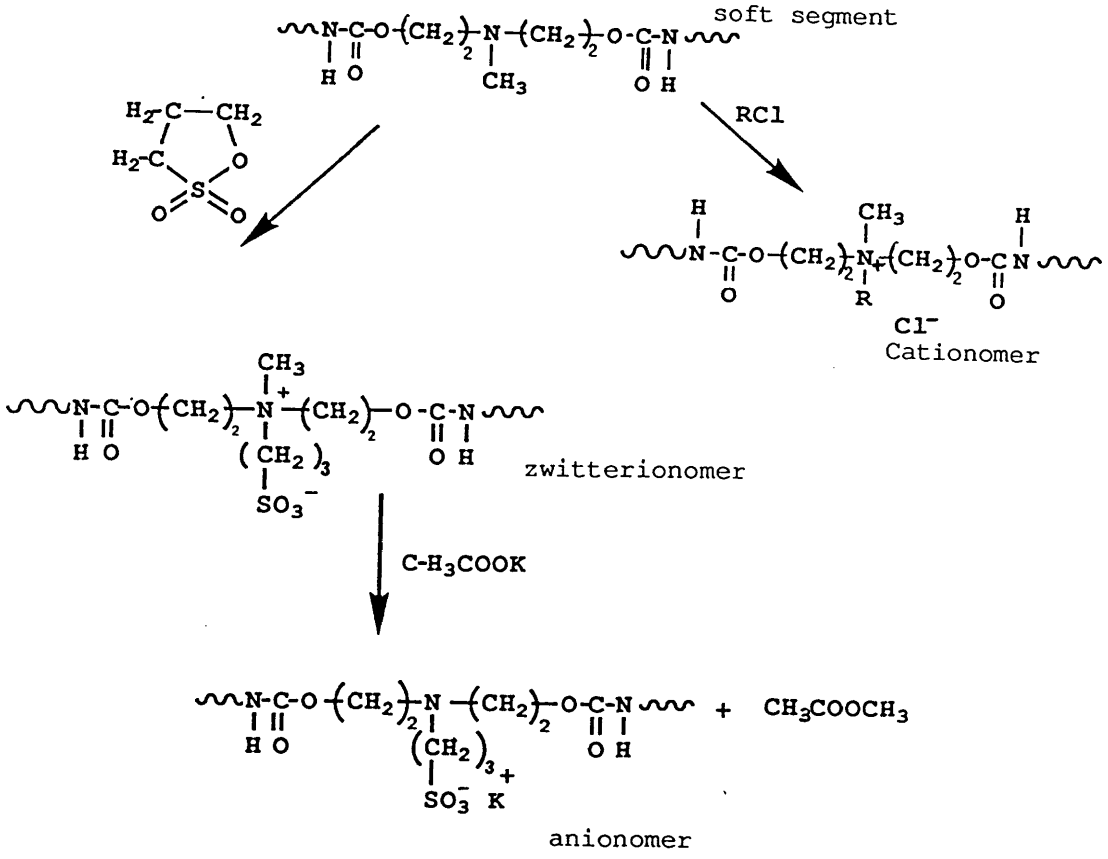
This is probably the oldest and most commonly used method for the preparation of polyurethane ionomers. It involves essentially the use of a tertiary amine-containing hard segment chain extender. Ionisation of the resulting polyurethane is accomplished by either reacting the polymer with various quaternisation agents

or dissolving in aqueous acids. This method was first used by Schlack for the preparation of ionic polyurethanes containing large number of ionic groups, called polyelectrolytes(32). For polyurethanes possessing polyether or polyester soft segments as well as the tertiary amine containing short-chain diols, quaternisation with alkyl halides yielded polyurethanes containing relatively few number of cationic groups in the chains, termed cationomers(38). When chain extenders containing secondary amine groups were reacted with sultones or lactones in the presence of bases, anionomers which had anionic groups in the chains with positively charged counterions were produced(39). If bifunctional quaternisation agents such as 1,4-bis(chloromethyl) benzene were used, chemical crosslinking of the chains resulted and three dimensional networks similar to those which exist in vulcanised rubbers were formed(40).

Cooper et.al. recently reported the use of tertiary amine hard segment chain extenders such as N-methyl diethanolamine(MDEA) for the preparation of polyurethane ionomers(34-37). The common two-step solution polymerisation route was employed for these segmented polyurethanes containing tertiary nitrogen groups. Ionisation was effected via quaternisation of the tertiary amines with alkyl halides to give cationomers. When the MDEA chain extended polyurethanes were reacted with γ-propane sultone, polyurethanes containing

quaternary ammonium ions closely linked to sulphonyl anions, called zwitterionomers, were produced. Reaction of the zwitterionomers with the appropriate metal acetate resulted in the formation of polyurethane anionomers. The general reaction scheme for the formation of these ionomers are shown in Fig.1.13.

Fig.1.13. Formation of Cationomer, Zwitterionomer and Anionomer.



While the preparation of ionomers via quaternisation of tertiary amine-containing chain extenders has been widely adopted, one drawback of this method is that the chain extender must contain a tertiary nitrogen atom, which may limit this method.

1.11.2. Polyurethane Ionomers using Bifunctional Ionic Chain Extenders

The use of bifunctional chain extenders for the synthesis of polyurethane ionomers has been known for a long time(33). This method is generally considered to be more effective than the tertiary amine route. The advantage of using this method is that the choice of monomers is much wider and the ionic content of the resultant polyurethanes can be controlled more readily. Therefore ionomers prepared by this route usually have better defined structures.

The requirement for this method is that the hard segment chain extender must carry some labile or reactive functional groups such as alkyl halides and epoxides, etc. Reactions of such bifunctional chain extenders with the appropriate reagents give the required ionic monomers. When alkyl halide-containing diols such as 3-chloro-propane-1,2-diol are used, ion incorporation can be achieved by nucleophilic substitution reaction with various nucleophiles(41,42)(Fig.1.14). For monofunctional alcohols possessing epoxide groups such as

2-epoxypropanol, reaction with the appropriate nucleophilic agents results in the ring opening reaction to give an ionic diol(Fig.1.15). Thus the epoxy ring opening reaction provides another convenient route for the preparation of difunctional ionic monomers for use in polyurethane ionomer synthesis.

Fig.1.14. Formation of Potassium-S-dihydroxypropyl Thiosulphate from 3-chloro-propane-1,2-diol.

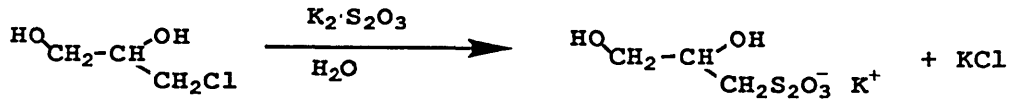
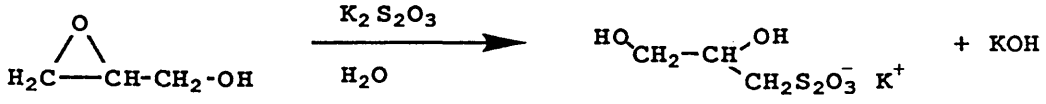


Fig.1.15. Formation of Potassium-S-dihydroxypropyl Thiosulphate from 2-epoxypropanol.

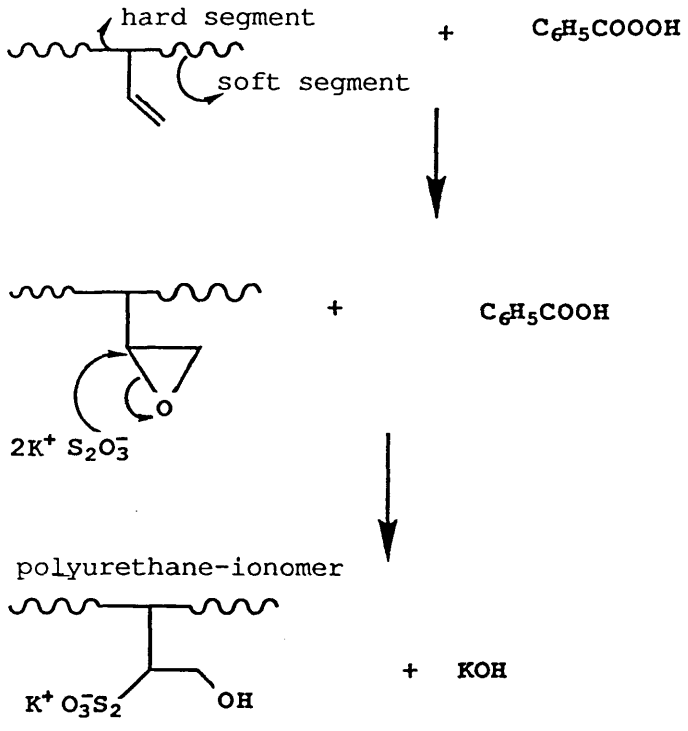


1.11.3. Epoxidation of Unsaturated Monomers and Polyurethanes

Although epoxidation of unsaturated diols such as cis-1,4-butene diol has been described in the past(43), its application in the synthesis of polyurethane ionomers is only recently developed in this Department(44,45). The epoxy ring is considered to be unstable due to its highly strained structure and can easily be opened by nucleophilic reagents such as thiosulphate and sulphite ions. It is commonly generated by the reaction of a carbon-carbon double bond with peroxybenzoic or peracetic acids.

Epoxidated polyurethanes can be prepared by epoxidation of the monomers or directly from the unsaturated polymers. In general, epoxidation of the monomers is much easier than that of the corresponding polymers. Butler reported that cis-1,4-butene diol reacted smoothly with m-chloroperoxybenzoic acid, but when it was incorporated into a segmented polyurethane hard block, this monomer was rendered unreactive towards oxidising agents(19). The reasons for the low reactivity of the double bond in the polymer may be due to the electron withdrawing effect of the neighbouring urethane linkages and possibly steric forces operating in the polymer. Nevertheless, these detrimental effects could be reduced by using polyurethanes having double bonds in the side chains instead(Fig.1.16).

Fig. 1.16. Formation of Polyurethane Ionomer by Epoxidation of Unsaturated Polyurethane.



Although epoxidation of unsaturated monomers can readily be achieved, the conditions employed for the polymerisation step could cause the opening of the unstable epoxy ring to produce trifunctional species, and thus lead to crosslinking of the polymer.

1.11.4. Other Routes to Polyurethane Ionomers

Apart from the three major routes described above, other methods for preparing polyurethane ionomers have also been proposed(46,47).

The reaction of N-chlorosulphonyl isocyanate (CSI) with unsaturated compounds is well known and has been applied to polyisoprene(48). Thus by treating the ester of cis-2-butene-1,4-diol with CSI to form the β-lactam derivatives followed by hydrolysis with tetra-n-butylammonium hydroxide, Egboh obtained ionic derivatives of the cis-2-butene-1,4-diol for use in polyurethane ionomers synthesis(46). This reaction, however, did not convert the unsaturated polyurethanes directly to ionomers due to the more favoured reaction of CSI with the labile hydrogen on the urethane linkage.

Another pathway to ion incorporation depends on a bimolecular nucleophilic reaction involving the urethane hydrogen(47). Using this method, polyurethane anionomers similar to those obtained in the tertiary amine route can be obtained by reaction of the nitrogen atom in the urethane linkage with sodium hydride and subsequent reaction with γ-propane sultone.

CHAPTER TWO STRUCTURE AND PROPERTIES OF SEGMENTED POLYURETHANES AND IONOMERS

2.1. Structure of Segmented Polyurethanes

Segmented polyurethanes are known to possess two-phase microstructures in which the discrete hard segment domains serve as thermally reversible crosslinks and/or filler particles for the soft segment matrix. The soft segments are responsible for the elastomeric character of the polymer, while the hard segments provide dimensional stability. Consequently, segmented polyurethanes exhibit elastomeric properties similar to crosslinked rubber but retaining the characteristics of thermoplastics.

The existence of a two-phase microstructure in polyurethanes was first indicated by Cooper and Tobolsky(49) from the anomalous mechanical properties exhibited by these copolymers. Since then, there has been a large volume of literatures regarding the characterisation of this heterogeneous microstructure (50-54). The general conclusion of these studies has been that microphase separation in these block copolymers is not complete and that phase inversion may also take place depending on the relative composition and experimental conditions. The extent of phase separation and domain morphology is believed to be the principal features controlling the unique and useful properties of segmented polyurethanes.

2.2. Factors Affecting the Degree of Phase Separation

The main driving forces for phase separation in segmented polyurethanes are the incompatibility of the two segments and the ability of the urethane groups to form interurethane hydrogen bonds. A number of factors which influence the extent of phase separation include copolymer composition, segment length and polarity, crystallisability of either segments, potential for soft segment-hard segment H-bonding, sample history, sample preparation method, etc. Obviously, the overall composition and segment length are determined by the method of synthesis whereas the chemical nature of the reagents used in the polyurethane synthesis are responsible for the segment polarity, crystallisability of either segments and degree of H-bonding between the two segments.

2.2.1. Effect of different Types of Polyol and Chain Extender

The type of polyol soft segment used can have a profound influence on the degree of phase separation of segmented polyurethanes. For instance, polar soft segments is expected to form strong interactions such as H-bonding with the hard segments and cause partial phase mixing.

Chang and Wikes(55) studied the morphology of several segmented polyurethanes using polypropylene glycol(PPG)

and polyethylene glycol(PEG) soft segments and found that PPG-based polymers had higher degree of phase separation compared to PEG-based polymers. This was attributed to the extra methyl group present in the PPG-based polymers which possessed a lower dipole moment and weaker dispersion forces and thus lower tendency towards hydrogen bonding with the urethane hard segments than the PEG-based polymers.

In the study of a series of polyether polyurethanes based on various polyols having different ether contents, Hwang et al(56) showed that polyether polyurethanes based on polyol with higher ether content were more compatible with the urethane hard segment, and generally resulted in poorer phase separation.

The difference between polyether glycol, polyester glycol and some hydrocarbon-based glycols is mainly associated with the varying degree of H-bonding present between the two segments and these will be discussed in Section 2.3.1.

Sung et al(57) investigated the effect of urea linkage on the phase separation of polyurethanes based on TDI and PTMG with ethylene diamine and butanediol chain extenders. These authors found that phase separation improved significantly for polymers based on ethylene diamine instead of butanediol. This was attributed to the increased number of H-bonds associated with the hard blocks.

2.2.2. Effect of Molecular Weight of Polyol and Diol

Another important structual variable which affects the degree of phase separation is the molecular weight of the polyol soft segment and diol chain extender. Sung et al(58) examined two polyether polyurethaneureas of different molecular weights and found that the hard segment domains in the lower molecular weight polymer were more interconnected than those in the higher molecular weight sample and that the soft segment of the low molecular weight polymer contained more solublised hard segment domains.

The effect of chain extender length on the structure of the hard segments has been investigated by Blackwell et al(59) using X-ray diffraction and conformational analysis. The results showed that for butanediol and longer diol chain extenders, the even diol polymers adopted the lowest energy fully extended conformations which allowed for H-bonding perpendicular to the chain axis. Such H-bonding network would not be possible with odd diol polymers in the extended conformation, and these adopted higher energy contracted conformations. Thus, polymers prepared from butanediol and higher even diols should exhibit better overall properties as the hard segments of these polymers can crystallise more easily in the lowest energy extended conformation, and hence larger driving force for phase separation. These results suggest that the strength of the H-bonds (physical crosslinking)

does not only depend on the concentration of urethane groups, but also on the steric conditions which either favour or hinder the intermolecular interactions.

2.2.3. Effect of Segment Concentration

One of the primary structual variables which directly affects the two-phase structure of segmented polyurethanes is the concentration of the segments. Leung et al(60) showed that increasing the hard segment content caused more hard segments to mix into the soft-phase. For a series of polyurethanes having constant soft segment molecular weight, increasing the hard segment content from low to high levels resulted in the polymer structure changed from one having a continuous soft segment matrix with dispersed hard segments to one having a continuous hard segment matrix with the dispersed soft segments in it.

The effect of hard segment content on the morphology of polybutadiene-based polyurethanes has been investigated by Macknight et al(61). The results showed that phase separation occurred in most samples with hard segment concentrations up to 75%. However, for samples with less than 33% hard segment content, incomplete phase separation was observed. Furthermore, phase inversion was observed at approximately 60% hard segment concentrations.

2.2.4. Effect of Isocyanate Type

Bogart et al showed that segmented polyurethanes based on the aliphatic counterpart of MDI, H_{12}MDI, generally exhibited less hard segment ordering or crystallinity (62). This lack of ordering was attributed to the fact that H_{12} MDI is produced as a mixture of 3 isomers. Substitution of the aliphatic H_{12}MDI for the aromatic MDI gave phase separated polyurethanes with greater interfacial area, presumably due to the greater compatibility of the two segments.

The effect of symmetry of the isocyanate on the degree of phase separation has been investigated by Sung et al (63). By studying the thermal behaviour of polyurethanes based on 2,4- and 2,6-toluene diisocyanate. These authors concluded that a greater degree of phase separation, with well-ordered domain structure, occurred in the polyurethanes based on the symmetrical 2,6-TDI.

2.2.5. Effect of Sample History

In addition to the structual variables, the degree of phase separation also shows a strong dependence on the thermal history of the polymer. Wilkes et al(64,65) studied the time-temperature dependence on the thermal and mechanical properties of segmented polyurethanes using DSC. The soft segment T_g was shown to be greatly affected by heat treatment. Immediately after annealing at 170°C for 5 minutes, the soft segment T_g was found to

be about 40°C higher than its original value which slowly decreased to its original value with time depending on the cooling rate. In some quenched samples, the phase separation only developed over a period of days. These findings indicated that phase separation is favoured at low temperature where enthalpic factors dominate the entropic factors.

The effect of prolong annealing from room temperature to around 120°C has been investigated by Cooper et al(66). Their results revealed that annealing generally gave rise to an endothermic peak at a temperature 20-50°C above that of the annealing temperature. This endotherm was assigned to the disruption of the ordered segments resulted from the reorganisation of lesser segment orders into more perfect arrangements upon annealing.

2.2.6. Effect of Chemical Crosslinking

The presence of any multifunctional impurities in the monomers or excess of diisocyanate can lead to small amount of chemical crosslinking in the final polymer. Chemical crosslinking can have a deleterious effect on the phase separation as well as the strength of segmented polyurethanes(67), which is contray to results observed in hydrocarbon elastomers where increased crosslinking usually results in improved mechanical properties, especially modulus. Chemical crosslinking in polyurethanes causes a spatial separation of chains which

reduces the chance of H-bonding. This adverse effect prevents the formation of domain structure and is believed to be the cause of poor mechanical properties.

2.2.7 Effect of Sample Preparation Method

It has been demonstrated that structual inhomogeneity could arise from component incompatibility or phase change during polymerisation in bulk, especially for hydrocarbon soft segment-containing polyurethanes owing to the extremely poor compatibility between their components(68).

The composition of the two-phase structure of segmented polyurethanes can also be influenced by the sequence of reactants mixing during the preparation. Polyurethanes prepared by the 'one-shot' process generally have a more dispersed hard segment arrangement than the 'prepolymer route'. Abouzahr et al(69) found that polyester based polyurethanes prepared by the 'one-shot' process had higher soft segment transition temperatures than those obtained by the 'two-step' process. This was attributed to the presence of a larger proportion of hard segments within the soft phase resulting in a higher T_g in the polyester based polyurethanes. This effect however was not observed for polymers based on polyethers presumably due to the less tendency of the polyethers toward hard-soft segment H-bonding.

2.3. Characterisation of Segmented Polyurethane Structures

Of the many analytical methods available, infrared and nuclear magnetic resonance spectroscopy seem to be the two techniques most commonly applied to elucidate the structure of polyurethane block copolymers. NMR is particularly useful since it will give information on the configuration of the polymer skeleton as well as on the presence of functional groups. The only limitation of this technique is that it will only detect a small range of functional groups.

In addition to obtaining structual information, ^{1}H NMR spectroscopy is a very useful method for detecting the presence of side reactions such as the formation of allophanate or biuret linkages which causes chemical crosslinking. Such crosslink sites can easily be identified since the N-H proton in different groups experience different chemical shifts in the NMR spectrum.

The NMR signal of the N-H group is generally very broad and often cannot be observed. This is due to the relaxation effect of the quadrupole of the ^{14}N atom. However, this problem can be solved by the right choice of solvents. It has been shown that when the NMR spectrum was obtained in relatively non-polar solvents such as chloroform or carbon tetrachloride, a model compound with allophanate or biuret linkage showed the resonance signal

of the N-H proton, whereas the one with urethane or urea linkage afforded no such signals(70). However, all compounds with those linkages showed very sharp signals when the measurement was carried out in polar solvents such as dimethyl sulphoxide or dimethyl acetamide, etc. This was probably due to the increased N-H distance caused by the solvation of the molecule and, consequently, to the weakened influence of the nitrogen quadrupole.

NMR spectroscopy is also very valuable for studying the different stages of reactions. Matthews and coworkers(71) used ^{1}H and ^{13}C NMR techniques to follow the initial end-capping and subsequent chain extension reactions in the synthesis of segmented polyurethanes. A number of weak signals were detected in the spectra and were identified as crosslink products resulting from side reactions. These were confirmed by chemical analysis which showed a deficiency of the isocyanate content even in the prepolymer formation stage.

2.3.1. Hydrogen Bonding in Polyurethanes

One of the characteristic feature of the urethane linkage is its ability to form hydrogen bonding which is important in determining the domain structure and the degree of phase separation. This normally occurs between the N-H and C=O group or the adjacent oxygen atom in the urethane linkage. However, if polyester or polyether is

part of the polymer, H-bonding between the N-H group of the hard segment and the ether oxygen or oxygen in the ester group of the soft segment is also possible which results in partial phase mixing(72). The incomplete phase separation has been demonstrated by soft-segment T_g analysis, infrared studies and x-ray scattering measurements, etc(60,73).

It has been shown that polyurethanes with polyester soft segments exhibited lower degree of phase separation than those with polyether soft segments(74-76). This was due to the more polar polyester soft segments which had higher affinity towards H-bonding with the urethane hard segment.

It is thus expected that polyurethanes having hydrophobic hydrocarbon soft segments should give very good phase separation due to the lack of potential for hard segment-soft segment hydrogen bonding and the extreme polarity difference between the urethane and hydrocarbon segments. Macknight and Cooper (11,77) has reported the use of hydroxy-terminated polybutadiene and polyisobutylene as soft segments and found that these materials had a higher degree of phase separation when compared with polyether or polyester polyurethanes. Similar characteristics have also been noted in polydimethylsiloxane-based polyurethanes(78).

Hydrogen bonding in polyurethanes has been the subject of numerous investigations mainly using infrared spectroscopy. Coleman et. al(79) studied a linear semicrystalline aliphatic polyurethane using Fourier Transform Infrared spectroscopy and found that H-bonding caused a shift in the N-H and C=O stretching frequencies to lower values compared with those observed when these groups are not H-bonded. Both the frequency shifts and intensity changes were characteristic of the type or magnitude of the hydrogen bonds formed and could be related to the degree of phase separation in the polyurethanes(80).

The extent and distribution of H-bonding in polyether polyurethanes have been investigated by Srichatrapimuk and Cooper(75). Their results indicated that at room temperature, about 80% of the N-H groups formed H-bonds while only 65% of the carbonyl groups participated in H-bond formation with the N-H groups. The rest of the N-H group took part in H-bonding with the ether oxygen. These authors also found that the hard-soft segment H-bond was weaker than the interurethane H-bond and dissociated first when the polymers were heated from room temperature. The interurethane hydrogen bonds were responsible for most of the high temperature H-bond dissociation. Nevertheless, a measurable amount of hydrogen bonding was found to remain at temperatures as high as 200°C.

2.3.2. Morphology of Segmented Polyurethanes

The existence of discrete hard-segment domains embedded in the matrix of soft-segments in segmented polyurethanes due to thermodynamic incompatability of the two segments is now widely recognised. Of the many methods used for studying the morphology of these segmented block copolymers, the most direct visual assessment of the microdomain structure is by electron microscopy.

The general understanding of the morphology of amorphous block copolymers is based on the concept developed for the polystyrene/polybutadiene block copolymer system(81,82). The characterisation of segmented polyurethanes, however, present additional complexicity due to the variable length of the two segments as well as possible hard-segment and/or soft-segment crystallinity.

Koutsky et al(83) studied the transmission electron microscopy of solvent etched and iodine stained polyether and polyester/MDI/ butanediol based polyurethanes. Their results showed that the hard segment domains were in the form of grains of 30-100 °A diameter. The domain structure found in these studies was consistent with results of other authors based on results of mechanical properties and X-ray measurements(84,85).

In another electron microscopy investigation of polyether/MDI/butanediol based polyurethane systems,

Schneider et al(86) showed that the hard segment domains had a fibrillar, spherulitic structure. The spherulitic domains exhibited a sub-structure of urethane rich aggregated fibrils of lateral dimensions about 300-600 °A in size, possessing little pronounced orientation interspersed by material of lower electron density, presumed to be the soft phase.

Thomas et al(87) examined a series of polyether polyurethanes using samples prepared from solvent casting using N,N'-dimethylformamide. These authors found that the hard segment phase composed of paracrystalline fibrils of lateral dimensions equal to the length of the hard segment. Furthermore, these fibrils aggregated into microdomains which were seen to associate into spherulitic structures. The morphological picture of these systems was in agreement with Schneider's model. Subsequent works on conventional transmission electron microscopy using cryo-ultramicrotome as the sample preparation technique further confirmed the micro-heterogeneous nature of segmented polyurethanes(88,89).

Another important technique for the characterisation of the microdomain structure in segmented polyurethanes is by X-ray scattering and diffraction measurements. This method was first applied by Bonart et al(90,91) using segmented polyurethanes. Bonart proposed hard-segment packing models in which the hard-segment units are

ordered laterally in order to maximise interurethane H-bonding. In such models, the hard-segment sequences were assumed to exist in rigid, extended configurations with lamellar or sheetlike microdomains.

Other models for the microdomain structure of segmented polyurethanes using small angle X-ray scattering techniques have also been proposed. For example, Koberstein and Stein(92) suggested the hard segment chains were present in either coil or folded configurations with the domain thickness corresponding to 2-4 hard-segment units.

2.4. Thermal Analysis of Segmented Polyurethanes

Differential Scanning Calorimetry (DSC) is one of the thermal analysis methods commonly used for the characterisation of polymers. This method essentially measures the heat flow within the polymer during a thermal scan or under isothermal conditions.

DSC is a very attractive technique for characterising the two phase structure of segmented polyurethanes. Since the two segments in these block copolymers have their individual glass transition temperatures in their pure states, the presence of hard segment domains in the soft segment will undoubtedly affect the T_g of the soft segment. Inclusion of hard segments into the soft-phase will raise the T_g of the soft-phase while inclusion of

soft-segments into the hard-phase will decrease the hard segment T_g(93). Usually, only the soft segment T_g can be observed by DSC because the change in heat capacity of amorphous hard segments at the glass transition is too small to be seen.

Therefore the purity of the soft segment, or the degree of phase separation can be assessed by measuring the temperature difference between T_g of the soft segment in the polyurethanes and T_g of the neat soft segment. Quantitative results for the extent of phase separation have been obtained by the enthalpy jump method(94,95). The idea of this method is that the heat capacity change (ΔC_p) at T_g is proportional to the mass of the polymer chains taking part in the transition. Soft segments dissolved in the hard phase are not expected to contribute to ΔC_p, since their mobility is restricted. Thus, the degree of phase mixing can be represented by the ratio

$$\Delta C_p(T_g)/\Delta C_p0(T_g)$$

where ΔC_p is the heat capacity change in the segmented polymer.

ΔC_p0 is the heat capacity change in the pure soft segment.

Lagasse (96) first observed individual glass transition temperatures of the soft and hard segments in polyurethanes containing polybutadiene soft segments.

This was later confirmed by Schneider and MacKnight(4,5) who found that the T_g of soft segment in these polyurethanes was independent of the hard segment content and was very close to that of the original hydroxy-terminated polybutadiene. Furthermore, the T_g's of these polymers were shown to be not sensitive to the thermal history of the polymers(77). All these results suggested that phase separation in polybutadiene-containing polyurethanes was almost complete.

One of the problem associated with the use of hydrocarbon soft segments is the difficulty in finding the right solvent for their preparation due to the extreme polarity difference between the components. This is probably why most of their synthesis were carried out in bulk(77,97). This incompatibility effect has been investigated by MacKnight et al(68,98) using three polybutadiene / toluene diisocyanate / butanediol based systems. In all cases, two hard-segment T_g's were observed which were attributed to the compositional non-uniformity as a result of the poor compatibility between the components of the system.

A peculiar thermal behaviour of some polyurethanes is associated with the melting peak of MDI/BD hard segment. In the DSC thermogram, multiple melting peaks are usually observed. The temperature and enthalpies associated with these endotherms have been shown to be dependent on the

thermal history of the sample(99,100). The endotherm at 120-190°C has been attributed to disruption of long-range order of the hard segment domains and that above 200°C has been typically assigned to melting of the microcrystalline regions of the hard domains(100,101).

2.5. Mechanical Properties of Segmented Polyurethanes

Segmented polyurethanes display a very high level of mechanical properties at room temperature, e.g., tensile strength and ultimate elongation are similar to values for conventional crosslinked rubber(102). It is generally accepted that the favourable mechanical strength and elastomeric properties of these segmented block copolymers are directly attributed to the nature of the hard segment domains which act as crosslink points in the network(103,104). Since the structure of such domains is governed by the degree of phase separation, any factors influencing the degree of phase separation may also affect the mechanical properties of these block polymers. In order to achieve optimum mechanical properties, it is desirable to have a highest possible degree of phase separation.

In contrast, phase mixing exerts an adverse effect on the mechanical properties of segmented polyurethanes. For every segment which is dissloved in an 'unlike' phase, there will be a corresponding reduction of two of the total number of physical crosslinks connecting the hard

and soft segment domains. The reduction in the number of physical crosslink points leads to a decline in the mechanical properties.

The mechanical properties of segmented polyurethanes can be optimised by carefully choosing the type of soft and hard segments, molecular weight of the two segments, method of synthesis, stoichiometric ratio between them and sample processing history, etc.

One of the fundamental factors which determines the mechanical properties of segmented polyurethanes is the hard segment concentration. Wang et al(105) studied a series of segmented polyether polyurethaneureas and showed that increasing the hard segment content or hard segment block length led to a higher modulus and lower ultimate elongation. This was attributed to the higher volume fractions and greater microcrystalline order in the hard segment domains which improved the domain cohesion and enhanced the filler effect.

Another structual variable which affects the mechanical properties is associated with the molecular weight of the soft segment. Speckhard et al(106) studied the properties of polyisobutylene-based polyurethanes and found that increasing the length of the soft segment led to poorer mechanical properties of the polymers. This was due to the larger domain sizes in the higher molecular weight

soft segment as indicated by small angle X-ray scattering measurements.

Ono et al showed that increasing the soft segment molecular weight of polyurethanes based on hydroxy-terminated polybutadiene decreased the tensile strength, modulus, tear resistance and hardness of the resulting polymers(107). This was interpreted in terms of the increase in urethane linkage with decreasing soft segment molecular weight, followed by an increase in intermolecular H-bonding sites which led to the growth of physical crosslinks.

Despite the general belief that increasing degree of phase separation leads to improvement in mechanical properties, polyurethanes based on hydrocarbons such as polybutadiene and polyisobutylene which are known to have a highly phase separated structure possess mechanical properties inferior to those of polyether or polyester polyurethanes. The main reason for the low mechanical properties of hydrocarbon-based polyurethanes is associated with the difficulties in synthesis due to the incompatibility of the non polar soft segment and the polar diol chain extender resulting in compositional heterogeneity and lower mechanical properties(108). Another possible reason for the poor mechanical properties in the hydrocarbon-based polymers is the absence of strain-induced crystallisation which often occurs in the soft segments of polyether polyurethanes.

Studies on polyisobutylene-based polyurethanes showed that increasing the hard segment content did not have any significant effect on the degree of phase separation of these highly phase separated polymers, but resulted in higher modulus and lower ultimate elongation as indicated by stress-strain data(11). Increasing hard segment concentration also resulted in a transition from rubber like behaviour to plastic yielding. This behaviour was attributed to a change from isolated to interconnected domain morphology.

2.6. Environmental Properties of Segmented Polyurethanes

Polyurethane block copolymers have found wide spread applications in a number of areas, for these polymers can be tailor-made to suit individual requirements by varying their chemical compositions. Therefore it is important to have some knowledge regarding the environmental stability of these materials.

Generally, polyurethanes based on polyether or polyester exhibit poorer hydrolytic stability and moisture permeability than polyurethanes based on hydrocarbon soft segments, such as hydroxy-terminated polybutadienes and polyisobutylenes(10,11). As expected, the ester group in polyester polyurethane is especially prone to hydrolysis.

In terms of oxidative stability, polyisobutylene is advantage compared with polybutadiene as soft segment. The poor oxidative stability of polybutadiene is due to the presence of unsaturation in the polymer and to the fact that the butadiene units in the chain may exist both in the cis- and trans- forms. The former problem can be eliminated by hydrogenation(5). Polyurethanes based on aromatic diisocyanate are known to suffer from UV induced degradation which cause reduction of molecular weight and tensile properties as well as yellowing, all of which can limit their applications. The photodegradation mechanism has been studied by Beachell and Chang(109) using electron spin resonance spectroscopy with urethane model systems. The degradation process has been attributed to the photo-decomposition of the α-hydrogen on the carbon next to the urethane nitrogen to give a conjugated azo-type of structure.

Nevertheless, this inherent weakness can be prevented by using an aliphatic diisocyanate such as 4,4'-dicyclohexylmethane diisocyanate, H_{12} MDI, which does not have the potential for conjugated structures. Consequently, polyurethanes based on aliphatic diisocyanates usually have improved light stability(110). Therefore a polyurethane copolymer based on polyisobutylene soft segment and H_{12} MDI would be excellent in terms of environmental stability.

2.7. Physical and Mechanical Properties of Polyurethane Ionomers

Polyurethane ionomers, obtained by introducing a relatively small amount of ionic groups into the hard segments of polyurethane copolymers, generally possess enhanced physical and mechanical properties. Effects such as increase in modulus, higher hard segment T_g and increase in melt and solution viscosity are known. When ions are incorporated, the segmental mobility of the polymer chain is reduced because of long range electrostatic forces between ions. Ionic groups also act as bulky side groups restricting the mobility of the polymer chain segments, or serve as interchain crosslink. In addition, the incorporation of ions increases the polarity difference between the soft and hard segments, thus increasing the driving force for phase separation. Ionisation also improves the hard segment domain cohesion through coulombic interactions of the ionic groups. The improved phase separation and domain cohesion are believed to be responsible for the improvement in mechanical properties. In contrast to the large volume of studies on the structure and properties of conventional non-ionic polyurethanes, there appeared to be only limited data available regarding the physical and mechanical properties of polyurethane ionomers(111-114).

One interesting property of many polyurethane ionomers not found in conventional polyurethane copolymers is their ability to disperse or sometimes dissolve in water(25). This specific behaviour is directly attributed to the presence of ionic groups which can be solvated by polar solvents such as water. Non-polar solvents are expected to solvate only the hydrophobic soft-segment leaving the ionic centre associated whereas solvents with high polarity such as water tend to solvate the ionic groups. In a mixed solvent system, e.g., acetone/water, increasing the water content will cause a gradual break up of ionic associations and at the same time an increase in association of the soft segments. Therefore, depending on the chemical structure, polyurethane ionomers can have the ability to swell, disperse or even dissolve in mixed solvent systems due to the variety of polymer-solvent interactions possible.

The morphology and mechanical properties of polyurethane ionomers are in general dependent on similar factors which govern the properties of conventional polyurethane copolymers. In polyurethane ionomers, however, ionic interactions are an additional factor which has to be taken into consideration. Most of the studies regarding the structure and properties of these ionic polyurethanes were done only in the past decade, and mainly concerned with the effect of ionisation on the

morphology and physical and mechanical properties of polyurethanes having various chemical compositions.

Hwang et al(114) studied the effect of hard segment content and the degree of ionisation on the extent of phase separation and properties of several series of polyether polyurethane zwitterionomers. These authors found that increasing the hard segment content in the non-ionic polyurethanes increased the tendency for phase mixing. On the other hand, ionisation greatly increased the degree of phase separation as shown by a lower and sharper T_g and a higher rubbery modulus in the ionomer samples. Ionisation was also shown to raise the hard segment softening point due to increased domain cohesion caused by the interaction of ionic forces between hard segments. In addition, there was a dramatic change in the tensile properties with increasing ionic content, varying from soft and rubbery to hard and strong thermoplastic elastomers.

In another investigation, Miller et al(113) reported the effect of ionisation on the properties of two polyether polyurethanes with different molecular weight soft segments. The results showed that for the polyurethane with shorter soft segments, ionisation increased the degree of phase separation whereas the degree of phase separation of the longer soft segment polyurethane was not affected upon ionisation. This was due to the presence of crystallinity in the longer soft

segment polymer which imposed such a large driving force for phase separation that no further increase in phase purity occurred. Increasing the degree of ionisation also improved the strength of the polyurethane with shorter segments while decreasing the ultimate elongation due to hard domain cohesion which reduced the ability to deform. However, no improvement in strength was observed for the longer soft segment polyurethane except that such polymer exhibited longer ultimate elongation.

The effect of ionisation on polyurethanes containing different types of soft segments has been investigated by Yang et al(34). Two series of polyurethane zwitterionomers having different ionisation levels based on poly(tetramethylene oxide) and hydroxy-terminated polybutadiene soft segments were prepared using the method described in Chapter one. The polyether-based non-ionic polyurethane was found to be less phase separated than the hydrocarbon-based polymer, as discussed earlier. Upon ionisation, the negatively charged end of the zwitterion was found to coordinate with both the positively charged end and the urethane N-H group. This led to effective enhancement of hard segment domain cohesion and resulted in better phase separation and higher tensile strength of the polyether polyurethanes. The enhanced domain cohesion, however, did not have any effect on the phase separation of the already highly phase separated polybutadiene-based

polymers, except for increasing its tensile strength. The degree of improvement in tensile strength was found to be greater for the polyether-based polymer than for the hydrocarbon-based counterpart. This was interpreted in terms of the different effects on the morphology of the two systems upon ionisation. The polyether-based polymer was shown to have an interconnected domain structure caused by interaction between the ether group of the soft segment and the urethane group in the hard segment which resulted in a lower surface tension at the interdomain interface. The large polarity difference between the urethane and the polybutadiene produced a high interfacial tension between the two segments and yielded more isolated domains. The interconnected domain structure, which gradually reinforced with increasing ionisation level, was thought to be responsible for the large improvement in tensile properties.

More recently, the use of polydimethylsiloxane as soft segment for the synthesis of polyurethane zwitterionomers was described by Xue-Hai et al(115). The use of this soft segment produced polyurethanes which have similar characteristics to those based on polybutadiene and polyisobutylene due to the large differences in polarity and also the lack of hydrogen bonding between the two segments. The behaviour and properties of these ionomers were consistent to those reported by Yang(34). Furthermore, the polyurethanes obtained using

polydimethylsiloxane soft segment have many attractive properties such as wide service temperature range due to the low T_g of this soft segment, good thermal and oxidative properties, good release properties, incompatibility with most organic compounds, and, for example, excellent electrical insulating properties.

2.8. Dilute Solution Behaviour of Ionic Polymers

Ionic polymers can generally be classified into two major categories: (1) substances which contain macromolecules carrying a large number of ionic groups are called "polyelectrolytes" and (2) those polymers that accommodate salt groups at relatively isolated positions along the chain are termed "ionomers"

The viscosity of dilute solutions of ionic polymers display a unique dependence on concentration which distinguishes them from their non-ionic counterparts. For the latter, the reduced viscosity $\eta sp/c$ increases only gradually with increasing concentration, whereas ionic polymers undergo a large increase in viscosity with dilution, sometimes reaching values at high dilutions which are many times the viscosity which would be expected for polymers in the absence of charges. This interesting phenonmenon is commonly called "polyelectrolyte effect".

(a) non-ionic polymers

From the theory of U-tube viscometers, the dynamic viscosity of a liquid η can be related to the flow time t as follows:

$$\eta = A\rho t - B\rho/t$$

where ρ = density of the liquid

A and B= constants for the particular viscometer used

The second term on the right hand side of this equation is known as the kinetic energy correction factor, and arises because part of the potential energy lost as the liquid level falls is converted into kinetic energy of flow and is not used in overcoming the viscous drag of the liquid. This term is generally very small and can usually be neglected. Therefore, it is clear that when a polymer is dissolved in a solvent, its viscosity and flow time can be related to that of the pure solvent by the following relationship:

$$t/t0 = \eta/\eta 0$$

where t and η = the flow time and viscosity of the polymer solution

t0 and $\eta 0$ = the flow time and viscosity of the pure solvent.

The dilute solution viscosity of most non-ionic polymers obeys the Huggins' and Kraemer's equations, i.e. their viscosity decreases with dilution(116,117).

$\eta sp/c = [\eta] + k' [\eta]^2 c$----Huggins (1942)

$\log \eta r/c = [\eta] - k'' [\eta]^2 c$---Kraemer (1938)

where $\eta sp = \eta - \eta 0/\eta 0$ = specific viscosity

$\eta r = \eta/\eta 0$ =relative viscosity

(b) polyelectrolytes

The presence of a large number ionic groups in the polymers produces materials which combine the properties of electrolytes and polymers. Their solutions show large conductance and ionic dissociation. The chain conformation of polyelectrolyte molecules in dilute solution may be markedly expanded by the electrostatic repulsion between the ions, and this effect results in a large increase in viscosity.

At high concentrations, the molecules are close to each other. They are not appreciably expanded, and the specific viscosity is approximately normal. As the concentration of the solution is decreased, the polymer molecules no longer fill all of the space and intervening regions extract some of the mobile ions. Net charges develop in the polymer chains causing them to expand. As this process continues with further dilution, the

expansive force increases. At very high dilution, the polymer molecules will have lost many of their mobile ions and will expand virtually to their maximum length.

Fuoss and coworkers(118) studied extensively some cationic polyelectrolytes prepared by quarternising poly-(4-vinyl pyridine) with butyl bromide. They showed that the rise in $\eta sp/c$ at low concentrations may be suppressed by addition of simple salts (e.g. KBr). A fixed low concentration of KBr was found to have little effect at high polymer concentrations where the concentration of bromide ions in the polymer greatly exceeded that of the added salt. However, as the concentration of the polymer was reduced, the added salt became effective in suppressing further loss of mobile ions from the polymer and $\eta sp/c$ ceased to rise.

(c) ionomers

Although there are numerous investigations on ionomers in the solid state, very few studies have been concerned with the solution properties of these ionic polymers which contain relatively small number of ionic groups. This may be due to the poor solubility of most commercially available ionomers which limits the range of solvents for the determination of their hydrodynamic parameters.

Results reported for carboxylate and sulphonate ionomers revealed very complex behaviour in which the

viscosity was shown to be strongly dependent on, for example, the polarity of the solvent, the nature of the cation and the concentration of the polymer solution(119-121). Typically these ionic polymers show strong ionic association in low polarity solvents at low polymer concentrations.

Otocka et al(121) conducted some investigations on the viscosity of carboxylic acid terminated polybutadiene neutralised with various cations. Despite the fact that some of these systems could only be dissolved in organic solvents with difficulty, these studies indicated intramolecular associations at ambient temperature which diminished with increasing temperature.

Most of the recent work on the dilute solution behaviour of ionomers were pioneered by Lundberg et al based on polystyrene sulphonates(122-124). Their results indicated two types of behaviour: (1) aggregation behaviour due to the dipole-diploe attraction in moderate polarity solvents such as THF, and (2) polyelectrolyte behaviour due to the coulombic interaction between ions and polar solvents such as DMSO and DMF. While these ionomers were regarded as polyelectrolytes of low charge density, they did not display typical "polyelectrolyte effect" in low polarity solvents. This was due to the fact that the metal sulphonate groups were largely un-ionised in solvents of low polarity. Therefore their solution behaviour was governed by ion-pair interactions,

and not free ions, as in the case of polyelectrolytes in aqueous solution. In solvents of high polarity, however, the "polyelectrolyte effect" was observed in most cases at low polymer concentrations. Furthermore, the nature of the cation was shown to affect the ability of the polyelectrolyte to expand its hydrodynamic volume at low polymer concentrations(123). The magnitude of the molecular expansion was noticed to be dependent on the ability of the counterion to dissociate from the backbone chain, which in turn, was directly related to the solvent structure.

Another example of the polyelectrolyte behaviour was reported by Rochas et al(125), who investigated the dilute solution viscosity of acrylonitrile methallylsulphonate copolymers in dimethylformamide. These polymers were found to display "polyelectrolyte effect" in salt-free DMF, similar to that observed for aqueous solutions of polyelectrolytes.

2.9. Gel Permeation Chromatography of Ionic Polymers

Gel permeation chromatography, also referred to as size exclusion chromatography, is a fast and reliable technique for the determination of molecular weight and molecular weight distribution of polymers. It was first introduced by Moore(126) in 1964 and has since been used extensively especially in the field of polymer science.

The method is not an absolute one and therefore requires calibration.

Benoit and coworkers(127) have established a universal calibration relationship between molecular weight and retention volume for a number of homopolymers and copolymers having various chemical and geometrical structures. According to Benoit, GPC separation is governed by the hydrodynamic volume which is proportional to the product $[\eta]$ x M, and is related to the solution properties as well as the size of the molecules. Using polymer standards, typically monodisperse polystyrene, a calibration curve of log $[\eta]$ M versus retention volume can be constructed. Since the intrinsic viscosity can be independently measured for any polymer, the molecular weight of an unknown polymer can be determined from the retention volume and the calibration curve. Any factors affecting the intrinsic viscosity $[\eta]$ will thus change the hydrodynamic volume and hence the retention volume at which a particular polymer appears.

GPC separations are generally dominated by steric exclusion. However, other secondary mechanisms such as adsorption, partition and incompatibility may also be present depending on the polarity of the solvent and the polymer and on the polymer-solvent and polymer-support interactions. For macromolecules carrying ionic groups, GPC separation is controlled not only by the above

parameters, but also factors such as concentration and type of ionic groups.

As discussed in the last section, both ionomers and polyelectrolytes show abnormal behaviour in dilute solution. These ionic polymers are also known to influence the chromatographic process because of intramolecular chain expansion and interactions with any surface charge on the stationary phase. Such surface charge is likely to be present on porous glass or silica in neutral or basic aqueous media. It has been reported (128-131) that intramolecular expansion and substrate repulsion both lead to early elution relative to non-ionic polymers and that these two effects can be suppressed by the addition of simple electrolyte.

Cha and Coppola et al(131,132) observed anomalous bimodal distributions in the elution of sulphonated polyacrylonitrile and other ionic polymers. By using a 0.1M solution of LiBr or LiCl in DMF, the chromatograms of the polyelectrolytes were found to have a more symmetrical shape and were eluted at much higher retention volumes than in pure DMF. Cha concluded that the multiple peaks were due to different charge distributions or concentrations on the polymer chains and could be eliminated by adding LiBr to the solvent. In addition, intramolecular electrostatic interaction of the sulphonated polymer reduced the retention volume in DMF indicating unusually large apparent molecular size. Upon

addition of the screening electrolyte, the retention volume was increased due to contraction of the polymer chains. Coppola suggested that in DMF, supermolecular association or aggregates were formed which were destroyed by the addition of lithium bromide.

In a GPC study of non-ionic acrylonitrile copolymers and polar monomers, such as ethyl vinyl ether using DMF as solvent, Kenyon et al (133) observed two GPC peaks for some polymers which were unpredicted from the polymerisation conditions. These bimodal type distributions were attributed to the association of the polar groups in polyacrylonitrile with polar solvent molecules causing a considerable increase in the hydrodynamic volume. Addition of LiBr greatly reduced the polymer-solvent interactions and led to single-peak distribution curves at a higher retention volume.

Dubin and Wright(134) found unusually large retention volumes for non polar polymers such as polystyrene in polar solvents such as DMF or polar polymer in solvents of low polarity. The explanation given by these authors was that non-polar polymers in polar solvents preferentially adsorbed on the polystyrene gel and exhibited a delayed elution. Similarly, polar polymers showed the same behaviour in solvents of low polarity.

By using a mixture of two or more solvents of different polarities, Lundberg et al (135) and Mori (136) were able

to find solvent systems for polymers that contained both non-polar and polar properties and thus overcome the adverse adsorption effect.

Two other important factors which influence the GPC separation of ionic polymers are related to the concentration of polymer and the ionic strength. Abad et al(137) studied the behaviour of sodium polystyrene sulphonate as a function of injected polyelectrolyte concentration using a silica support and water as eluent. These authors observed a non-linear increase in the retention volume with increasing injected sample concentration. The mechanism of separation was interpreted in terms of electrostatic and hydrodynamic interactions. At low injected polyion concentrations, electrostatic repulsive interactions played a significant role in the elution of negatively charged sodium polystyrene sulphonate since there were negatively charged silanol groups on the silica support. As the concentration of polyelectrolyte was increased, the polymer chains became more folded and the diffusion of a polymer molecule into a pore of a given dimension became easier.

The effect of ionic strength of the solvent on the aqueous GPC of sodium polystyrene sulphonate and small neutral and charged molecules using porous glass supports was investigated by Cooper et al (138). From their studies of three different ionic strengths using

phosphate buffer solution, Cooper found that the retention volumes of non-ionic species were not affected by altering the ionic strength of the solvent. On the other hand, increasing the phosphate concentration of the buffer dramatically increased the retention volumes of all the charged molecules. The increase in retention volume was suggested to be partly caused by the decrease in site-site repulsion on the polyelectrolyte. This resulted in smaller molecular dimensions partly due to charge-charge interactions between the charged solute and the charged glass support surface.

CHAPTER THREE EXPERIMENTAL

3.1. Purification of Solvents and Reagents

All solvents and reagents were purified according to methods given in standard text books(139,140). Solvents used as reaction medium were dried in suitable drying agents before distillation. Solvents employed for the purpose of washing were generally used without further purification.

3.1.1. Dimethyl Sulphoxide (DMSO)

DMSO (Aldrich Chemical Co. Ltd.) was dried over powdered calcium hydride for one week. It was then distilled under reduced pressure and stored over fresh Linde molecular sieve, type 4A, prior to use.

3.1.2. D^6-DMSO

D^6-DMSO (Aldrich Chemical Co. Ltd.) was supplied in $1cm^3$ sealed ampoules and was used without further purification.

3.1.3. N,N'-Dimethyl Formamide (DMF)

DMF (BDH Ltd.) was dried over barium oxide powder for one week before being distilled under reduced pressure and was stored over Linde molecular sieve, type 4A, before use.

3.1.4. Tetrahydrofuran (THF)

THF (Aldrich Chemical Co. Ltd.) was dried over powdered calcium hydride for 48 hours and distilled prior to use.

3.1.5. Absolute Alcohol and Ethanol 96

Absolute alcohol and Ethanol 96 (James Borrough Ltd.) were used as supplied.

3.1.6. Toluene

Toluene G.R. (May and Baker) was used as supplied.

3.1.7. Diethyl Ether and Acetone

Diethyl ether and Acetone (May and Baker) were used as supplied.

3.1.8. 3-Chloro-propane-1,2-diol (CPD)

CPD (Fluka) was distilled under reduced pressure and stored over Linde molecular sieve, type 4A, prior to use.

3.1.9. Potassium Thiosulphate ($K_2S_2O_3$)

$K_2S_2O_3$ (Fluka) was used as supplied.

3.1.10. Potassium Sulphite (K_2SO_3) and Sodium Sulphite (Na_2SO_3)

K_2SO_3 and Na_2SO_3 (Fluka) were used as supplied.

3.1.11. Glycidol(2-epoxypropanol)

Glycidol (Aldrich Chemical Co. Ltd.) was used as supplied.

3.2. Purification of Monomers

3.2.1. Butane-1,4-diol (BD)

BD (BDH Ltd.) was dried over Linde molecular sieve, size 4A, for one week, then distilled under reduced pressure and stored over fresh molecular sieve until required.

3.2.2. Diphenylmethane-4,4'-diisocyanate (MDI)

MDI (Bayer) was distilled under reduced pressure and stored at -20°C prior to use.

3.2.3. Polyether Glycols (BDH Ltd.)

Polypropylene glycols of molecular weights 1025 and 2025 (PPG 1025 and PPG 2025), polyethylene glycol of molecular weight 1000 (PEG) and polytetramethylene glycol of molecular weight 1000 (PTMG) were all dried at 100°C in a rotary evaporator under reduced pressure for six to nine hours before being stored in sealed containers prior to use. This step was taken to remove any trace of moisture present which would otherwise have reacted with the isocyanate groups during the synthesis of polyurethanes.

3.3. Drying Agents and Other Chemicals

3.3.1. Anhydrous Calcium Hydride (CaH_2)

CaH_2 (BDH Ltd.) was used as received.

3.3.2. Anhydrous Barium Oxide (BaO)

BaO (BDH Ltd.) was used as received.

3.3.3. Molecular Sieves

Linde molecular sieves (BDH Ltd.) were heated in an oven at 200°C for 24 hours prior to use.

3.3.4. Nitrogen

Oxygen-free nitrogen (B.O.C.) was passed through series of vessels containing concentrated sulphuric acid, potassium hydroxide pellets and anhydrous calcium chloride in order to dry the gas, before reaching the reaction flask.

3.3.5. Catalyst

Di-n-butyltin dilaurate (Aldrich Chemical Co. Ltd.) was used as a catalyst in the synthesis of polyurethanes. It was used as received without further purification.

3.4. Synthesis of Potassium-S-1,2-dihydroxypropyl Thiosulphate (TDOL).

The synthesis of TDOL has been studied by two methods. The first experiment involved the nucleophilic attack of thiosulphate ions on 3-chloro-propane-1,2-diol. In the second method, TDOL was prepared via the ring opening reaction of glycidol by the attack of thiosulphate ions.

3.4.1. Reaction between 3-Chloro-propane-1,2-diol and Potassium Thiosulphate

Powdered potassium thiosulphate (57.10g, 0.361mol) was dissolved in 70cm^3 of water and CPD (22.12g, 0.200mol) added , followed by a further 70cm^3 of water. The solution was refluxed gently for 2 hours and cooled. Any trace of unreacted CPD was extracted with diethyl ether (2x20cm^3). The water was then removed by rotary evaporation under vacuum at 100°C. After cooling, the product was extracted from the inorganic salt with DMF (3x100cm^3). The DMF extracts were centrifuged until clear and reduced in volume by rotary evaporation to yield a viscous colourless oil. The oil was dissolved in 30cm^3 of water to give a colourless solution. Ethanol (60cm^3) was added to the solution to form an emulsion from which the product crystallised after stirring for 1-2 hours. The yield was maximised by cooling the solution overnight in a refrigerator at 4°C. The product was collected by

filtration and washed with cold ethanol before being dried in vacuum (yield =78%).

The product could be recrystallised from boiling ethanol, though this was generally not found to be necessary.

3.4.2. Reaction between Potassium Thiosulphate and Glycidol

To an aqueous solution of potassium thiosulphate (19.1g, 0.1mol) in 40cm^3 water containing a few drops of phenolphthalein in a two-neck flask, glycidol (7.4g, 0.1mol) was added dropwise over 10 minutes through a pressure equilising funnel at 60°C. The pink colour developing due to the formation of hydroxyl ions was continuously discharged by the addition of dilute hydrochloric acid (0.5M). The mixture was kept at 60°C for about 30 minutes until no sign of any pink colour appeared. The mixture was then cooled and washed with diethyl ether to remove any unreacted glycidol or trifunctional species that could formed as a side-product. Water was then removed by rotary evaporation to leave a colourless viscous oil from which the product was extracted with hot ethanol (Yield=26%).

3.5. Synthesis of Potassium-S-1,2-dihydroxypropyl Sulphonate(SDOL)

Potassium sulphite(47.48g, 0.300mol) was dissolved in 60cm^3 of water and 3-chloropropane-1,2-diol,CPD(22.12g, 0.200mol) in 50cm^3 of water was added. The solution was refluxed gently for 2.5 hours and cooled. Diethyl ether (2x20cm^3) was added to extract any traces of unreacted CPD. Water was then removed by rotary evaporation at 80°C. After cooling, the resulting SDOL was extracted from the inorganic salts with warm DMSO (3x100cm^3). The DMSO extracts were centrifuged until clear and removed by rotary evaporation under vacuum at 100°C to yield a viscous colourless oil. The oil was dissolved in 20cm^3 of water. Absolute alcohol (50cm^3) was added to the solution to form an emulsion from which the product crystallised after standing for 1-2 hours. The product was collected by filtration and washed with cold ethanol before being dried in a vacuum desiccator at room temperature (yield=72%).

3.6. Synthesis of Sodium-S-1,2-dihydroxypropyl Sulphonate (SDPS)

The synthesis was similar to that of SDOL, substituting potassium sulphite with sodium sulphite, except in the method of extraction. Due to the slightly higher solubility of SDPS compared with SDOL, it was extracted

from the inorganic salt with hot DMF instead of DMSO. After rotary evaporation of the DMF, a white solid was left which was washed thoroughly with acetone before being dried in vacuum at room temperature (yield=75%).

3.7. Determination of Hydroxyl Content in Various Polyols

The polyol was weighed and dissolved in 10cm^3 of dioxane by warming to approximately 50°C in a conical flask. When the solution cooled to room temperature, acetyl chloride(1.5M in toluene, 10cm^3) was added from a pipette. The solution was swirled gently, and was chilled further to 0°C. Pyridine(2cm^3) was added from a pipette, the flask was then capped, shaken and placed in a hot water bath at 60°C for 1 hour(Shaked vigorously every 10 minutes). The solution was cooled in an ice-bath and chilled distilled water(25cm^3) was carefully added. The solution was then allowed to cool in the ice-bath for a further 30 minutes with occasional shaking to decompose the excess reagent. A few drops of indicator solution(0.1% of cresol red solution in 50% ethanol) was added and the resultant solution was titrated against NaOH(0.5M alcoholic) solution until the first definite violet colour appeared. The end point was taken when the violet colour stayed without slow fading. A duplicate blank determination was made under identical conditions but omitting the polyol sample. Each analysis was carried

out at least twice and the average value was taken. The values of the polyol equivalent weight as calculated using the equation below are tabulated in Table 3.1. The term polyol equivalent weight is defined as the weight of polyol(in gram) which contains one gram equivalent of hydroxyl group. If the polyol chains are assumed to be linear with no side branching and that a hydroxyl group terminated at each end of the chains. Then the hydroxyl equivalent is one-half the average molecular weight of the polyol and one-third the average molecular weight of trifunctional polyol,etc...

$$\text{Equivalent Weight of Polyol} = \frac{1000 \times Wt}{M(B-S)}$$

where Wt=weight of polyol used

M=molarity of NaOH

B=volume required for the blank titration (cm^3)

S=volume required for the sample titration (cm^3)

Table 3.1. Result of hydroxyl analysis.

Polyol Type	Experimental	
	Equivalent wt.	Molecular wt.
PTMG1000	485	970
PEG1000	491	982
PPG1025	545.5	1091
PPG2025	918	1836

The experimental values of polyol equivalent weight were used in all the synthesis of segmented polyurethanes.

3.8. Synthesis of Segmented Polyurethanes with Various Types of Soft Segment

It is understood that the phase morphology as well as the mechanical and physical properties of polyurethanes are affected by the concentration and the type of soft segment present. To study their effect on the properties of polyurethanes, various soft segments have been incorporated into the polymers. Table 3.2 summarises the type and quantity of monomers used in the step growth polymerisation. A typical method of preparation of segmented polyurethanes based on MDI, PPG 1025 and BD is as follows:

A solution of PPG 1025 (13.86g, 0.0127mol) in 40cm^3 DMSO was added to MDI (10.01g, 0.04mol) in 20cm^3 DMSO over 10 minutes at 100°C under nitrogen. After 1 hour the mixture was cooled to 60°C and a solution of BD (2.43g,0.027mol) in 40cm^3 of DMSO was added over 10 minutes followed by 0.05g of di-n-butyltin dilaurate. Reaction was continued for another 2 hours at this temperature under nitrogen after which there was no increase in molecular weight as checked by GPC. The final polymer was then precipitated from a large excess of distilled water and washed for 1-2 hours with fresh distilled water. It was then dried in vacuum at room temperature for 2 weeks before being stored in the dark at 4°C.

Table 3.2. Monomer ratios used for non-ionic segmented polyurethanes.

Polymer code	Polyol Type	Mass of Polyol used/g	Mass of MDI used/g	Mass of BD used/g
PTMG-0	PTMG1000	12.32	10.01	2.43
PE-0	PEG1000	12.47	10.01	2.43
PP-0	PPG1025	13.86	10.01	2.43
PP-02	PPG2025	23.32	10.01	2.43

3.9. Synthesis of Polyurethane Ionomer based on MDI, PPG 1025 and TDOL. (PP-100-Th/BD)

A solution of PPG 1025 (13.86g, 0.0127mol) in 40cm^3 DMSO was added to MDI (10.01g, 0.04mol) in 20cm^3 DMSO over 10 minutes at 100°C under a nitrogen atmosphere. The mixture was stirred for 1 hour at 100°C. It was then cooled to 60°C and a solution of TDOL (6.11g, 0.027 mol) in 40cm^3 of DMSO was added over 10 minutes followed by 0.05g of di-n-butyltin dilaurate. Reaction was continued for another 2 hours at 90°C under nitrogen. The final polymer was then precipitated from toluene (1500cm^3) and washed for 1-2 hours with 500cm^3 of fresh toluene. It was then dried in vacuum at room temperature for 2 weeks before being stored in the dark at 4°C.

3.10. Synthesis of Polyurethane Ionomer Series with Various Ratios of TDOL to BD based on MDI, PPG 1025, TDOL and BD.

The method used was similar to that used for the preparation of PP-100-Th/BD substituting TDOL for various ratios of TDOL/BD. Except for PP-75-Th/BD, the resultant polymers were precipitated from water rather than toluene. The molar ratios of monomers used for the series are summarised in Table 3.3.

Table 3.3. Ratios of monomers used for polyurethane ionomer series based on MDI, PPG1025, BD and TDOL.

Polymer code	Mass of PPG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of TDOL used/g
PP-100-Th/BD	13.86	10.01	----	6.11
PP-75-Th/BD	13.86	10.01	0.61	4.58
PP-50-Th/BD	13.86	10.01	1.22	3.06
PP-25-Th/BD	13.86	10.01	1.83	1.53
PP-0	13.86	10.01	2.43	----

3.11. Synthesis of Polyurethane Ionomer based on MDI, PPG 1025 and SDOL.

A solution of polypropyleneglycol 1025(13.86g,0.013mol) in 20cm^3 DMSO was added to MDI(10.01g, 0.04mol) in 20cm^3 DMSO over 10 minutes at 60°C under a nitrogen atmosphere.

The mixture was stirred for 1 hour at 100°C. It was then cooled to 60°C and a solution of SDOL (5.25g, 0.027mol) in 60cm^3 of DMSO was added dropwise over 10 minutes, followed by 0.05g of di-n-butyltin dilaurate. The mixture was then heated for another 2 hours at 90°C. The resultant polymer was precipitated from toluene(1000cm^3) and finally dried in vacuum at room temperature.

3.12. Synthesis of different Series of Polyurethane Ionomers with Various Ratios of SDOL and BD using different Soft Segments.

The methods used for the following series of ionomers were similar to that of PP-100-S/BD. Tables 3.4, 3.5, 3.6 and 3.7 summarise the quantity of various monomers used.

Table 3.4. Ratios of monomers used for polyurethane ionomer series based on MDI, PTMG, BD and SDOL.

Polymer code	Mass of PTMG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of SDOL used/g
PTMG-100-S/BD	12.32	10.01	----	5.25
PTMG-50-S/BD	12.32	10.01	1.22	2.62
PTMG-25-S/BD	12.32	10.01	1.83	1.31
PTMG-10-S/BD	12.32	10.01	2.19	0.52
PTMG-0	12.32	10.01	2.43	----

Table 3.5. Ratios of monomers used for polyurethane ionomer series based on MDI, PEG, BD and SDOL.

Polymer code	Mass of PEG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of SDOL used/g
PE-100-S/BD	12.47	10.01	----	5.25
PE-50-S/BD	12.47	10.01	1.22	2.62
PE-25-S/BD	12.47	10.01	1.83	1.31
PE-10-S/BD	12.47	10.01	2.19	0.52
PE-0	12.47	10.01	2.43	----

Table 3.6. Monomer ratios used for polyurethane ionomer series based on MDI, PPG 1025, BD and SDOL.

Polymer code	Mass of PPG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of SDOL used/g
PP-100-S/BD	13.86	10.01	----	5.25
PP-50-S/BD	13.86	10.01	1.22	2.62
PP-25-S/BD	13.86	10.01	1.83	1.31
PP-10-S/BD	13.86	10.01	2.19	0.52
PP-0	13.86	10.01	2.43	----

Table 3.7. Monomer ratios used for polyurethane ionomer series based on MDI, PPG 2025, BD and SDOL.

Polymer code	Mass of PPG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of SDOL used/g
PP-100-S/BD2	23.32	10.01	----	5.25
PP-50-S/BD2	23.32	10.01	1.22	2.62
PP-25-S/BD2	23.32	10.01	1.83	1.31
PP-10-S/BD2	23.32	10.01	2.19	0.52
PP-02	23.32	10.01	2.43	----

3.13. Synthesis of Polyurethane Ionomer Series based on MDI, PPG 1025, BD and SDPS with Various Ratios of BD and SDPS

The method used was similar to that used for the SDOL ionomer series substituting SDOL for SDPS. The reactant ratios for the series are shown in Table 3.8.

Table 3.8. Monomer ratios used for polyurethane ionomer series based on MDI, PPG 1025, BD and SDPS.

Polymer code	Mass of PPG used/g	Mass of MDI used/g	Mass of BD used/g	Mass of SDPS used/g
PP-100-SDP/BD	13.86	10.01	----	4.81
PP-50-SDP/BD	13.86	10.01	1.22	2.41
PP-25-SDP/BD	13.86	10.01	1.83	1.20
PP-0	13.86	10.01	2.43	----

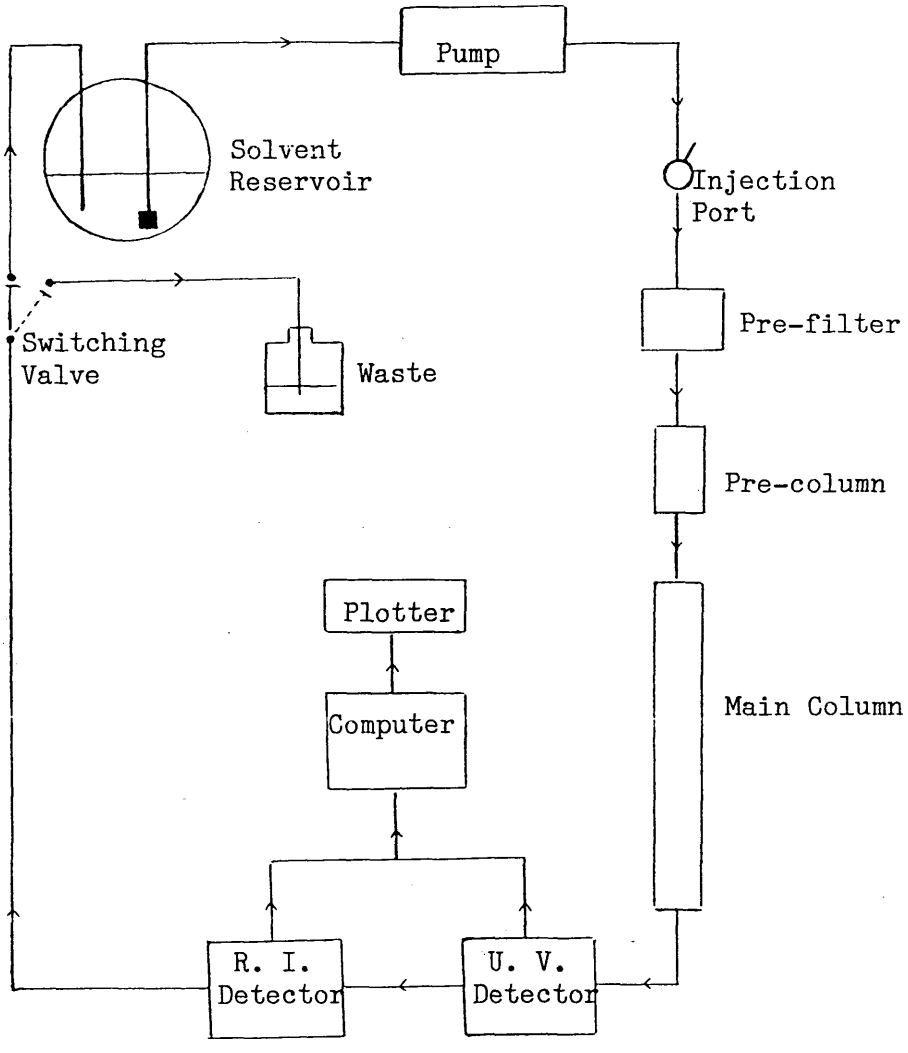
3.14. Sample Casting

Thin films of polymers approximately 1mm thick were prepared by solution casting from DMF onto dust-free petri glass dishes. The solvent-containing polymers were first of all dried at 50°C under atmospheric pressure for three days and then under reduced pressure for two weeks at the same temperature.

3.15. Gel Permeation Chromatography

The GPC apparatus is shown diagrammatically in Figure 3.1. Basically the system consists of a solvent reservoir from which solvent (DMF) was pumped by a HPLC metering pump (Altex model 110A) at 1.0cm^3 per minute to a column system composed of a pre-filter (Anachem, 2 μm), a pre-column (Polymer Laboratory PL Gel 50x7.5 mm, 5 μm and 10 μm particles of mixed porosity) and a main column (PL Gel 300x7.5 mm, 5μm particles of mixed porosity). Sample injection was made through a HPLC valve (Rheodyne 7125 syringe loading injector valve) with a 20 μl injection loop fitted between the pump and the column. The eluted sample was passed first of all to an ultra-violet detector (Cecil CE 2012 reference channel variable wavelength UV moniter) with a 8μl flow cell, then to a refractive index detector (Knauer differential refractometer) before it was collected in a waste bottle. Cycling of the solvent between runs was made possible by

Fig.3.1 Apparatus Used for Gel Permeation Chromatography.



means of a switching valve installed between the UV detector and the waste collector.

Data collection was carried out by a Trilab 2000 computer (Trivector systems Ltd.) at a rate of 1 point per second. As well as collecting raw data, Trilab 2000 was also used to perform molecular weight analysis calculations to give various molecular weight averages by means of a basic program using the calibration data obtained from standard polystyrene samples of narrow molecular weight distribution.

Notes on sample injection:

An approximately 0.3% w/v polymer sample was dissolved in DMF. Any undissolved impurities or dust particles were filtered off before the sample was injected into the column. As the concentration of the ionomers used has a marked influence on the retention volume , all the weighings were carried out accurately when making up the polymer solutions.

3.16. Microanalysis

Microanalysis was carried out by the Microanalytical Laboratory, Department of Chemistry, Imperial College.

This is a very useful and accurate method for checking the elemental content of low molecular weight materials.

However, it is not a very reliable method in the case of polyurethanes due to a number of inevitable side reactions which can occur during polymerisation. This method was used, nevertheless, as a further check for purity of the polymers.

3.17. Proton Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR spectra were obtained using a Perkin-Elmer R32 90 MHz NMR spectrometer. Samples were dissolved in deuterated DMSO (approximately 5% w/v) and filtered directly into 5mm NMR tubes. A typical scan was from 0-10ppm relative to TMS using a scan time of 450s. Off scans were also made for checking the presence of allophanate groups (10.6ppm) in polyurethanes.

3.18. Infra-red Spectroscopy

Infra-red spectra were recorded on a Perkin-Elmer 457 scanning spectrometer. The spectra of brittle and powdery materials were obtained using a disc pressed from the sample and KBr powder (approximately 0.5% w/w polymer in KBr) . Spectra of rubbery samples were taken using thin films of the polymer.

IR spectroscopy was also used for checking the purity of all reagents and to follow the extent of reaction. For instance, the amount of isocyanate present during the synthesis of polyurethanes could be closely monitored by

noting the disappearance of the -NCO peak at 2260cm^{-1} with time. In such cases, liquid samples were injected into KBr cells, and solid samples were cast from a suitable solvent onto either NaCl or KBr plates, before using the spectrometer for scanning.

3.19 Stress-strain Measurements

Stress-strain tests were performed on a Polymer Laboratories-Minimat MK2 Materials Tester. The system was interfaced with an IBM Personal System/2 Model 30 computer for data storage. Dumbbell shaped test pieces were used and all tests were carried out at a cross-head speed of 10mm per minute at room temperature. A plot of force versus extension was recorded from which the tensile modulus(E), ultimate tensile strength(T.S.) and % of elongation at break were easily obtained. All tests were carried out in duplicate and the average value of two tests was taken.

3.20. Solution Viscometry

Viscosity measurements were carried out using a standard Ubbelohde suspended-level viscometer at various fixed temperatures in a thermostated water bath. Using a syringe, polymer solutions were filtered directly into the viscometer before any measurement was taken. This was to remove contamination by dust particles or impurities

which could otherwise drastically affect the results. About 15 minutes of temperature equilibration was allowed prior to each flow time measurement. Each flow time was measured at least three times at each concentration and the average value was taken.

3.21. Thermogravimetric Analysis

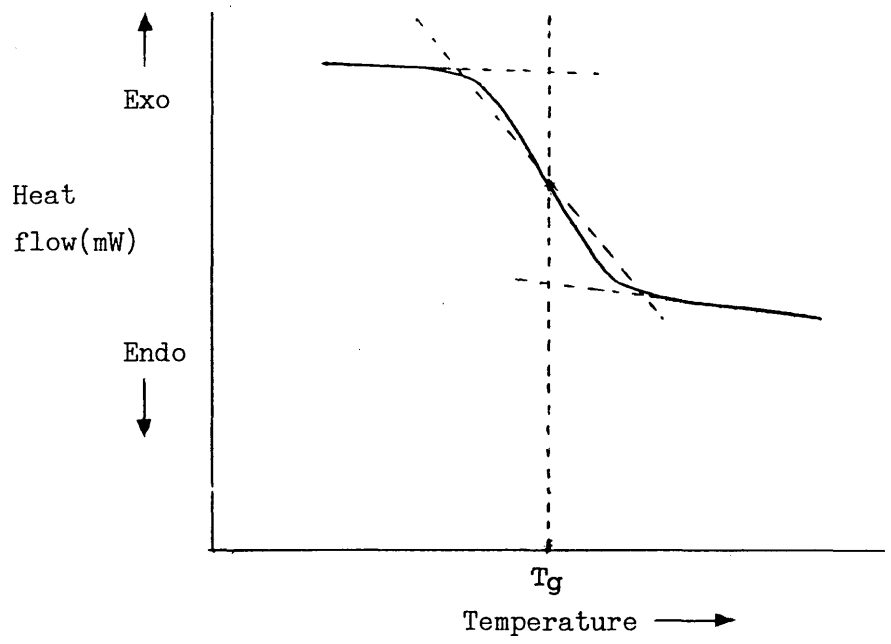
Thermogravimetric analysis studies were performed using a Perkin-Elmer TGS-2 Thermogravimetric system coupled with a Perkin Elmer DSC-2. Approximately 5mg of material was used for each run. The heating rate was at 10°C per min from room temperature to 300°C, under a nitrogen atmosphere in all cases. The system was calibrated against several standard metallic alloys before use. The instrument gave a direct plot of % sample weight retained vs temperature and from this plot, the thermal stability of the materials could be assessed.

3.22. Differential Scanning Calorimetry

DSC thermograms were recorded using a Du Pont 910 Thermal Analyser with a DSC cell attachment. Temperature scanning experiments were performed at a scanning rate of 10°C per minute at temperatures between -150°C and 150°C. An approximately 10mg sample was put in an aluminium sample pan and placed in the DSC cell together with an empty pan as a reference. The heat flow, temperature and

time were monitored throughout the experiment and stored in the instrument memory for later analysis. Glass transitions were designated as the mid point of the two tangents of the discontinuous points as shown in Figure 3.2.

Fig. 3.2. Method Used for Determining the Position of T_g.



3.23. Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis was performed using a Polymer Laboratories DMTA. A universal temperature programmer coupled with the DMTA unit together with an interface were used to control the running of the instrument and to carry out data processing. A small rectangular strip sample was clamped in a dual cantilever bending mode using a small torque wrench set. A forced

oscillation of 10Hz was used and temperature scanning was conducted from -100°C to 150°C at a rate of 5°C per minute.

Temperatures profiles of dynamic storage modulus (E'), loss modulus (E") and damping factor tan δ were obtained. The glass transition temperature (T_g) was identified as the tan δ peak.

3.24. Equilibrium Water Uptake Measurements

A thin film of polymer sample approximately 1mm thick was dried in an vacuum oven until a constant weight was reached. It was then placed in a sample tube containing the appropriate solvent, water or ethanol, and placed in a constant temperature water bath at 30°C. The sample was removed at periodic intervals and dried between filter papers before the weight was rapidly recorded. This process was continued until an equilibrium weight was achieved. The experiment was done in duplicate for each sample and the average final equilibrium value was calculated. A graph of % mass gain vs time was plotted and the equilibrium uptake value was taken when the % mass increase was less than 0.1% per hour.

3.25. Scanning and Transmission Electron Microscopy (SEM and TEM)

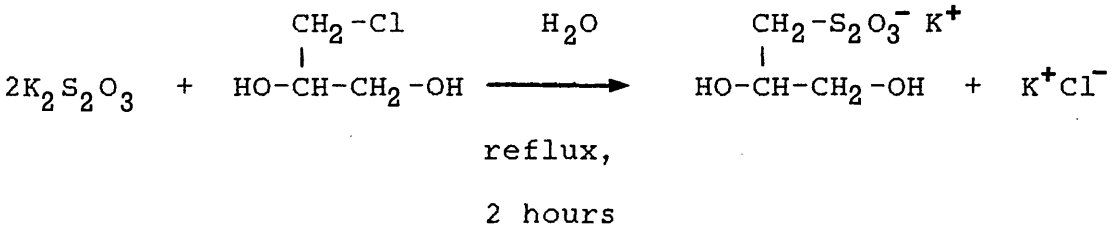
SEM was performed using a Jeol T200 Scanning Electron Microscope with an electron accelerating voltage of 10kV. Samples were prepared by fixing a small disc of the polymer approximately 1cm diameter onto a cylindrical aluminium support. To prevent local charging of the poorly conducting polyurethane, all specimens were vacuum coated with a thin layer of gold by sputtering.

TEM was performed using a Jeol 100CX Transmission Electron Microscope operating at 100kV. Ultrathin films were prepared by solution casting from DMF directly onto 400 mesh copper grids. Precautions were taken to minimise electron beam damage to the samples by using a low density beam.

CHAPTER FOUR RESULTS AND DISCUSSION

4.1. Preparation of Potassium-S-1,2-dihydroxypropyl Thiosulphate (TDOL)

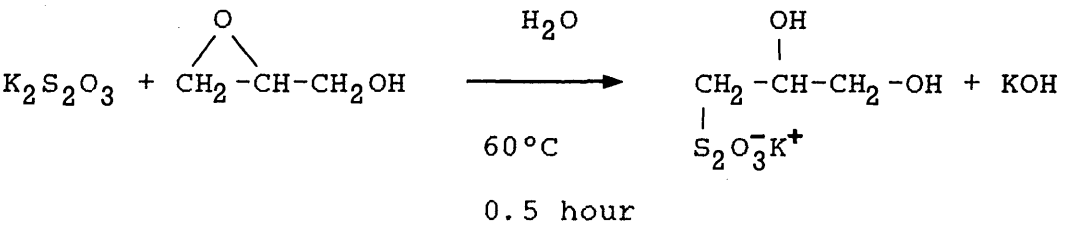
The new ionic diol, TDOL, belongs to a class of S-alkyl salts known as Bunte salts after its discoverer in 1874(141). Its chemistry and properties have been reviewed in depth by Milligan and Swan(142). Two methods have been tried for the preparation of this ionic diol. The first method, developed by Bunte, essentially involved the nucleophilic attack of thiosulphate ions on an alkyl chloride precursor. The substrate used in this case is 3-chloro-propane-1,2-diol. Details of this method are described in Section 3.4.1.



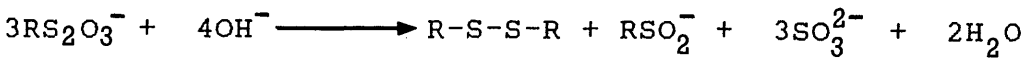
The thiosulphate ion is generally considered to be very nucleophilic. It reacts with its substrate exclusively on the sulphur atom, even though it has three terminal oxygens and only one sulphur available for bonding. This may be explained in terms of the amount of atomic overlap in the two atoms. Being a larger atom compared to oxygen,

the sulphur atom has a relatively more diffuse lone pair of electrons which can give greater atomic overlap with the 2p orbital of the carbon atom in the S_N2 transition state than the smaller and with more tightly held electron pair oxygen atom.

The second route attempted for the synthesis of TDOL was the nucleophilic attack of thiosulphate ions on the epoxy ring of glycidol. The detailed procedure is given in Section 3.4.2.



This method, however, gave only 26% yield of the product compared to 78% obtained by the former route. The low yield obtained from this method may be due to the highly unstable epoxy ring which can easily be opened by the side product KOH before it was neutralised with dilute hydrochloric acid(see Section 3.4.2). Furthermore, any trace of the side product KOH present may also attack the product TDOL resulting in the formation of disulphide and other side products(142).



Infrared spectroscopy showed that the TDOL which has been formed was heavily contaminated with impurities. On the whole, this cannot be regarded as a satisfactory method for the synthesis of TDOL.

4.2. Characterisation of TDOL

TDOL in the pure state is a white crystalline solid and is very soluble in water, readily soluble in DMSO and DMF, slightly soluble in boiling ethanol, but insoluble in less polar solvents such as acetone, THF or chloroform. Its identity was confirmed by elemental analysis, infrared and ^{1}H nuclear magnetic resonance spectroscopy.

The elemental analysis result of TDOL presented in Table 4.1. shows that the experimental figures are close to the calculated values. Thus the purity of TDOL is proven.

Table 4.1. Elemental analysis result for TDOL.

Element	C(%)	H(%)	S(%)
Found	15.80	3.02	27.56
Calculated	15.93	3.10	28.32

The IR and NMR spectra of TDOL are given in Fig.4.1. and Fig.4.2. respectively. The IR spectrum of TDOL shows several bands that have been reported as characteristic of alkyl thiosulphates(143).

A strong sharp band at 535cm^{-1} and a strong broad band at 650cm^{-1} are assigned as SO deformations. A weak but sharp peak at 420cm^{-1} is assigned as the SS stretch and a strong sharp band at 1030cm^{-1} as a SO stretching frequency. A broad strong band centred at 1210cm^{-1} probably includes the other SO vibration identified by Simon and Kunath(143).

The ^{1}H NMR spectrum of TDOL can readily be assigned as follows: the secondary hydroxyl proton, H(a), is a doublet centred at 4.6ppm, the primary hydroxyl proton, H(b), is a triplet centred at 4.35ppm, the methine proton, H(c), is seen as a multiplet centred at 3.65ppm, the methylene protons adjacent to the thiosulphate, H(d), is a doublet centred at 3.32ppm and the methylene protons next to the primary hydroxyl group, H(e), is a double doublet centred at 2.90ppm.

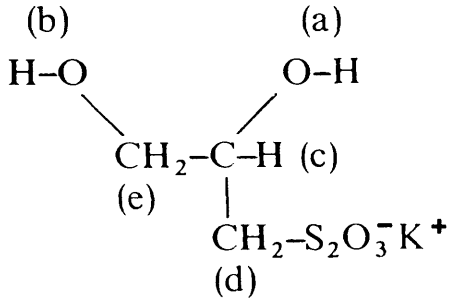


Fig. 4.1. IR spectrum of TDOL

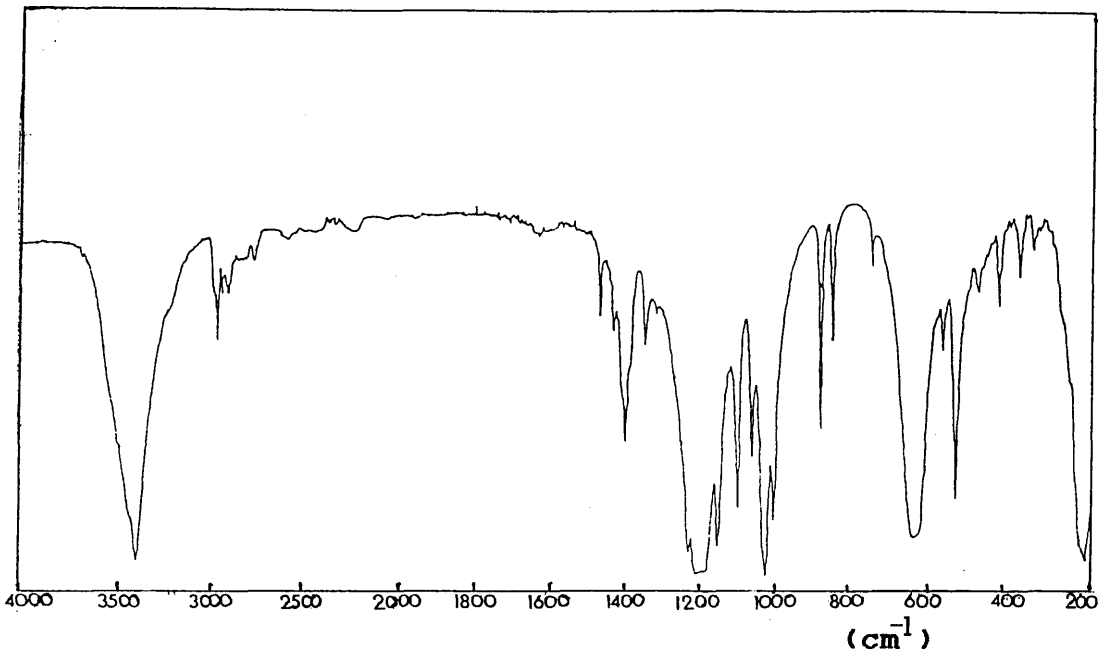
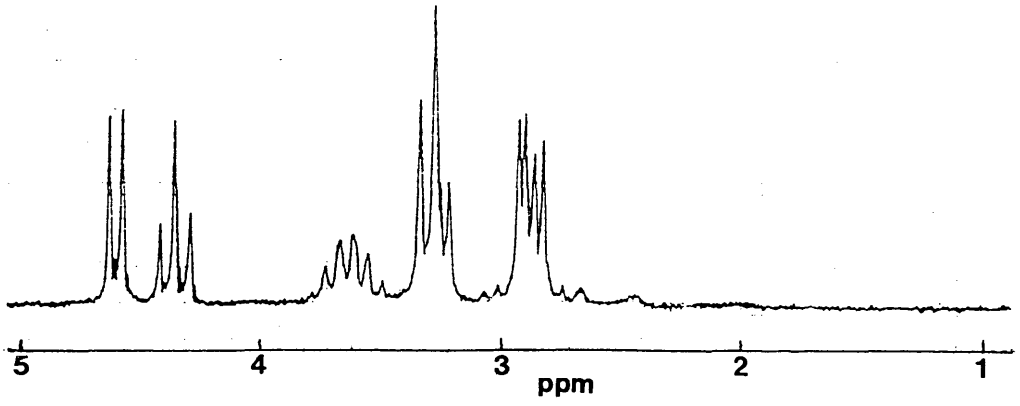


Fig.4.2 ^1H NMR spectrum of TDOL



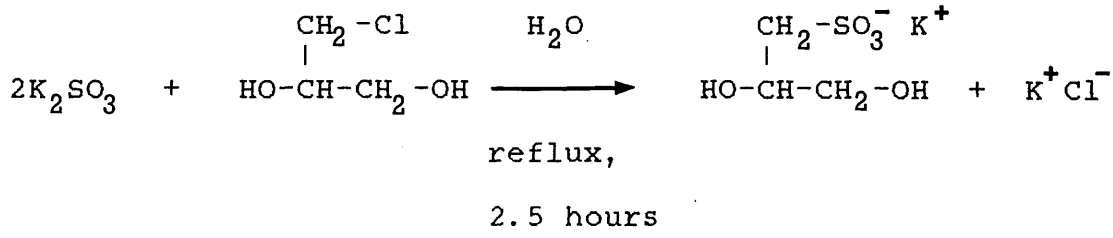
4.3. Preparation of Potassium-S-1,2-dihydroxypropyl Sulphonate(SDOL) and Sodium-S-1,2-dihydroxypropyl Sulphonate(SDPS)

The good nucleophilicity possessed by the thiosulphate ion has led to the exploration of more possible nucleophiles for use in the synthesis of new ionic diols. One of the most promising nucleophile is the sulphite ion which has a structure closely resembling to that of the thiosulphate ion.

Streitwieser and Heatcock have tested the correlation between basicity and nucleophilicity of a series of bases with some common substrates by plotting the rate constants against the corresponding pKa values(144). These authors showed that the sulphite group was more basic than the thiosulphate ion and that the nucleophilicity of the sulphite group was almost as good as the thiosulphate ion. Therefore, the use of a sulphite ion as an attacking group in the S_N2 reaction involving CPD was investigated.

The reaction conditions used for the synthesis of SDOL and the sodium salt analogue, SDPS, were similar to that used for TDOL. To allow for the slightly lower nucleophilicity of the sulphite ion, an extra 0.5 hour was given for the reaction. As discussed earlier, the sulphite ion is expected to react with its substrate wholly on the sulphur atom because of the more diffuse

nature of the lone pair of electrons of the second row elements compared to those of the first row.



4.4. Characterisation of SDOL and SDPS

Both SDOL and SDPS are crystalline white solid when pure. The solubility of both SDOL and SDPS in various solvents is slightly lower than that of TDOL. For example, SDOL was found to be only slightly soluble in DMF and virtually insoluble in ethanol and other less polar organic solvents.

The elemental analysis results of both SDOL and SDPS are presented in Table 4.2 and Table 4.3, respectively. The results indicate the correct amount of elements present in both compounds.

Table 4.2. Elemental analysis result for SDOL

Element	C(%)	H(%)	S(%)
Found	17.62	3.24	15.54
Calculated	18.53	3.60	16.47

Table 4.3. Elemental analysis result for SDPS

Element	C(%)	H(%)	S(%)
Found	20.22	3.93	17.98
Calculated	19.62	4.68	17.20

The structure of SDPS has been further confirmed by mass spectroscopy. MH^+ (FAB) for SDPS=179.

There are no difference in the IR and ^1H NMR spectra between SDOL and SDPS. The IR and NMR spectra of SDOL are presented in Fig.4.3 and Fig.4.4 respectively. The IR spectrum of SDOL bears a close resemblance to that of TDOL. The major difference being that the sharp peak at 420cm^{-1} due to SS stretch in the spectrum of TDOL was absent in that of SDOL. Two strong sharp bands at 520cm^{-1} and 620cm^{-1} have been assigned to SO deformations, a strong sharp peak at 1040cm^{-1} and a strong broad band centred at 1200cm^{-1} to SO stretching frequencies. Other major absorptions may be assigned readily by reference to standard texts(145).

The NMR spectrum of SDOL is assigned as follows: H(a) is a doublet centred at 4.87ppm. H(b) is a triplet centred at 4.6ppm, H(c) is a multiplet centred at 3.85ppm. Due to the chiral centre present at the central carbon, the pro-chiral centres on either side can effect geminal splitting of the protons. The protons at C1 are split by the methine proton at the chiral centre and experience a

Fig.4.3 IR spectrum of SDOL

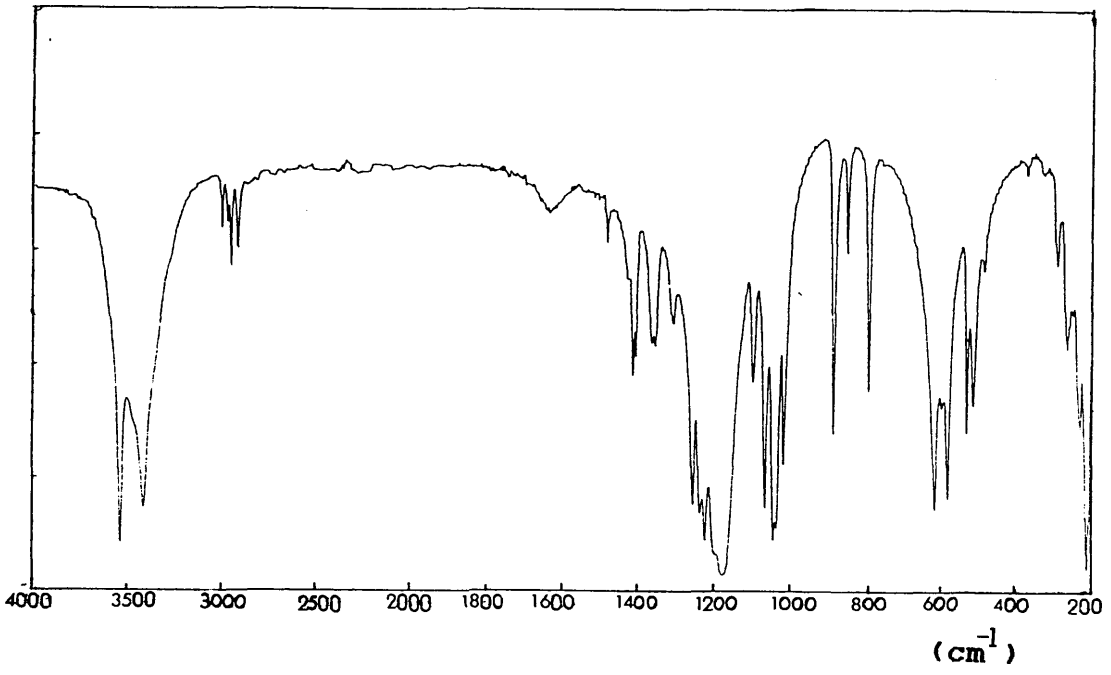
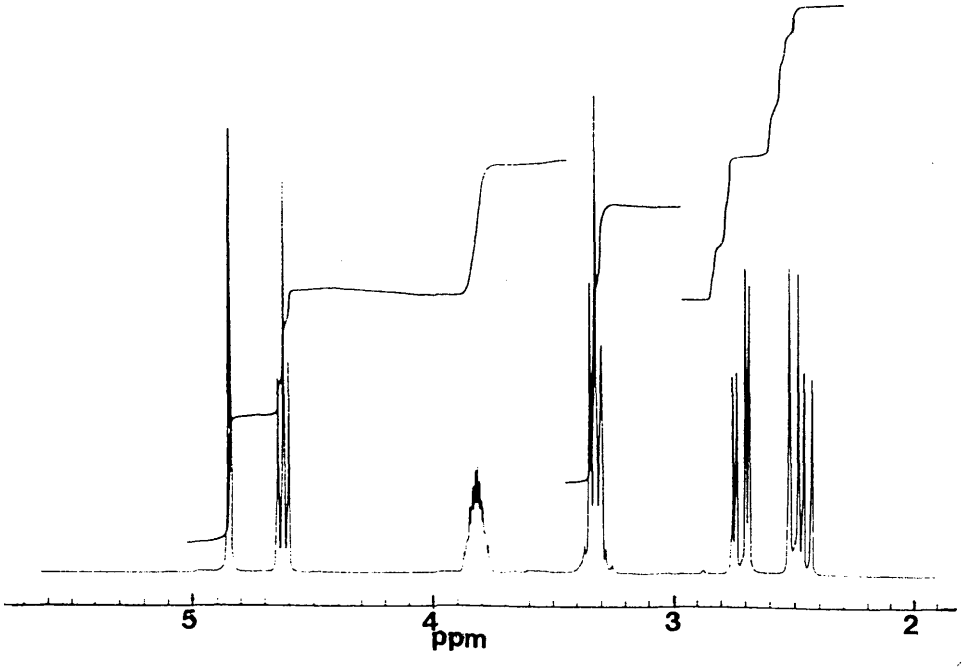
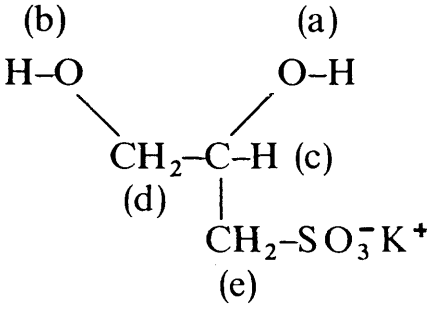


Fig. 4.4 ^{1}H NMR spectrum of SDOL



splitting by the adjacent hydroxyl proton forming a double doublet. Geminal splitting results in 8 lines to the resonance pattern for H(d). Similarly, the protons adjacent to the sulphonate H(e) are split into a double doublet. A triplet is observed at 3.34ppm, however, due to resolution limitation.



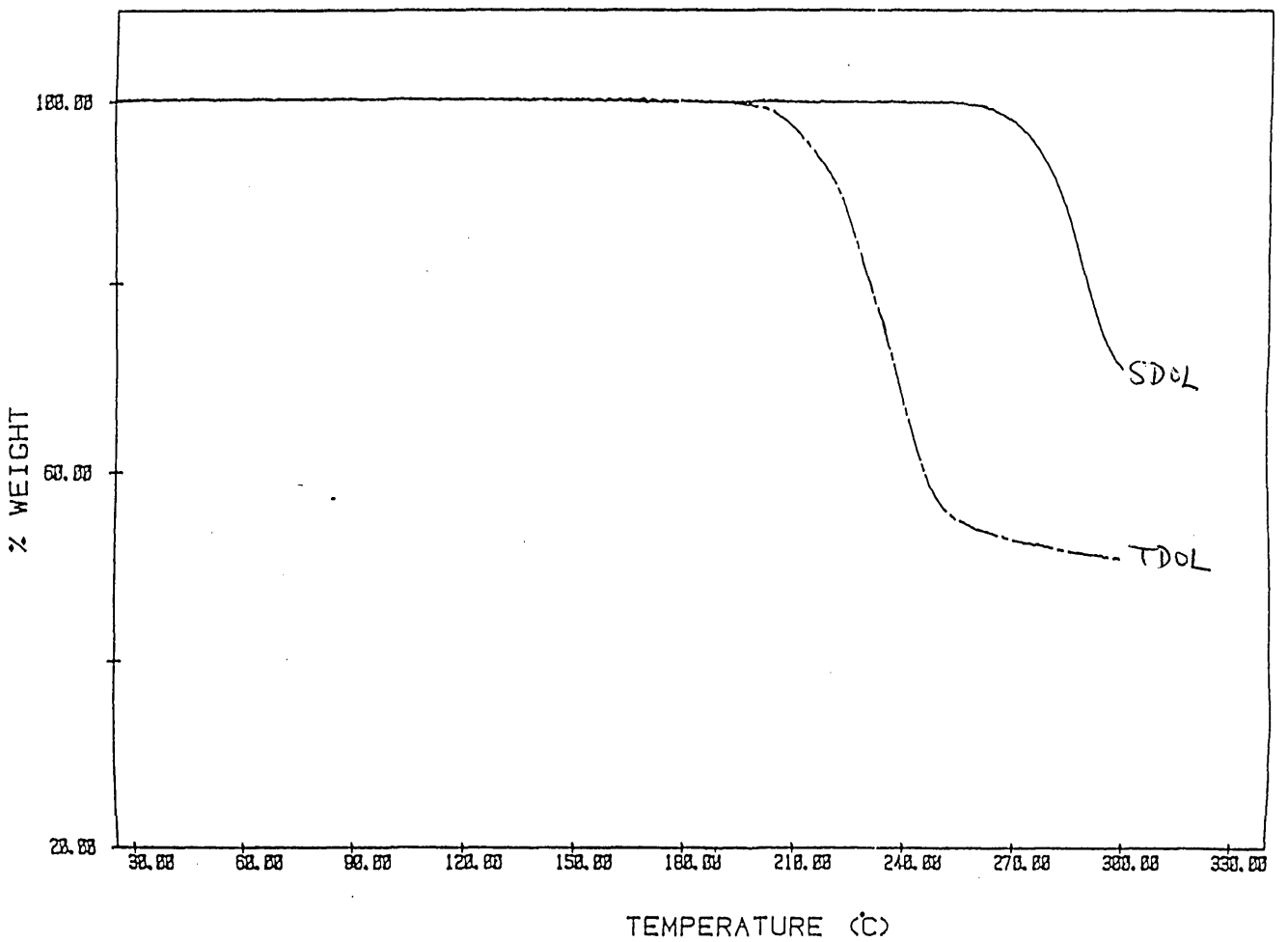
4.5. Thermal stability of TDOL and SDOL

As the ionic diols were subjected to relatively high temperatures during the synthesis of ionomers, the thermal stability of both TDOL and SDOL were assessed by means of thermogravimetric analysis. The results are shown in Fig.4.5. The thermal stability at 5% weight loss for the two ionic diols are tabulated in Table 4.

Table 4.4. Thermal stability of TDOL and SDOL as determined at 5% weight loss

Diol	Temperature at 5% weight loss
TDOL	208
SDOL	281

Fig.4.5 TGA thermograms of TDOL and SDOL



The results show that SDOL is very stable with vitually no weight loss up to 270°C. On the other hand, decomposition of TDOL started at a much lower temperature. The lower decomposition temperature of TDOL is reflected in the ease with which the S-S bond of the thiosulphate group is broken. This may be attributed to the weaker S-S bond compared to the better overlap C-C bond. The longer S-S bond length relative to the C-C bond may have contributed to the difference in the bond dissociation energies(146).

D 298 S-S=101.7kcal mol, D 298 C-C=145.0kcal mol,

D 298 C-S=182.0kcal mol.

All these results suggest that although the thermal stability of TDOL is much less than that of the SDOL, both SDOL and TDOL seem to be stable to fairly high temperature in the solid state. However, isothermal scan is expected to give a better understanding of the thermal stability of these ionic diols. Such scans were not available due to the lack of computer software. It has been reported that sodium S-ethyl and S-benzyl thiosulphates decomposed to give sodium dithionate and the coressponding disulphide at 100°C in the solid state(147). On the other hand, Milligan and Swan emphasized that the alkali metal salts are usually fairly stable, even at 100°C in aqueous solution(142).

4.6. Synthesis and Characterisation of Polyurethane Ionomers

Nomenclature Used for different Series of Polyurethane Ionomers

Polymer Composition	Polymer Code		Hard Segment Content(wt.%)
	Ionic	Non-ionic	
PP1025/MDI/BD/TDOL	PP-X-Th/BD	PP-0	~50
PP1025/MDI/BD/SDOL	PP-X-S/BD	PP-0	~50
PP2025/MDI/BD/TDOL	PP-X-Th/BD2	PP-02	~36
PP2025/MDI/BD/SDOL	PP-X-S/BD2	PP-02	~36
PE1025/MDI/BD/SDOL	PE-X-S/BD	PE-0	~50
PTMG1025/MDI/BD/TDOL	PTMG-X-Th/BD	PTMG-0	~50
PTMG1025/MDI/BD/SDOL	PTMG-X-S/BD	PTMG-0	~50
PP1025/MDI/BD/SDPS	PP-X-SDP/BD	PP-0	~50

X is the % of ionic diols in the chain extenders. e.g. for the synthesis of PP-100-Th/BD, only TDOL was used in the chain extension step, whereas for the synthesis of PP-50-Th/BD, 50% of the TDOL was substituted with butane-1,4-diol. For non-ionic (control) polymers, samples with the same code represent polymers of identical composition.

Sample Code	mole % of ionic groups in the polymers
X=10	3.4
X=25	8.5
X=50	17.1
X=75	25.6
X=100	34.1

Study of extent of polymerisation using GPC:

The extent of polymerisation in the formation of polyurethanes and their ionomers has been followed by Gel Permeation Chromatography. Fig. 4.6 and Fig. 4.7 show the GPC chromatograms of PP-0 and PP-25-Th/BD at different polymerisation times. The results indicate that for both polymer systems, there seem to be no further increase in molecular weight after a reaction time of four hours. In the synthesis of PP-25-Th/BD and all other ionomers, due to the presence of a less reactive secondary hydroxyl group in TDOL and SDOL or SDPS, a reaction time of ten hours was used in an attempt to push the polymerisation to completion. The peculiar shape of the chromatograms of PP-25-Th/BD will be discussed in Section 4.9.

Fig.4.6 GPC Chromatogram of PP-O
at Various Reaction Times

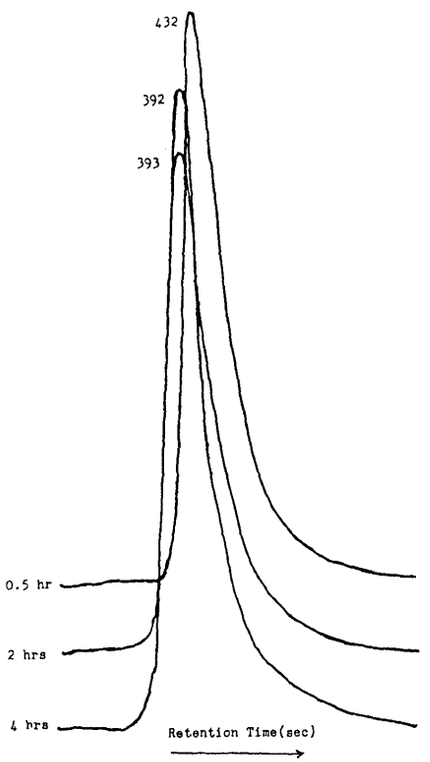
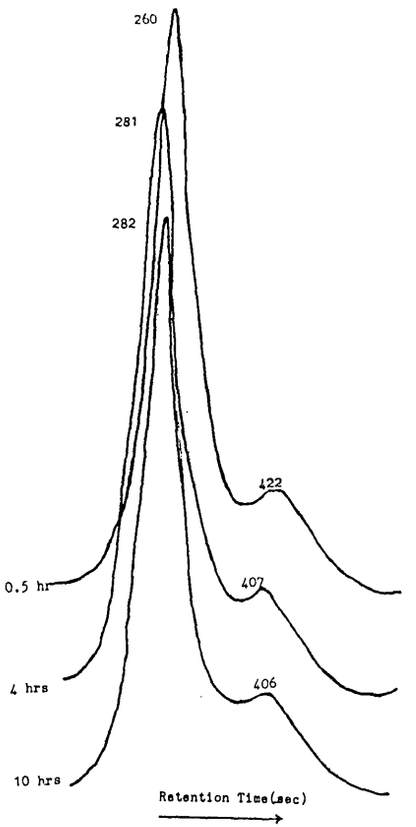


Fig.4.7 GPC Chromatogram of PP-25-Th/BD
at Various Reaction Times



Elemental analysis of polyurethanes and ionomers:

Elemental analysis results for both the non-ionic polyurethanes and the ionomers were found to be of limited use, possibly due to the occurrence of side reactions during synthesis. This technique was nevertheless used as a further check for sample purity and for monitoring the possibility of solvent retention in the polymers.

Solubility of polyurethanes and ionomers:

The solubility of the PP-X-Th/BD series of ionomers in various solvents is briefly summarised in Table45.

Table 4.5. Solubility of non-ionic and ionic polyurethanes

Solvent	PP-0	PP-50-Th/BD	PP-100-Th/BD
DMF	Fully soluble	Fully soluble	Fully soluble
DMA	Fully soluble	Fully soluble	Fully soluble
DMSO	Fully soluble	Fully soluble	Fully soluble
THF	Fully soluble	Slightly	Barely
Water	Insoluble	Insoluble	Slightly
Toluene	Insoluble	Insoluble	Insoluble
Benzene	Insoluble	Insoluble	Insoluble
Diethyl ether	Insoluble	Insoluble	Insoluble
Ethyl acetate	Insoluble	Insoluble	Insoluble

The results show that all the polymers are fully soluble in highly polar solvents such as DMF, DMA and DMSO which are typical of segmented polyurethanes. These solvents are compatible with the non-polar MDI residues, slightly polar polyether soft segments and the highly polar ionic groups which make up the polymer molecules. THF, which is a solvent for many segmented polyurethanes, does not dissolve the higher ionic content polymers. Its polarity is not high enough to dissolve the large number of ionic groups in these polymers. Other low polarity solvents such as toluene, benzene or diethyl ether are unable to dissolve any of the polymers due to the incompatibility of these solvents with one or more of the groups present in these polymers.

One interesting feature of PP-100-Th/BD is that this ionomer is slightly soluble in water, giving a cloudy solution with a solid residue when the solution is saturated. This is in marked contrast to the non-ionic polyurethane which is virtually insoluble in water with an equilibrium water uptake of only 3.8% at 30°C. All this behaviour is attributed to the dominating effect of the highly polar thiosulphate groups, depressing the solubility in low polarity solvents and enhancing water solubility.

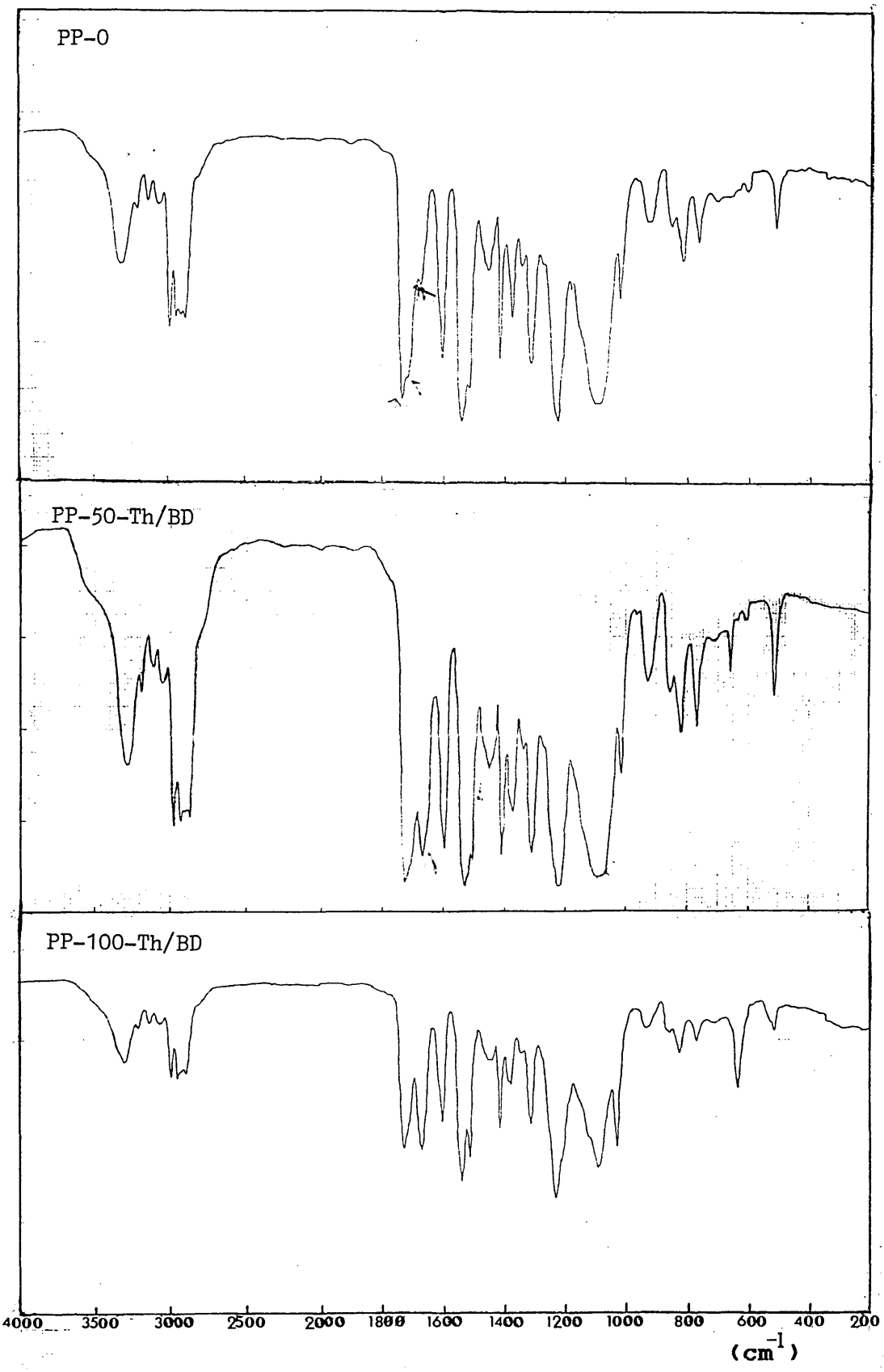
4.7. Infrared Analysis of different Series of Polyurethane Ionomers

Infrared spectroscopy is a crucial technique for the identication of various functional groups present in the polymers. Sample preparation can be carried out in a number of ways depending on the physical state of the material. For all polyurethanes prepared in this study, both ionic and non-ionic, the IR spectra were obtained using thin films of the polymers cast from DMF.

The IR spectra of the PP-X-Th/BD series of ionomers are presented in Fig. 4.8. Comparison of the spectra of the three polymers reveals two major differences. A peak at around 640cm^{-1} in the spectra of PP-50-Th/BD and PP-100-Th/BD is probably due to the SO deformation seen at 650cm^{-1} for TDOL. This is also demonstrated by an increase in intensity of this peak with ionic content seen in the spectra of PP-100-Th/BD. No other bands due to the alkyl thiosulphate group are observed, probably due to the large number of other absorptions present.

The other difference between the three spectra lies in the carbonyl region. PP-0 displays a weak peak at 1670cm^{-1} which may be due to carbonyls involved in hydrogen bonding and a strong peak at 1730cm^{-1} for the free carbonyls. The intensity of the weak peak at 1670cm^{-1} increases with increasing ionic content which suggests that there may be more urethane carbonyls involved in

Fig. 4.8 IR Spectra of PP-X-Th/BD Series of Ionomers

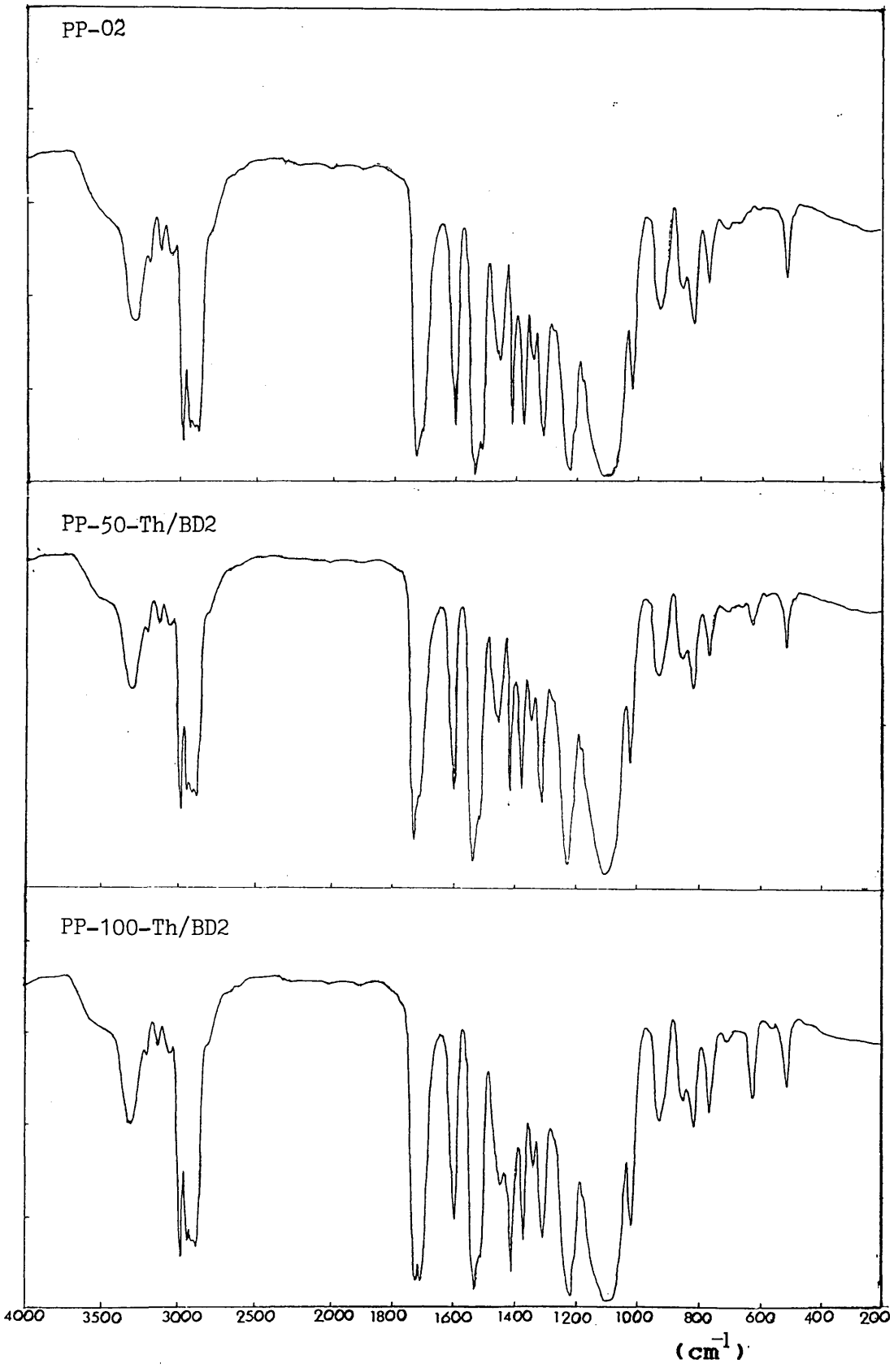


H-bonding in the higher ionic content polymers. Nevertheless, there are still about half of the carbonyl groups which appeared to be non-bonded, even for PP-100-Th/BD, assuming both the bonded and non-bonded peaks have similar absorption coefficients. All three polymers display a broad band at around 3340cm^{-1} typical of N-H groups involved in hydrogen bonding.

These results thus suggest that for the non-ionic control polymer, most of the urethane N-H groups are involved in H-bonding with proton acceptors other than the urethane carbonyls, possibly with the ether oxygens in the soft segments. Incorporation of ionic groups seems to cause more urethane carbonyls to take part in H-bonding and the number increases with increasing degree of ionisation.

Figure 4.9 shows the IR spectra of the PP-X-Th/BD2 series of ionomers. The spectra of this series generally have similar features to those of the PP-X-Th/BD series apart from the carbonyl absorption region. In both the spectra of PP-02 and PP-50-Th/BD2, there is a carbonyl peak at 1730cm^{-1} corresponding to free carbonyls and a very weak peak at around 1700cm^{-1} possibly due to carbonyls involved in H-bonding . The spectrum of PP-100-Th/BD2, on the other hand, shows two absorption peaks of approximately equal intensities at these two frequencies.

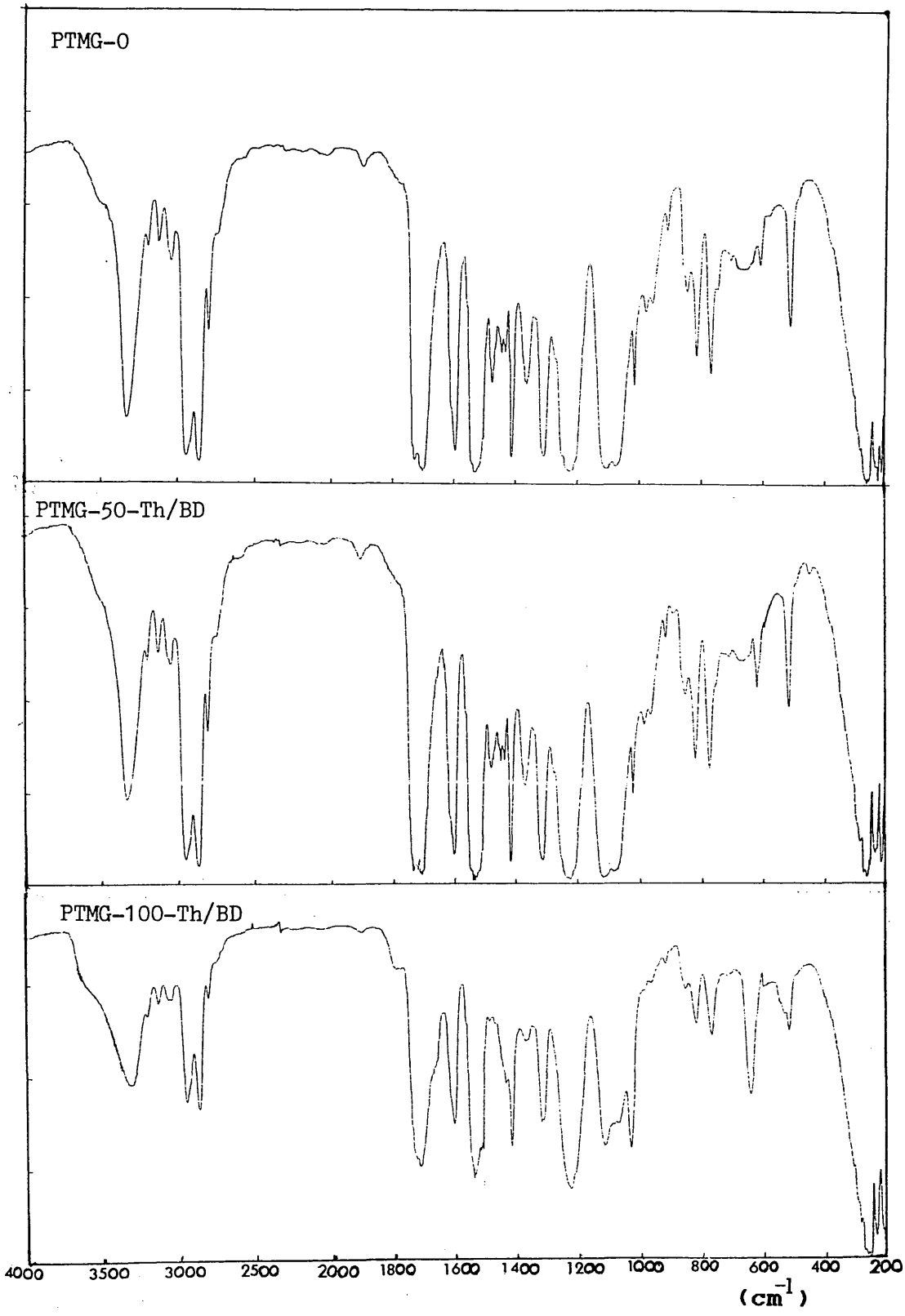
Fig.4.9 IR Spectra of PP-X-Th/BD2 Series of Ionomers



The frequency of the bonded carbonyl peak in this series of ionomers appears to be somewhat higher than that of the PP-X-Th/BD series. The shift of frequency resulting from H-bonding depends on the strength of the H-bonds. In general, stronger H-bonds cause a greater shift than weaker bonds. For instance, in polyester polyurethanes the H-bonds between the carbonyls of the polyester soft segments and the urethane N-H are weaker than those between the urethane carbonyls and urethane N-H and absorb at a frequency closer to that of the free carbonyl(148). The difference in frequency shift between these two series of ionomers, however, cannot be due to H-bond strength as the urethane carbonyls are the only type present in both series. Another possible interpretation is related to the hard segment domain morphology between the two series of ionomers. The PP-X-Th/BD series of ionomers is likely to have a more interconnected domain structure compared to the higher molecular weight soft segmented-based PP-X-Th/BD2 series (58). Perhaps this interconnected domain structure causes a difference in the strength of the H-bonds. It is also important to note that the hard segment concentration of the PP-X-Th/BD2 series of ionomers is slightly lower than that of the PP-X-Th/BD series as shown in Section 4.6.

The IR spectra of the PTMG-X-Th/BD series of ionomers are given in Fig. 4.10. In common to the other two series, the most interesting part of these spectra lies in the

Fig.4.10 IR Spectra of PTMG-X-Th/BD Series of Ionomers



carbonyl absorption region. Both spectra of PTMG-0 and PTMG-50-Th/BD show two peaks at around 1730cm^{-1} and 1700cm^{-1} with the latter peak more intense. The spectrum of PTMG-100-Th/BD on the other hand, reveals some rather peculiar features. A main absorption peak is observed at around 1700cm^{-1}, together with a shoulder peak at around 1670cm^{-1} . The presence of the shoulder peak at 1670cm^{-1} indicates that there may be three types of carbonyls present in the system. The first peak at 1730cm^{-1} was observed in all three series of ionomers. The second peak at 1700cm^{-1} was revealed in the PP-X-Th/BD2 series and this series of ionomers and possibly in PP-0, while the shoulder peak at 1670cm^{-1} observed in PTMG-100-Th/BD was also detected in the PP-X-Th/BD series of ionomers.

By carefully re-examining the spectrum of PP-0 in Fig.4.8, a feature similar to that of the PTMG-100-Th/BD system is just visible, i.e. the presence of three carbonyl absorption peaks, but with the main peak at 1730cm^{-1} compared to 1700cm^{-1} as observed in the PTMG-100-Th/BD system. All these observations seem to indicate that there are indeed three types of carbonyls present in some of the polymers. The peaks at 1730cm^{-1} and 1700cm^{-1} are thought to be due to free and H-bonded carbonyls respectively. The third peak at 1670cm^{-1}, however, may well be due to a completely different type of carbonyl. This has been subsequently identified as the

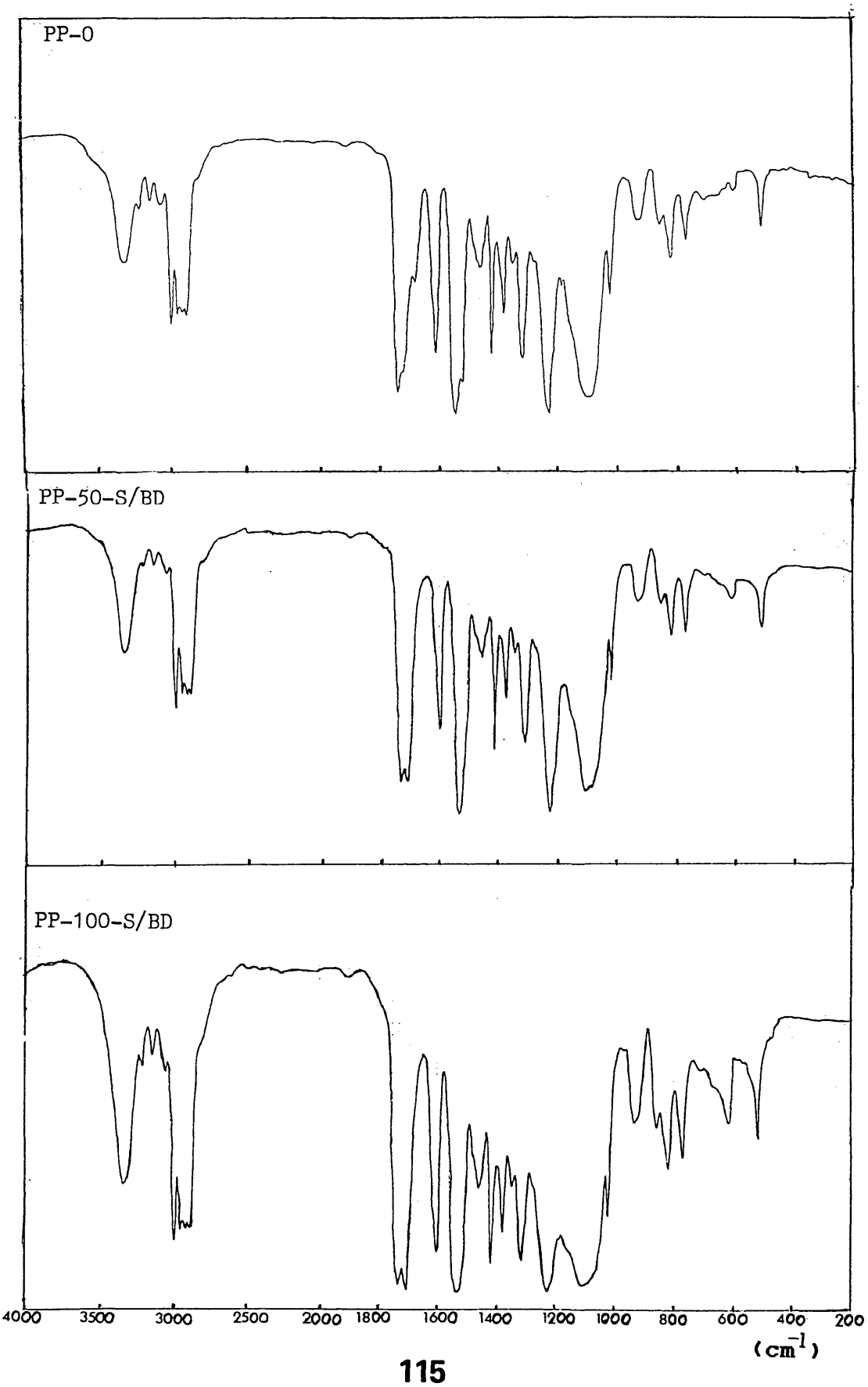
carbonyl of DMF which was used as casting solvent for all the polymers.

Fig. 4.11 illustrates the IR spectra of the PP-X-S/BD series of ionomers. The presence of the sulphonate group can be identified as an absorption peak at around 610cm^{-1} due to SO deformation whose intensity increases with increasing ionic content. Looking at the carbonyl absorption region of this series of ionomers, the bonded and non-bonded peaks at 1700cm^{-1} and 1730cm^{-1} in PP-50-S/BD are of nearly equal intensity, while the bonded carbonyl peak in PP-100-S/BD seems to be slightly more intense than the non-bonded peak.

The infrared analysis results for the various series of ionomers can thus be summarised as follows: For the PP-X-Th/BD series of ionomers, there appears to be some DMF present in all the polymers, the amount increases with increasing ionic content. The introduction of ionic groups does not seem to have any effect on the H-bonding behaviour and therefore the degree of phase separation of this series of polymers. This is not surprising as DMF is a good solvent for both the hard and soft segments and solvation of both segments by this solvent will undoubtedly interfere with the balance of H-bonding between the two segments.

On the other hand, introducing ionic groups into all the other series of ionomers caused an increase in the

Fig.4.11 IR Spectra of PP-X-S/BD Series of Ionomers



number of urethane carbonyls taking part in H-bonding, and consequently an increase in the degree of phase separation which is similar to results of other investigators(111-114). The effectiveness of the ions in improving the degree of phase separation in the various series of ionomers appears to be in the order PP-X-Th/BD2 < PP-X-S/BD < PTMG-X-Th/BD assuming the slightly lower hard segment content in the PP-X-Th/BD2 series does not have any significant effect on the H-bonding behaviour.

4.8. ^{1}H NMR Analysis of PP-X-Th/BD Series of Ionomers

The information obtained from the ^{1}H NMR spectra of polymers is generally rather limited compared to those obtained from the spectra of simple organic molecules such as TDOL and SDOL. This is due to the fact that many resonance peaks in polymers fall into a small range of region on the scale of the NMR spectrum that often cause overlapping of signals. Therefore only a few of the isolated peaks can be positively assigned with reference to model compound study(149).

The ^{1}H NMR spectra of the PP-X-Th/BD series of ionomers are shown in Fig.4.12-Fig.4.14, respectively. The spectrum of butane-1,4-diol is also presented in Fig.4.14 for the purpose of comparison. The spectra of all the polymers can be assigned qualitatively as follows. The resonance signal at δ=1.1ppm is due to the methyl protons

Fig.4.12 ^{1}H NMR Spectra of PP-0 and PP-25-Th/BD

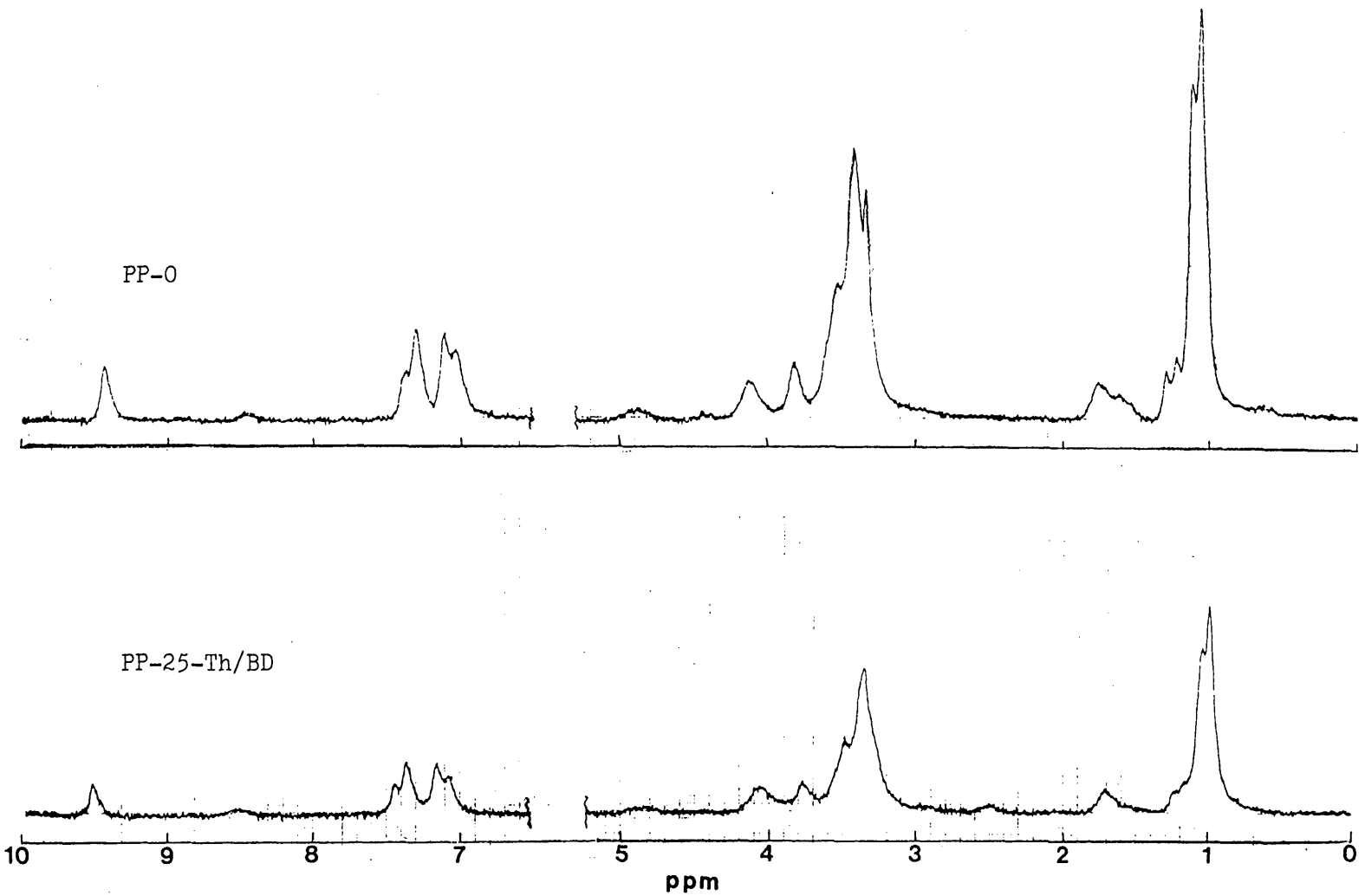


Fig.4.13 ^{1}H NMR Spectra of PP-50-Th/BD and PP-100-Th/BD

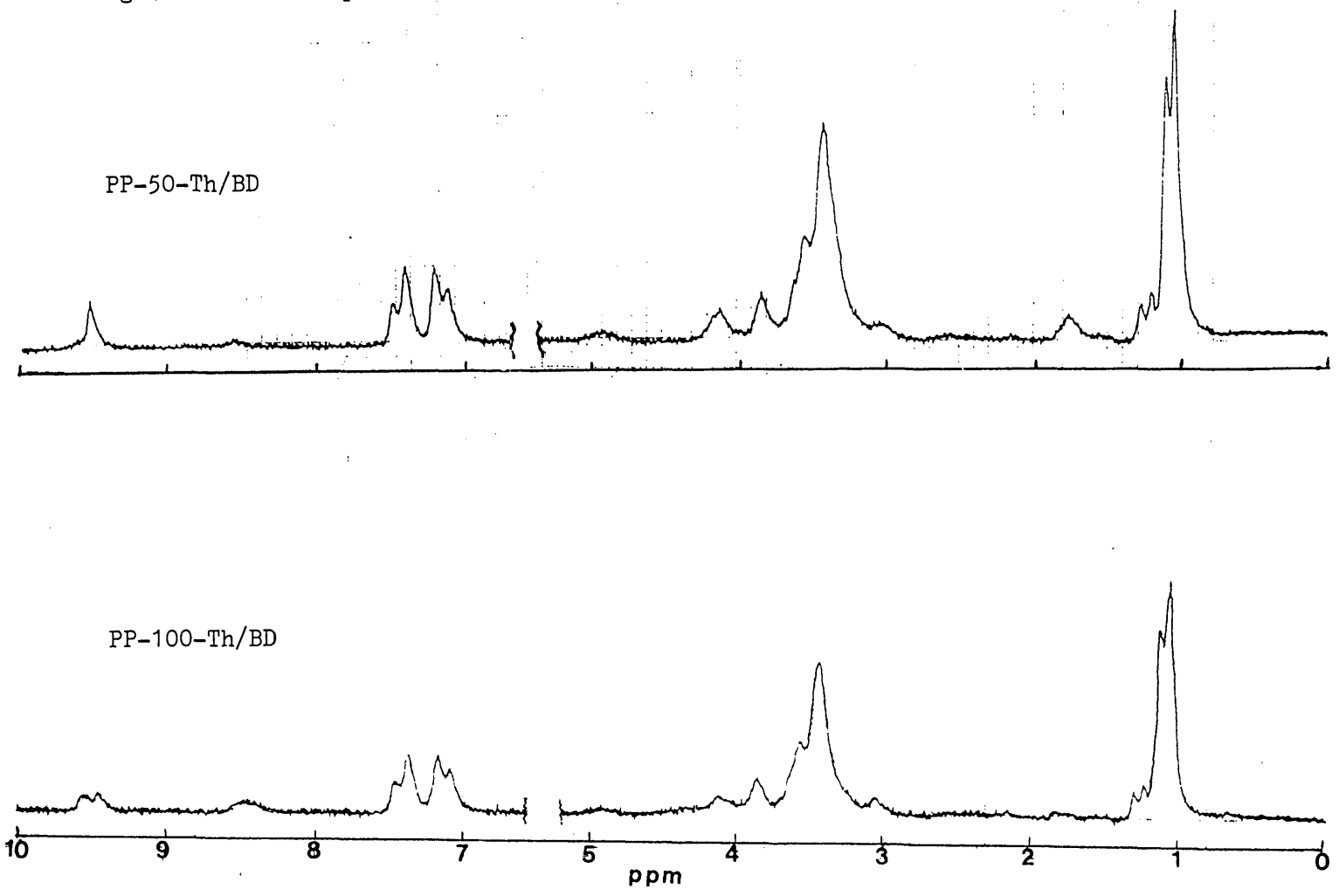
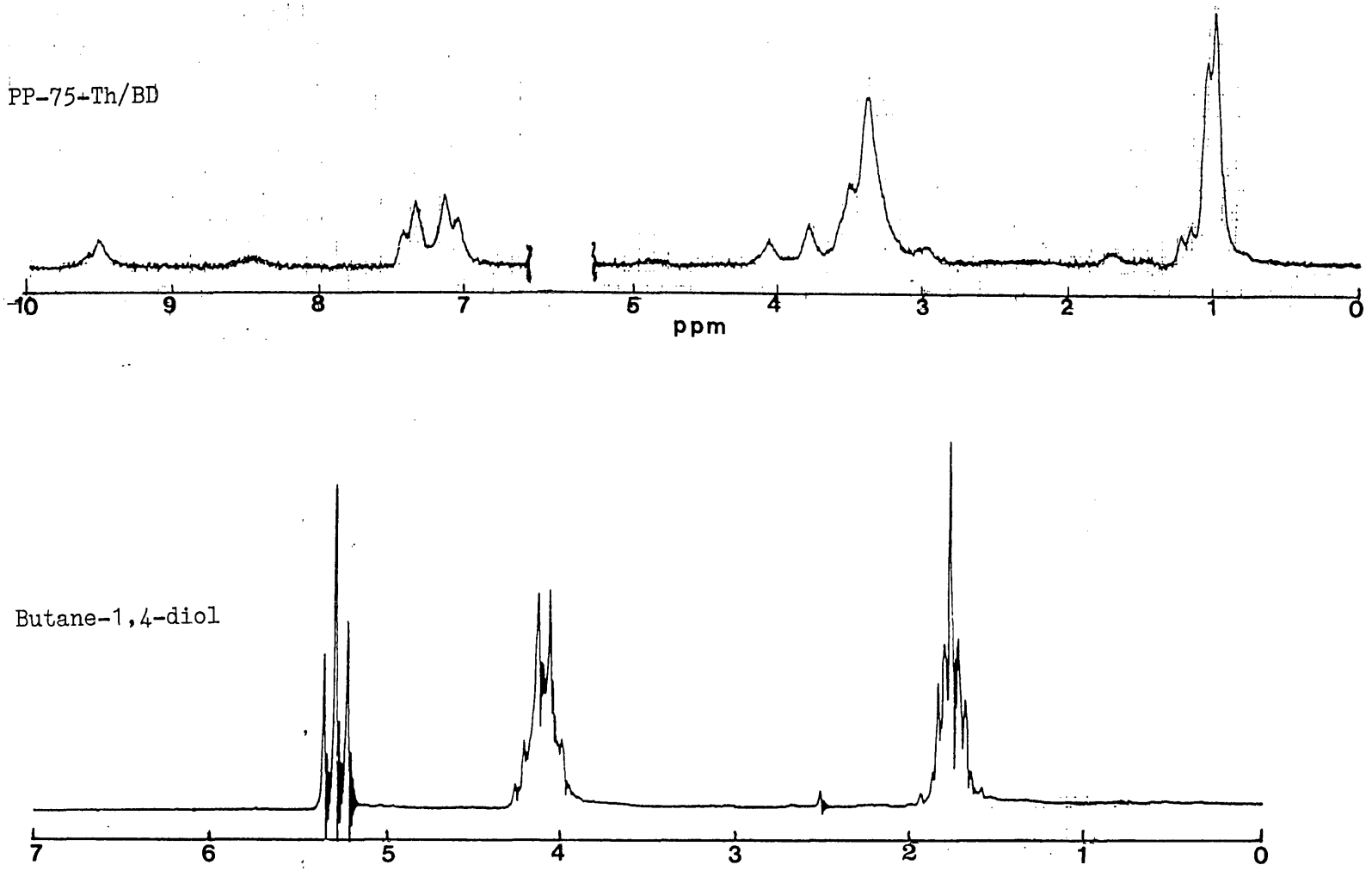


Fig.4.14 ^{1}H NMR Spectra of PP-75-Th/BD and Butane-1,4-diol



in polypropylene glycol. The peak at δ=1.75ppm corresponds to the central methylenes (CH_2) in the butane-1,4-diol hard segments. The resonance peak of the terminal methylenes (CH_2O) in the butane-1,4-diol hard segment is possibly that at around δ=4.1ppm. All signals fall into the region δ=3ppm to δ=5ppm make positive assignment difficult as this is the most crowded region on the NMR scale. Two other regions that can be assigned with certainty are that at δ=7.2ppm due to the aromatic protons and that at around δ=9.45ppm which corresponds to the urethane proton. Rather surprising, the signal of urethane proton is observed as a singlet for all the polymers except for PP-75-Th/BD and PP-100-Th/BD in which the presence of doublet is just visible. Based on the number of different diol residues adjacent to the urethane group which include PPG, BD and TDOL, there should be more than one signal present in all the systems. Furthermore, the unsymmetrical structure of both PPG and TDOL should yield even more multiple peaks. These complex signals would be expected to show up in a higher resolution spectrum.

The major difference between the spectra of the series of ionomers is the gradual decrease of the peak area at δ=1.75ppm and δ=4.1ppm with increasing ionic content due to the butanediol residue. In the spectrum of PP-100-Th/BD, the complete disappearance of the signal at δ=1.75ppm confirmed the identity of this signal as only

TDOL was used in the chain extension step. However, the peak at δ=4.1ppm is still visible in the spectrum of PP-100-Th/BD although the area has decreased considerably. This peak is likely to be an overlap of more than one signal, and possibly includes the methylene resonance in polypropylene glycol. A very weak but detectable resonance signal has been observed at around δ=8.5ppm in all the spectra. This is assigned as the resonance of urea protons resulted from the reaction of isocyanate with traces of water. The presence of relatively low levels of urea indicate the need for more precaution on eliminating moisture during the synthesis.

4.9 Gel Permeation Chromatography of Polyurethane Ionomers

The main purpose for employing GPC is to analyse the molecular weight and molecular weight distribution of polymeric materials. For most non-ionic polymers, the relative molecular weights and distributions can be conveniently obtained from the calibration curve of $[\eta]$ M vs retention time. The relative molecular weights of the various non-ionic polyurethanes as determined by this method are shown in Table 4.4.

Table 4.4 Molecular weights and distributions of various non-ionic polyurethanes determined by GPC

Polymer Code	Molecular Weight		Polydispersity * (D)
	$\bar{M}n$	$\bar{M}w$	
PP-0	12736	55402	4.35
PP-02	8692	38070	4.38
PTMG-0	13436	47026	3.50
PE-0	10489	28320	2.70

*D, the polydispersity is equal to ($\bar{M}w/\bar{M}n$)

The result shows that the molecular weight of all the polymers is on the low side, particularly the PP-02 polymer which is likely to have a significant effect on many of the properties of the polymers. There are many factors which influence the molecular weight of the polymers obtained by step growth polymerisation as discussed in Chapter One. These mainly concern with the purity of monomers and solvents, reactant balance, presence of moisture, side reactions, etc. In the present study, all the necessary measures have been taken to avoid the occurrence of these unwanted effects. For instance, hydroxyl analysis has been performed on all the polyols as described in Section 3.7. This analysis is crucial as the functionality of the polyols has been proved to vary considerably from batch to batch. Furthermore, all the reactants have been extensively

dried and purified prior to use and precuations have been taken to minimise the presence of moisture in the reaction medium. Despite all the steps taken, the observed results indicate that some adverse effects may still exist in the present polymer systems.

GPC separation of ionic polymers, on the other hand, is much more complicated owing to the various interactions between ions and polymer or solvent or column material. The presence of these interactions often lead to apparent molecular weight which is much higher than that of the same polymer without any ions, and in most cases resulted in anomalous molecular weight distributions(131,135,150). Therefore molecular weight interpretation from GPC for ionic polymers would be totally misleading without considering such interactions.

4.9.1 Effect of Ionic Groups on the Retention Time

The observed results for the polyurethane ionomers investigated in this project show some very unusual elution behaviour with GPC. Fig.4.15 and Fig.4.16 illustrate, respectively, the GPC chromatograms of the PP-X-Th/BD series of ionomers at three different concentrations using DMF as eluent. The dramatic effect of ionic groups on the elution behaviour is immediately recognised when comparing the chromatogram of the ionomers to that of the control polymer PP-0.

Fig.4.15 GPC Chromatograms of PP-O and PP-25-Th/BD at 3 different Concentrations

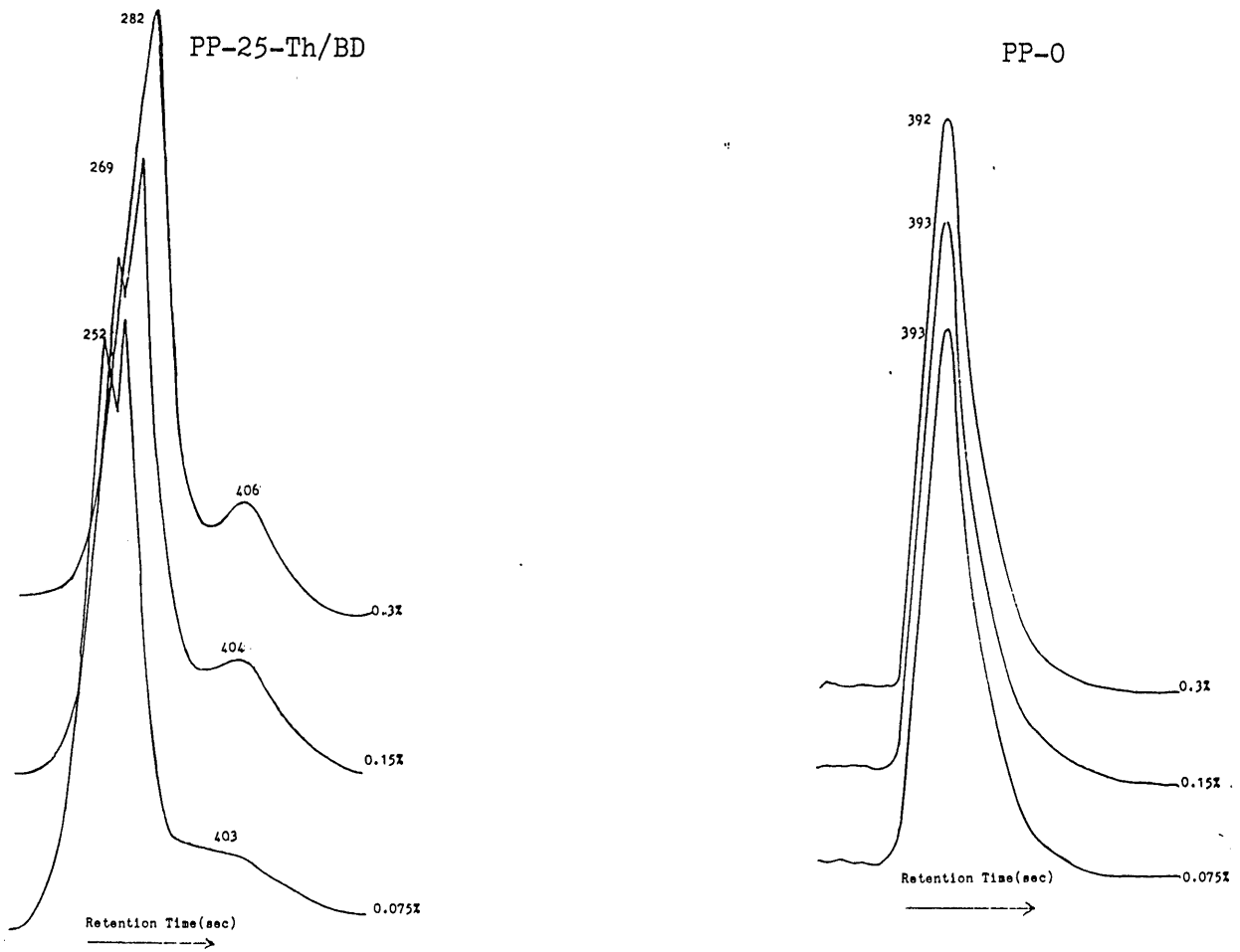
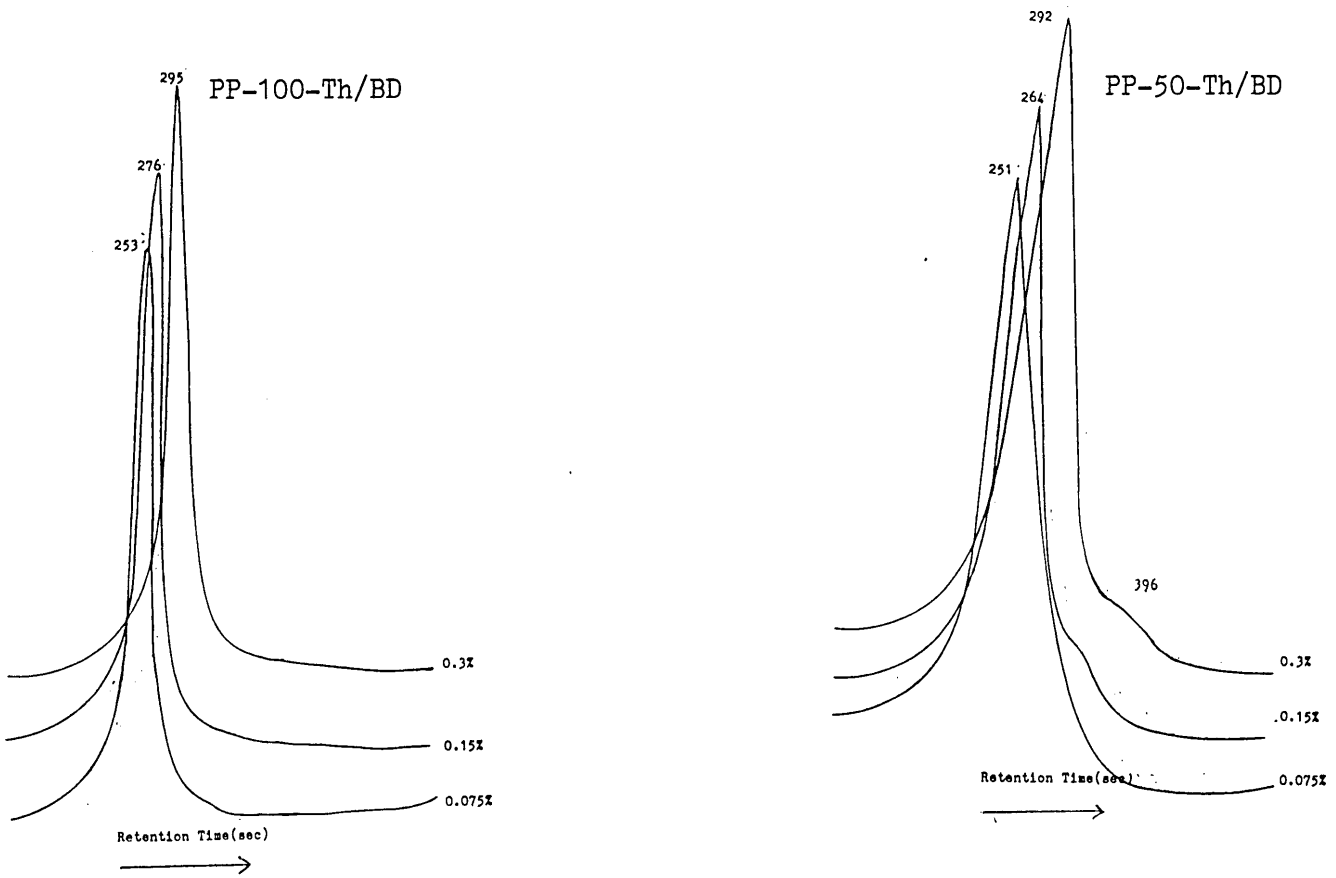


Fig.4.16 GPC Chromatograms of PP-50-Th/BD and PP-100-Th/BD at 3 different Concentrations



Two major differences between the ionomers and the control polymer are noticed:

(a) bimodal-type distributions and varying peak positions at sample concentration of 0.3% are observed in the chromatograms of all the ionomers.

(b) the position and shape of the peaks of all the ionomers are found to change with sample concentrations.

The chromatograms show that the retention time of the ionomers is much smaller than that of the control polymer at the same concentration(0.3%). In addition, more than one peaks are seen in the chromatograms of PP-25-Th/BD and PP-50-Th/BD which is totally unexpected. Based on the polymerisation conditions, the ionomers should have molecular weight similar to that of the control polymer and a unimodal distribution.

Several factors may be responsible for the apparent high molecular weight of the ionomers. First of all, in good solvents such as DMF both the ionic and non-ionic polyurethanes generally take a moderately open conformation due to solvation and intramolecular associations between urethane groups. The presence of ionic groups along the polymer chain of the ionomers cause them to expand compared to the non-ionic polymer. The amount of chain expansion depends on the concentration of ionic groups in the polymer. Hence the amount of chain expansion in PP-100-Th/BD should be more than that of PP-50-Th/BD or PP-25-Th/BD. The fact that

all the ionomers seem to have similar range of retention times suggests that there must be other effects involved apart from electrostatic repulsion.

One more probable cause for the multiple peaks is due to the intermolecular associations between the ionic groups which give rise to the formation of aggregates composed of different number of individual chains. This will cause a much greater increase in molecular weight and is likely to be the major factor responsible for the abnormal increase in molecular weight. The stability of the ionic aggregates depends on the electrostatic force and therefore on the number of ionic groups holding the different chains together. For the lower ionic content polymers, there are fewer ionic groups (fewer association points) and it is possible for the aggregates to break down. In addition, intramolecular association between the urethane groups in the polymer chains can also take place which results in a more closed-chain conformation. The ionic groups in the closed-chains have less tendency to participate in any intermolecular association. This postulation is demonstrated clearly in the chromatograms of PP-25-Th/BD and PP-50-Th/BD. It must be noted that even in PP-25-Th/BD, the number of unassociated chains is much smaller compared to the number of aggregates.

4.9.2. Effect of Sample Concentration on the Retention Time

The second interesting behaviour exhibited by the ionomers is their shorter retention times with decreasing sample concentrations. The behaviour of ionic polymers in dilute solutions depends strongly on the ionic strength of the solution and therefore on the concentration of the ions present. At lower concentrations, i.e. lower ionic strength, DMF acts effectively as a poorer solvent for the highly polar ionomers and there is a strong tendency for intermolecular associations to take place between polymer chains. As the concentration increases, molecular motions can pull apart the larger aggregates. Consequently, the aggregates at higher concentrations are of smaller sizes and appear at higher retention times. For PP-25-Th/BD, the low ionic concentration of this polymer resulted in less stable aggregates as discussed above. The break down of larger aggregates to form smaller ones may be the origin of the multipeaks observed in this system.

Another minor difference between the chromatogram of the ionomers and that of the control polymer is that the sharp front with a low molecular weight tail type of distribution commonly observed for non-ionic polymers becomes the opposite way round in the chromatogram of the ionomers. This phenomenon can be interpreted as follows: As the ionomers flow through the column, those in the

front become more diluted and the resulting aggregates are more stable and of larger sizes. Hence they are excluded from the pores and travel through the column faster. Similarly, the ionomers at the back also experience a similar dilution effect. The larger aggregates formed thus tend to catch up with those in the front and thus result in less tailing in the chromatogram.

4.9.3. Effect of Lithium Bromide on the Retention Time

Fig.4.17 shows the chromatograms of the PP-X-Th/BD series of ionomers in DMF containing 0.5% lithium bromide. The addition of LiBr seems to have no effect on the retention time of the non-ionic polyurethane. On the other hand, the retention of the ionomers are drastically changed in the presence of the electrolyte. Upon addition of LiBr, all the abnormal behaviour previously observed in the ionomers disappeared completely and a normal distribution curve is obtained. The function of LiBr is to screen the ionic groups and thus diminishes the repulsive forces and allows the polymer chains to take on a smaller hydrodynamic volume, observed as an increase in retention time. Furthermore, addition of LiBr effectively shields the charges on the polymer chains which makes ionic aggregation impossible and hence the polymers are eluted as single species. These results are in good agreement with findings by other workers(130,131).

4.9.4. Effect of Temperature on the Retention Time of Ionomers

The chromatograms of the PP-X-Th/BD series of ionomers at 80°C in DMF are presented in Fig. 4.18. A close inspection of these chromatograms reveals a number of differences from those obtained at room temperature. The retention time for all the ionomers appears to be marginally shorter at high temperature. This is to be expected as the viscosity of the polymer solution depends strongly on the temperature. For PP-25-Th/BD, the intensity of the peak at 374s, observed at 406s at room temperature, which corresponds to the elution of single chains is much greater than that obtained at room temperature. Increasing the temperature thus seems to reduce the stability of the ionic aggregates. A similar effect is observed in PP-50-Th/BD. For PP-100-TH/BD, in addition to the broadening of the peak which is due to the break down of larger aggregates, there appears to be a slight shoulder at around 374s. This corresponds to the elution of single polymer chains even for these highly associated ionic aggregates.

Fig.4.18 GPC Chromatograms of PP-X-Th/BD series at 80 C

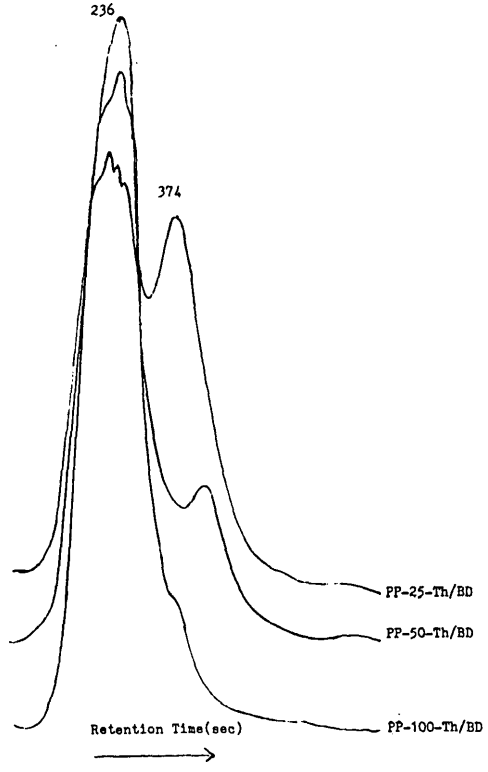
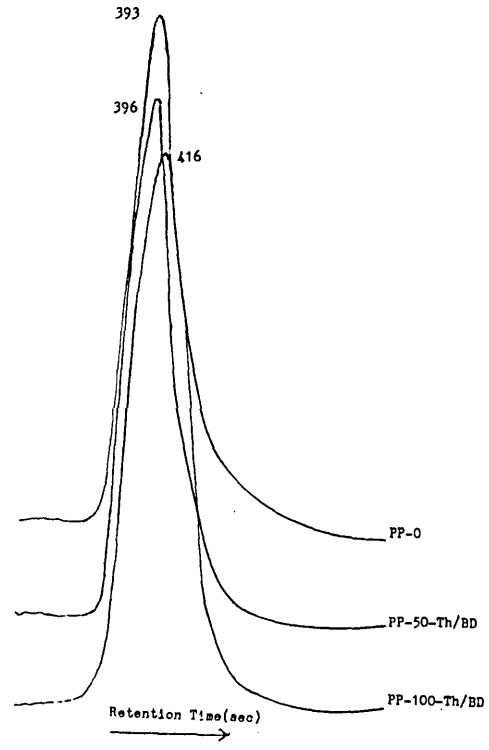


Fig.4.17 GPC Chromatograms of PP-X-Th/BD series containing 0.5% LiBr



4.10. Dilute Solution Viscosity of Polyurethane Ionomers

Discussion in Section 2.9 has shown that GPC separation is directly influenced by the viscosity as well as the molecular weight of the polymer. Results obtained from GPC study suggest that the abnormal solution behaviour may also be present in the viscosity profile of the ionomers. Viscosity measurements of a number of ionomers under various conditions have indeed demonstrated several types of unusual behaviour. The various effects which have been examined include ion concentration, solvent, counterion and the presence of an electrolyte.

Fig. 4.19 shows a plot of reduced viscosity, $(\eta/\eta 0)$, vs concentration for the PP-X-Th/BD series of ionomers in DMF at 25°C. The results indicate that with the exception of PP-0, all the ionomers show an initial fall in reduced viscosity with decreasing concentration, reaching a minimum before starting to rise again. The interpretation for this is that at high concentrations molecular interactions are more favourable than electrostatic interactions. The ionomer chains thus take on a more random conformation and normal viscosity behaviour is observed. That is, the viscosity decreases with decreasing concentration. As the concentration decreases, there are increasing volume for the counterions which tend to distribute themselves at longer distances from

Fig.4.19 Reduced viscosity vs concentration for PP-X-Th/BD in DMF at 25°C

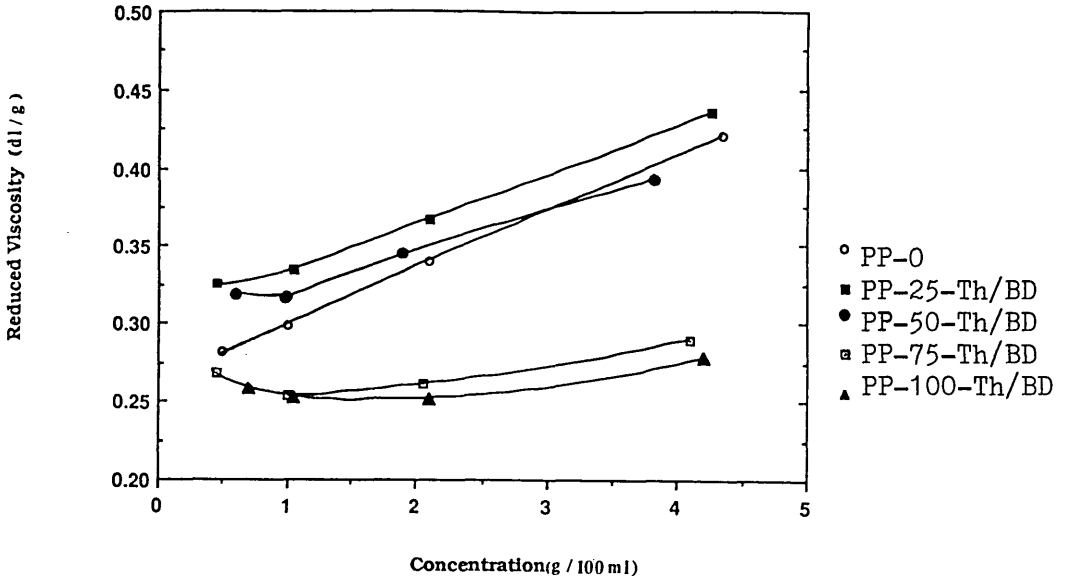
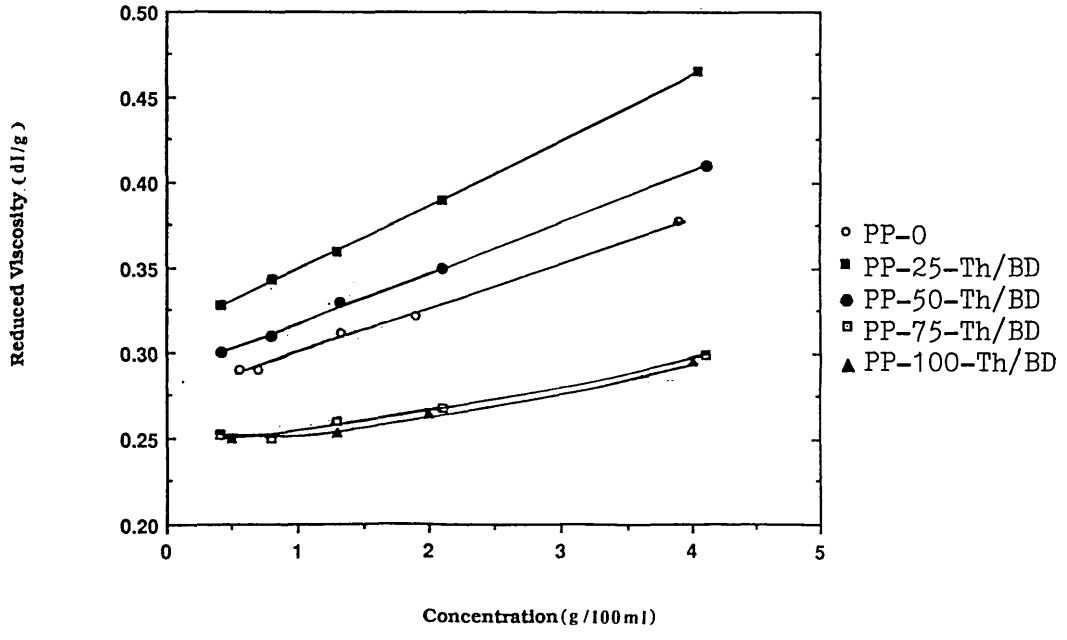


Fig.4.20 Reduced viscosity vs concentration for PP-X-Th/BD in DMF + 0.5% LiBr at 25°C



the ions on the chains. Hence shielding of the fixed charges will be reduced, and electrostatic repulsion will increase, which tends to expand the polymer chain. This is an example of the polyelectrolyte effect. This behaviour is most prominent in PP-100-Th/BD and in PP-75-Th/BD with their high ionic contents, where there is a slight increase in the reduced viscosity with decreasing concentration.

The concentration at which the reduced viscosity starts to rise sharply corresponds to the onset of ionic aggregation which results in a large rise in viscosity. This concentration has roughly been reached in this study. The ionic aggregation begins at different concentrations reflect the different stabilities of the aggregates. Ionomers with higher ionic content tend to form more stable aggregates. For PP-100-Th/BD, ionic association starts at around 1% whereas for PP-25-Th/BD, this occurs at roughly 0.5% .

The effect of 0.5% lithium bromide on the viscosity behaviour of the PP-X-Th/BD series of ionomers in DMF at 25°C is illustrated in Fig.4.20. Upon addition of LiBr, the viscosity of all the ionomers appears to behave as conventional non-ionic polymers. This can easily be explained based on the same argument used when discussing the GPC results. Thus, 0.5% of LiBr has effectively shielded the ionic groups on the ionomer chains and prevents any electrostatic repulsions between ions and

any ionic associations between polymer chains. Similar effects of LiBr on the viscosity behaviour of ionomers have been reported by other workers(125,151).The results also show a gradual decrease in viscosity with increasing ionic content of the ionomers, suggesting a decrease in molecular weight which is consistent with the GPC results shown in Fig.4.17. Here the retention time increases with increasing ionic content of the ionomers.

The high solubility of PP-100-S/BD and PP-100-SDP/BD in water enables the viscosity measurement of these two ionomers to be carried out in aqueous solution. These two ionomers, which contain rather high concentration of ionic groups, may in fact be referred to as polyelectrolytes with low charge density. The results for PP-100-S/BD and PP-100-SDP/BD presented in Fig.4.21 and Fig.4.22 show the effect of different levels of LiBr on the viscosity behaviour of these two systems. In the absence of LiBr, both PP-100-S/BD and PP-100-SDP/BD display typical polyelectrolyte behaviour in dilute aqueous solution. Electrostatic repulsion of charges along the polymer chain causes the chain to expand to achieve greater separation of like charges resulting in an increase of viscosity with decreasing concentration. A continuing decrease in concentration will eventually reach a point where an individual polymer chain becomes fully extended and acts as a rigid rod.

Fig.4.21 Reduced viscosity vs concentration for PP-100-S/BD in water at 25°C

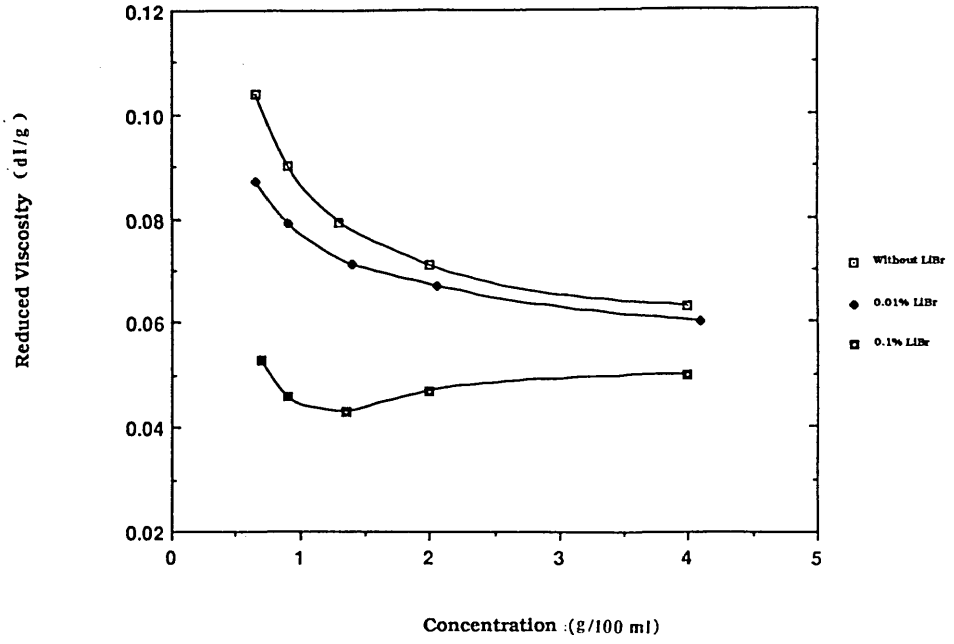
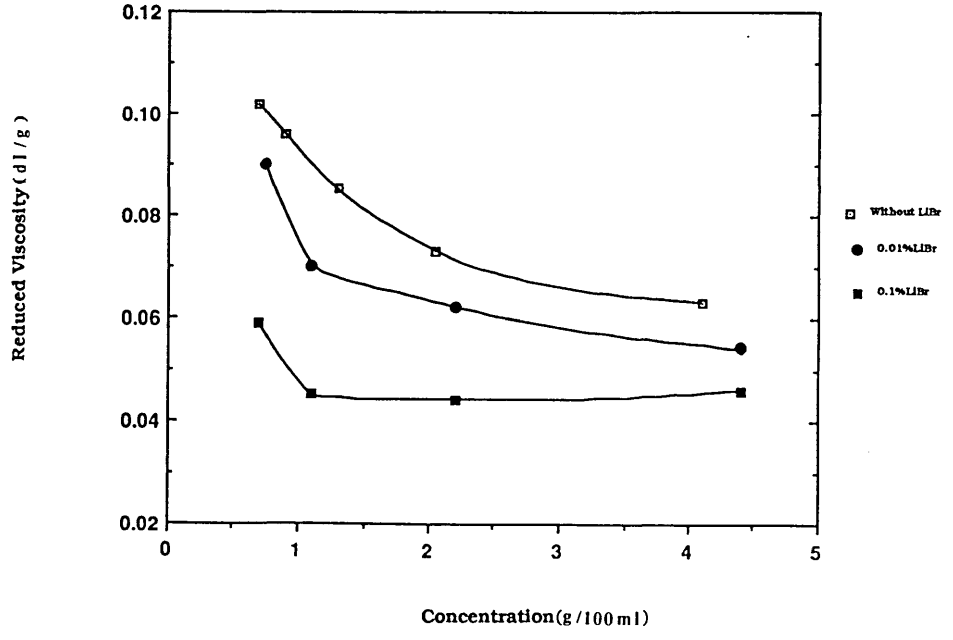


Fig.4.22 Reduced viscosity vs concentration for PP-100-SDP/BD in water at 25°C



Comparing the two systems in the absence of any inorganic salt, it is evident that the rise in reduced viscosity in PP-100-S/BD is much sharper than that of PP-100-SDP/BD. The increase in reduced viscosity is directly related to the strength of the counterion binding the sulphonate group. A potassium ion, which is slightly larger than a sodium ion, will have slightly less binding strength to the sulphonate group than the sodium ion and therefore exhibits a slightly greater "polyelectrolyte effect" The results also indicate that the ability of the LiBr to neutralise and shield the sulphonate ions depends on the concentration of the added salt. While little effect on the viscosity is seen at very low levels of addition, a clear difference is observed at a level of 0.1%. In order to completely eliminate this polyelectrolyte effect, as much as 0.5% of the electrolyte may be required, as shown in the PP-X-Th/BD ionomer system.

4.11. Equilibrium Water Sorption of Polyurethane Ionomers

One of the potential applications of polyurethane ionomers is in the biomedical area such as wound dressings. It is generally accepted that rapid wound healings is provided by dressings which maintain wounds in a moist state(152). In this respect, it is desirable to study the various factors which determine the amount

of water uptake in these highly polar ionic polymers. Results obtained so far include the effects of soft segments, ionic contents, type of anions and counterions and sample history on the water uptake behaviour of polyurethane ionomers.

Fig. 4.23 presents a plot of water uptake vs time for the four non-ionic control polyurethanes based on various soft segments. The equilibrium uptake values of which are tabulated in Table 4.6. The results show that the equilibrium water uptake values of the polymers are in the increasing order PTMG-0 < PPG-0 < PPG-02 << PEG-0. Apart from the PEG-0 polymer, all three polyether polyurethanes have water uptake values below 5%. As expected, the PTMG-0 polymer which contains the fewest number of ether linkage among the four polymers exhibits the least amount of water sorption. The PP-0 polymer which has a higher ether content exhibits approximately twice the amount of water uptake compared to the PTMG-based system. On the other hand, increasing the molecular weight of the soft segment pushes the equilibrium uptake value up even further, shown by the higher water uptake value of PP-02. These figures indicate that the water sorption behaviour in polyether polyurethanes is strongly dependent on the ether content of the polyol used. Water uptake in these polymers mainly proceeds through the binding of water molecules to the polyether oxygen. Although the urethane linkage is more

polar than the ether linkage, solvation of the urethane linkage is less favourable as these are directly linked to the aromatic structure which is highly incompatible with water.

Table 4.6. Equilibrium water uptake for non-ionic polyurethanes at 30°C

Polymer code	Equilibrium water uptake (%w/w)
PP-0	3.8
PP-02	4.3
PTMG-0	1.7
PE-0	41.0

Rather surprisingly, replacing the PTMG soft segment with PEG produces a striking increase in water uptake values. These values are in good agreement with results obtained by Schneider(153) who attributed the large increase in water uptake to the occurrence of specific interactions between water and the ether oxygens in PEG which are not possible in other polyether-based polyurethanes. This hypothesis is further reinforced by the fact that the homopolymer polyethylene oxide is the only member in the homologous polyether series that is water soluble(154).

The effect of ionic content on the level of equilibrium water uptake for the PP-X-Th/BD series of ionomers is

Fig.4.23 Equilibrium water uptake for non-ionic polyurethanes at 30°C

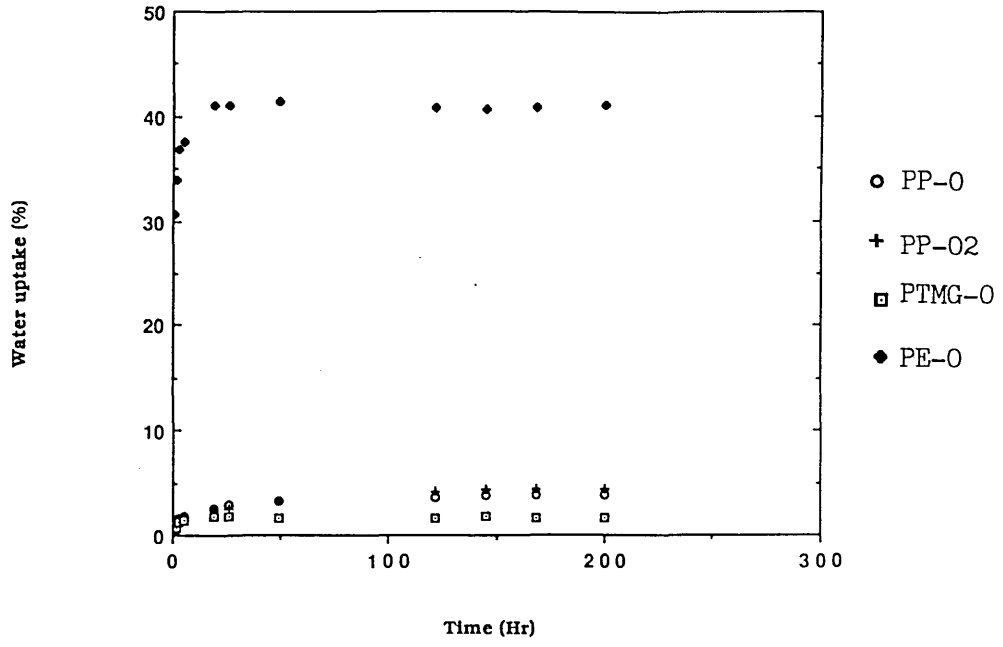
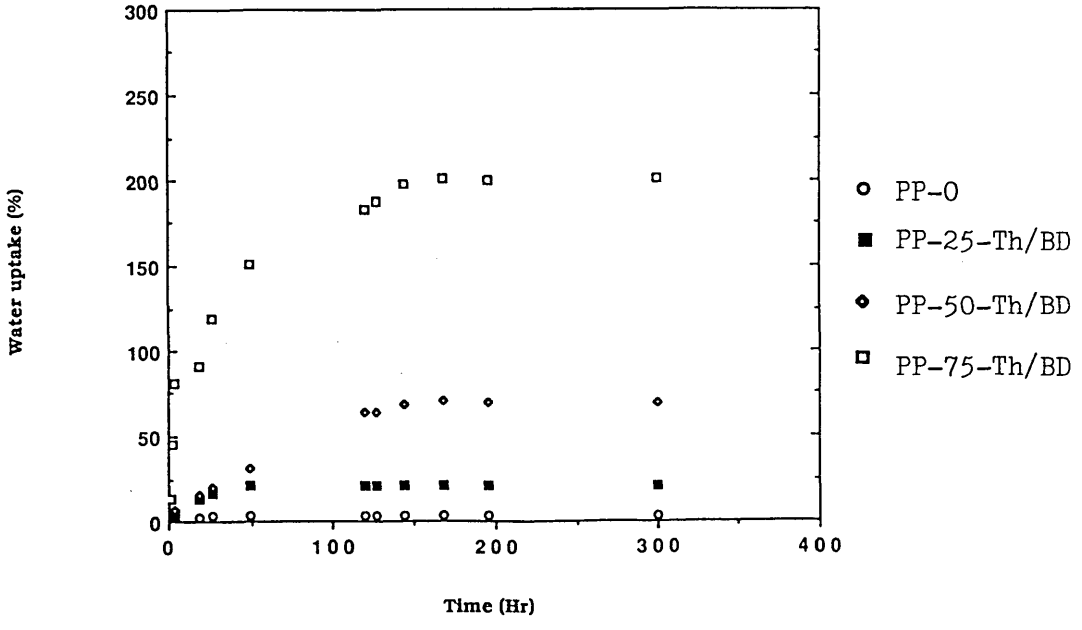


Fig.4.24 Equilibrium water uptake for PP-X-Th/BD at 30°C



illustrated in Fig. 4.24 and the values are tabulated in Table 4.7. The results show that the level of water absorbed increases with increasing ionic content. Data for PP-100-Th/BD could not be obtained as this polymer turned into a gel-like solid with virtually no mechanical strength shortly after it was immersed in water. The observed trend is to be expected as the thiosulphate group has a high affinity for water with solvation energy much higher than that of the ether oxygen. The incorporation of ionic groups creates additional solvation sites for water which results in an increase in water uptake of the polymers. The increasing number of solvation sites with increasing ionic content explains the large increase in water uptake values for the ionomers with high ion contents.

Table 4.7. Equilibrium water uptake for PP-X-Th/BD series at 30°C

Polymer code	Equilibrium water uptake (%w/w)
PP-0	3.8
PP-25-Th/BD	21.2
PP-50-Th/BD	70.1
PP-75-Th/BD	200.5
PP-100-Th/BD	-----

Fig. 4.25 and Table 4.8 show the equilibrium water uptake behaviour of the same series of ionomers after

heat treatment at 120°C for 24 hours. The results indicate clearly that heat treatment causes a pronounced increase in the water uptake level compared to the untreated polymers. The increase is more dramatic in the high ionic content polymers. Furthermore, PP-100-Th/BD, which broke up into a gel before heat treatment, is now completely stable in water. This polymer was found to swell many times of its original size after reaching equilibrium uptake value.

Table 4.8. Equilibrium water uptake for PP-X-Th/BD at 30°C (heat treated at 120°C for 24 hours)

Polymer code	Equilibrium water uptake (%w/w)
PP-0	3.8
PP-25-Th/BD	98.5
PP-50-Th/BD	186.4
PP-75-Th/BD	442.6
PP-100-Th/BD	780.3

The large increase in water uptake after the thermal treatment may be due to decomposition of the thiosulphate group to give disulphide linkages which results in chemical crosslinking(147). The presence of chemical crosslinking creates intervening space (free volume) within the polymer network in which water molecules can penetrate. This also explains the fact that the high ionic content ionomers were not soluble even in strongly

polar solvents such as DMSO or DMF after thermal treatment, which is due to the presence of large number of chemical crosslinkages.

The equilibrium water uptake results for the PP-X-S/BD series of ionomers are shown in Fig.4.26 and Table 4.9, respectively. Generally speaking, the PP-X-S/BD ionomers exhibit higher water uptake than the PP-X-Th/BD ionomers. For example, PP-75-S/BD and PP-100-S/BD are readily soluble in water, whereas PP-100-Th/BD is only slightly soluble and PP-75-Th/BD is quite insoluble, with an equilibrium uptake value of about 200%. These differences reflect the slightly more ionic character of the sulphonate ion compared to the thiosulphate ion.

Table 4.9. Equilibrium water uptake for PP-X-S/BD series at 30°C

Polymer code	Equilibrium water uptake (%w/w)
PP-0	3.8
PP-25-S/BD	9.7
PP-50-S/BD	129.9
PP-75-S/BD	-----
PP-100-S/BD	-----

Fig. 4.25 Equilibrium water uptake for PP-X-Th/BD at 30°C (heat treated at 120°C for 24 hours)

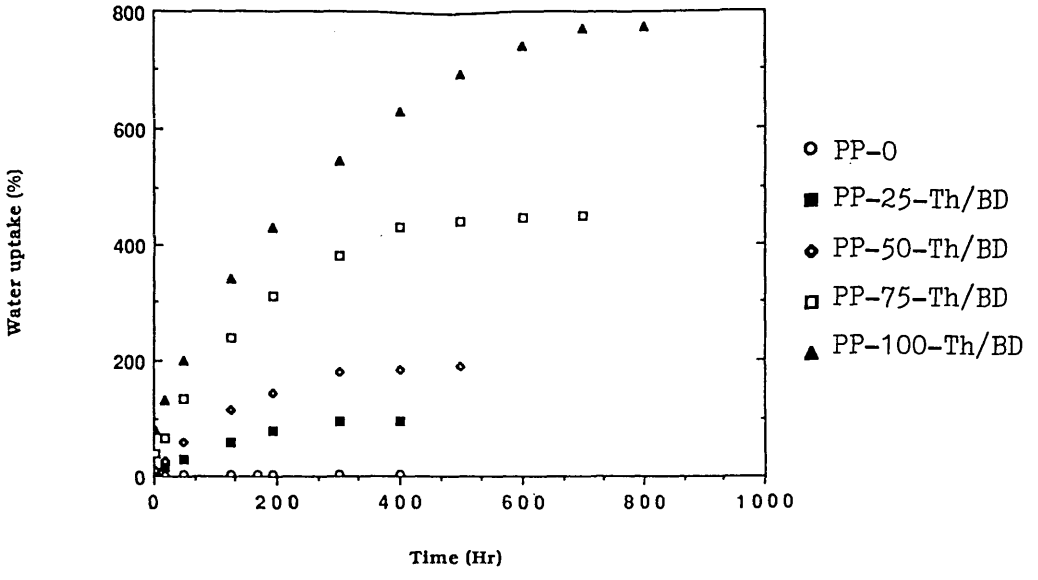
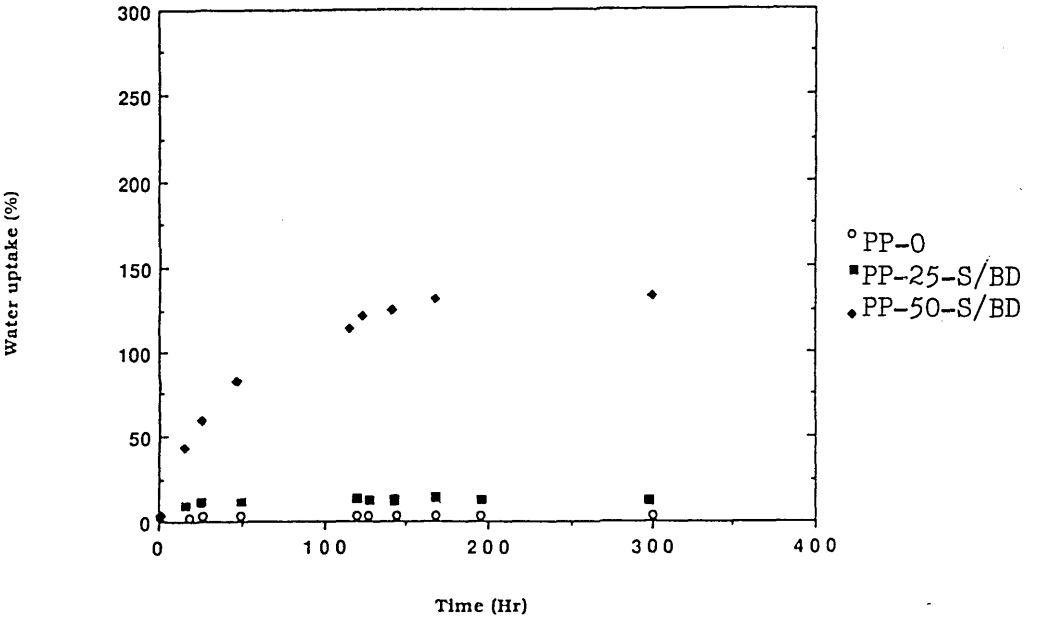


Fig.4.26 Equilibrium water uptake for PP-X-S/BD at 30°C



4.12 Differential Scanning Calorimetry Analysis of Polyurethane Ionomers

The thermal transitions and extent of phase separation of the non-ionic polyurethanes and two series of the ionomers have been evaluated using DSC analysis in conjunction with dynamic mechanical thermal testing. The DMTA results will be discussed and compared with values obtained by DSC in the next section.

The DSC thermograms of the non-ionic polyurethanes are illustrated in Fig. 4.27 and the values of the transitions are tabulated in Table 4.10. For the purpose of comparison, thermograms of the pure polyglycol soft segments have also been obtained (Fig. 4.28 and Table 4.11) as literature values for these polyether glycols seem to differ considerably, possibly associated with a molecular weight effect. For instance, values ranging from -115°C to -40°C were reported for polyethylene glycol(155).

Table 4.10 DSC data for non-ionic polyurethanes

Polymer code	Glass transition	
	T_g(°C)	Width of transition(°C)
PP-0	-11	23
PP-02	-35	30
PTMG-0	-38,42	33,17
PE-0	-25	31

Fig.4.27 DSC thermograms of non-ionic polyurethanes

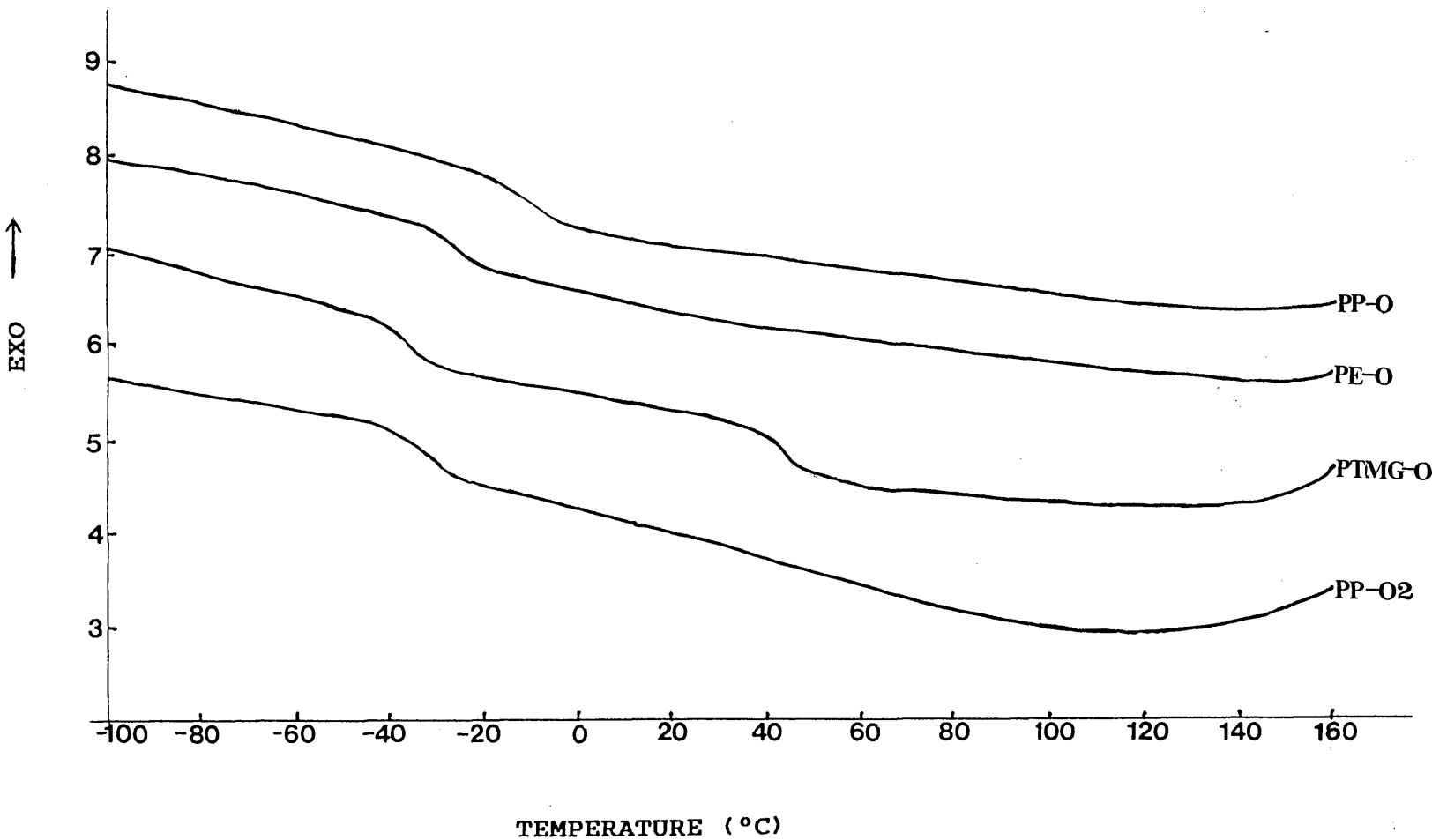


Fig.4.28 DSC thermograms of various polyols

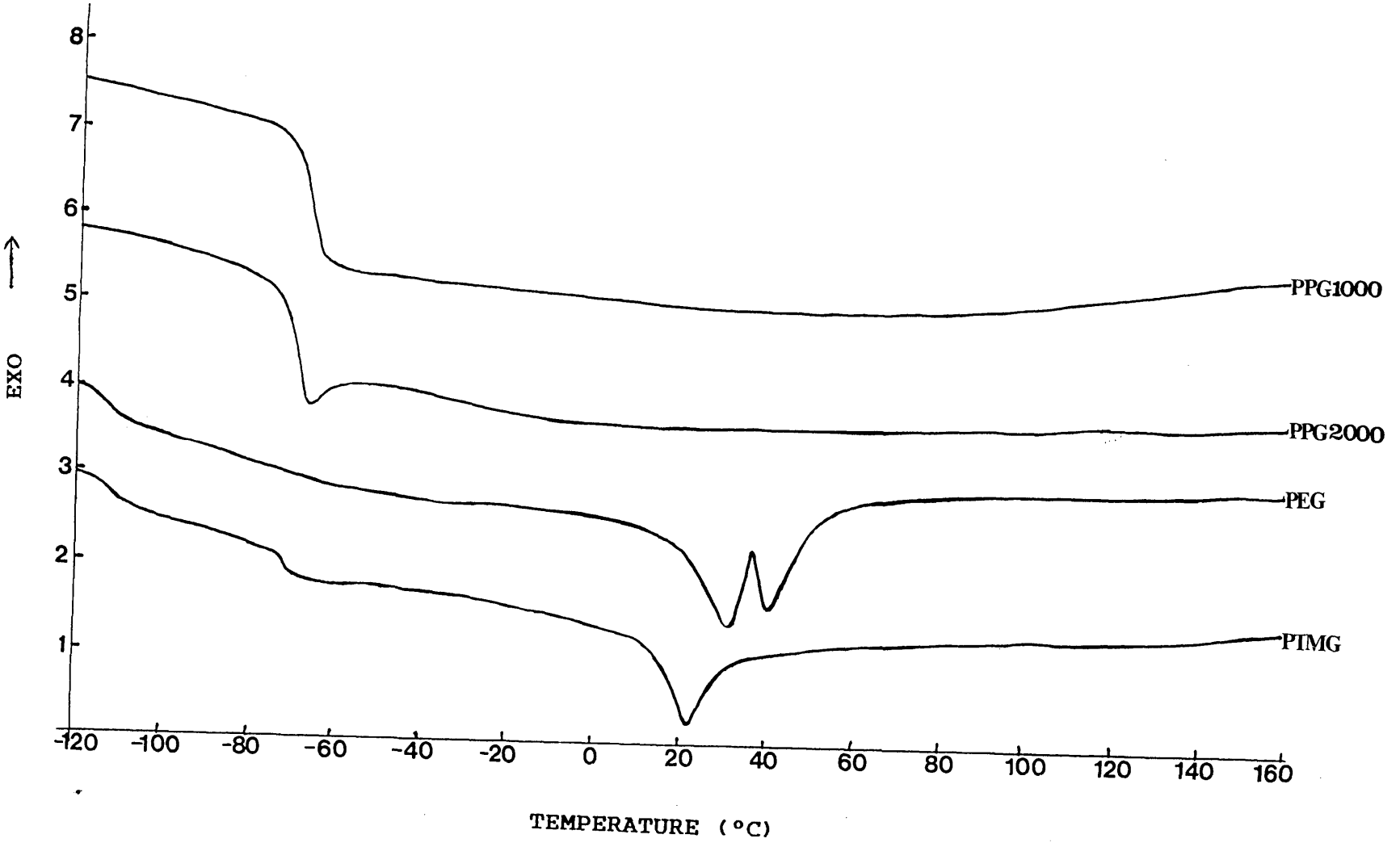


Table 4.11 DSC data for various polyols

Polymer code	Glass transition	
	T_g (C)	Width of transition(°C)
PPG1000	-68	10
PPG2000	-70	6
PTMG	-72	10
PEG	-115	8

The result shows that except for PTMG-0, all polymers exhibit single transition temperatures significantly above those of the pure macroglycols, thus suggesting that there are considerable degree of phase mixing between the two segments. This is in mark contrast to the high degree of phase separation commonly reported for polyether-based polyurethanes(55-58). Comparison of the two polymers based on PPG indicates that the T_g is lowered, and therefore there is better phase separation by increasing the molecular weight of the polyether glycol. This is due to the reduced probability of the hard segments dissolving in the soft phase. The results also reveal that for the PEG- and PTMG-based polymers, reducing the ether content of the soft segments results in a lower soft segment T_g and the appearance of a transition at around 37°C corresponding to the T_g of the hard segments. The existence of these two transitions is typical of phase-separated block copolymers. This is due to the PTMG-0 polymer which contains less ether oxygen

and thus has less tendency to form hydrogen bonds between the two segments. All these observations are consistent with results obtained by Cooper et al(56).

The phase morphology of segmented polyurethanes can be influenced by a variety of elements. Two effects, other than those mentioned in Chapter Two, are thought to be responsible for the high degree of phase mixing in the present systems. The first effect suspected to cause the phase mixing is related to the molecular weight of the polymers. It can be seen from the GPC results that all the polymers synthesised have relatively low average molecular weights and broad distributions. The resulting polymers, therefore have comparatively short segments and consequently there is a higher tendency for the two phases to interdiffuse.

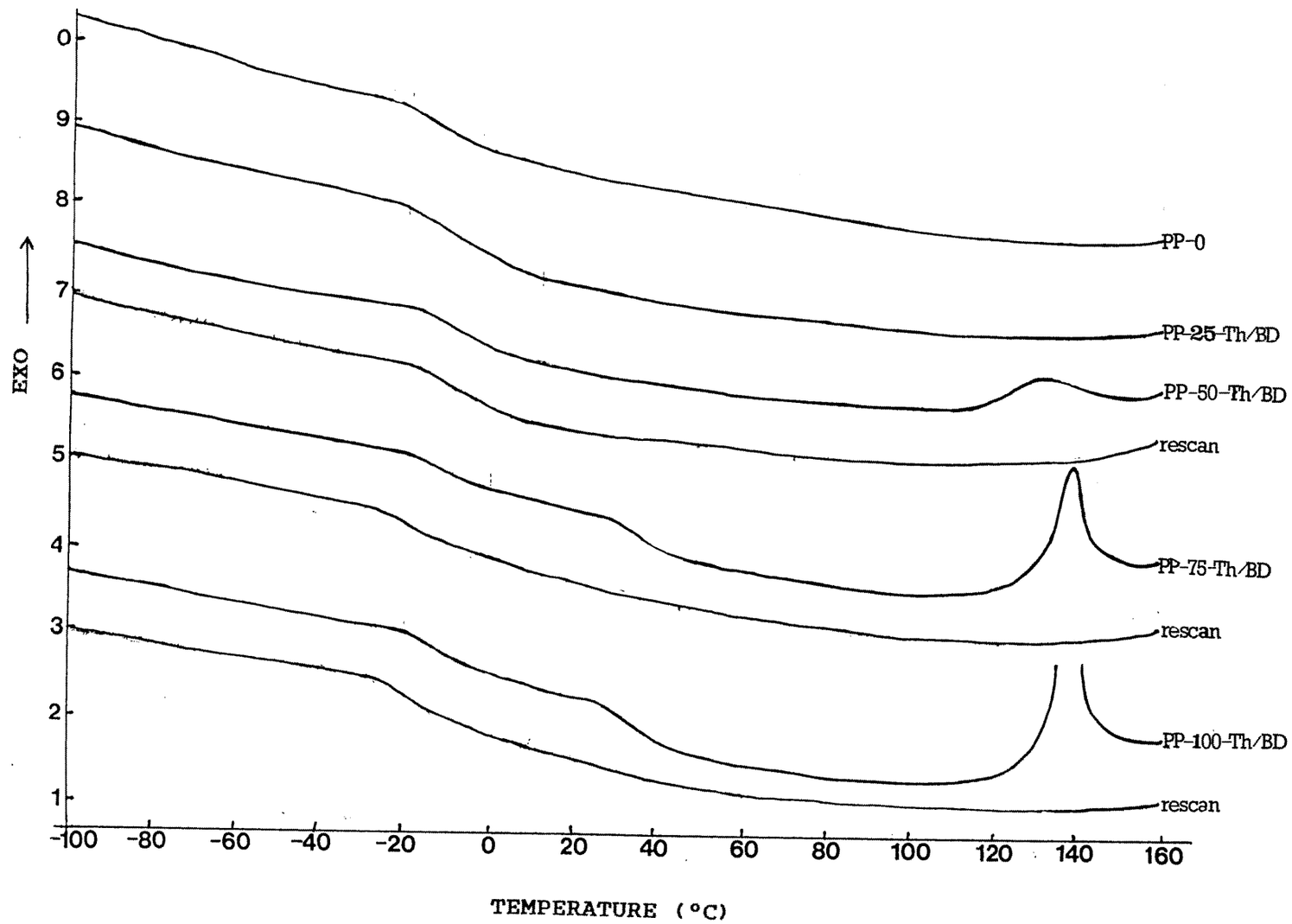
Fedors(156) applied the Flory Huggins theory of thermodynamics of polymer mixtures to poly(styrene-butadiene) block copolymer systems and predicted the minimum molecular weight required for a two-phase structure using the solubility parameters of the two blocks. However, there was some doubt about the accuracy of these results as unlike simple polymer mixtures, the individual segments in block copolymers are chemically linked to each others. The validility of this theory becomes even more uncertain for segmented polyurethanes which are complicated by the presence of H-bonding and crystallisability of the segments. There is

no precise evidence of the contribution of these effects. The results nevertheless suggest that there is a limit to the molecular weight of block copolymers, below which phase separation will not be possible.

The second likely factors for causing the phase mixing is associated with the choice of casting solvent used. For a block copolymer $(AB)_n$, a solvent which is good for A only will tend to 'precipitate' B first during solvent evaporation. Hence discrete domains are formed that become dispersed in the continuous matrix of the 'expanded' segment A, and vice versa. On the other hand, the use of a good solvent for both segments such as DMF, will encourage phase blending as both segments are equally solubilised in the solvent(157,158). Coote(159) reported that a trace of solvent was retained in most of his polyurethanes cast from DMF despite extensive drying under vacuum. This resulted, in many cases, in a deterioration of mechanical properties of the polymers. Nevertheless, DMF has been reported as a common casting solvent for polyurethanes in which good phase separation was attanied(87,93,95).

Fig.4.29 and Table 4.12 illustrates the DSC thermograms and values of transition temperatures of the PP-X-Th/BD series of ionomers. The results reveal several differences between the non-ionic polyurethane and the ionomers. The thermogram of PP-25-Th/BD shows a transition at a slightly higher temperature than that of

Fig.4.29 DSC thermograms of PP-X-Th/BD series



PP-0. The width of the transition of the ionomer is also larger which is indicative of a higher degree of phase mixing. A slightly higher transition temperature than that of the PP-25-Th/BD is observed in the thermogram of PP-50-Th/BD. Interestingly, there seems to be a slight exotherm at around 140°C in the thermogram of PP-50-Th/BD. The thermograms of PP-75-Th/BD and PP-100-Th/BD look generally alike in that both ionomers show two transition temperatures. These transitions are slightly further apart and narrower for PP-100-Th/BD. In addition, the slight exotherm in the thermogram of PP-50-Th/BD becomes more intense in the thermograms of the higher ionic content polymers. However, this exotherm disappeared completely in all the re-scan thermograms.

Table 4.12 DSC data for PP-X-Th/BD series

Polymer code	Glass transition	
	T_g(°C)	Width of transition(°C)
PP-0	-11	23
PP-25-Th/BD	-4	36
PP-50-Th/BD	0	34
PP-75-Th/BD	-4,35	34,22
PP-100-Th/BD	-8,36	30,12

All the above observations can be interpreted in the following ways. Incorporation of a small amount of ionic groups into the polyurethane results in an increase in

the glass transition temperature of the highly phase-mixed non-ionic polymer PP-0. Both PP-25-Th/BD and PP-50-Th/BD behave effectively as homopolymers and the introduction of bulky ionic groups simply restricts the mobility of the polymer chains and results in an increase in T_g. Further increase in ion concentration, however, increases the polarity difference between the two segments to a degree that they become incompatible with each other and phase separation takes place. This is indicated by the appearance of two segment transition temperatures in the thermograms of PP-75-Th/BD and PP-100-Th/BD.

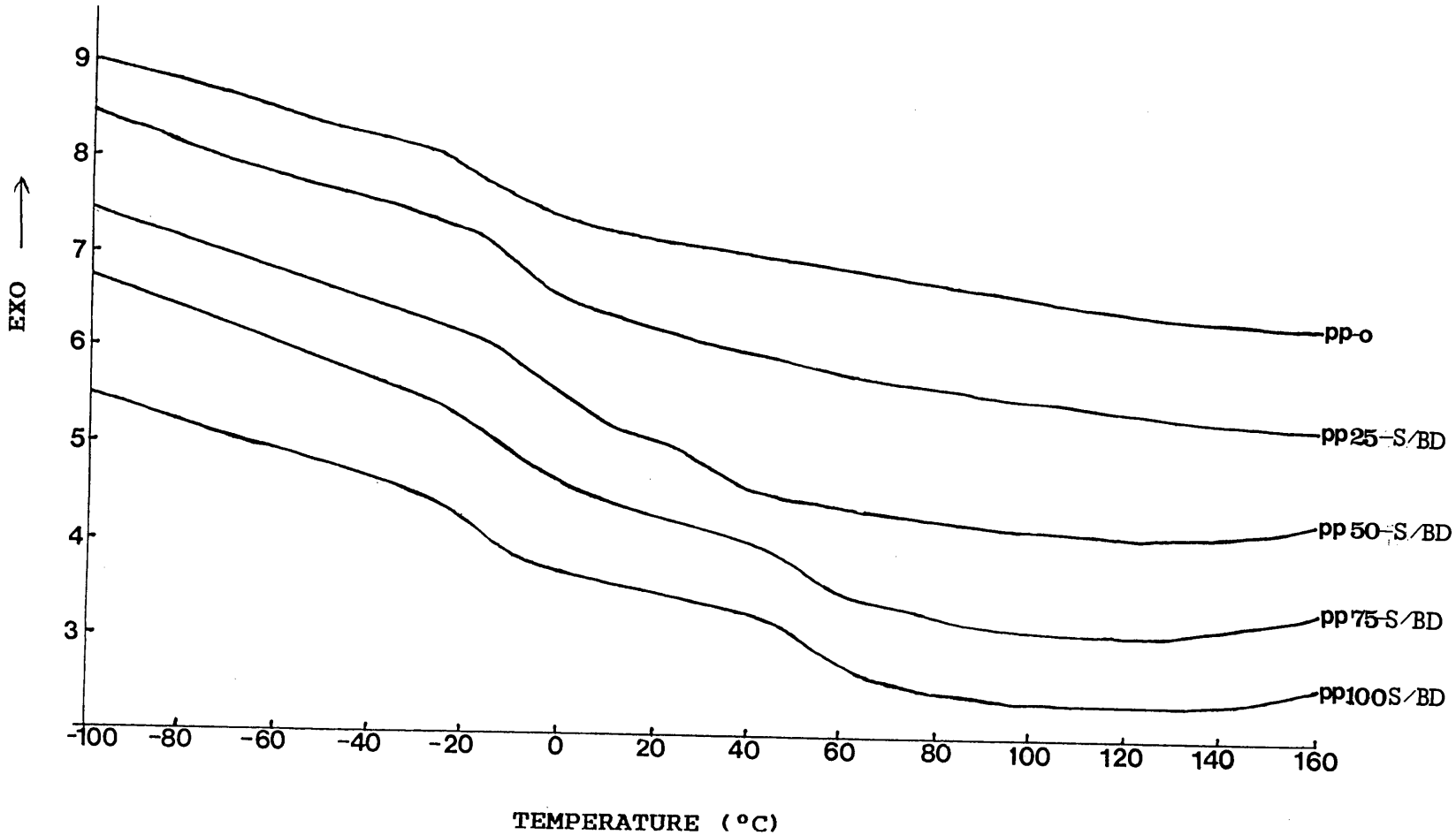
With regard to the exotherm at around 140°C for the three high ionic content ionomers, two explanations are suggested. The first interpretation as given by Butler(19) in a related study is that substantial rearrangement in the ionomers occurred at this temperature which resulted in a more ordered ionic structure. This exotherm was observed only in PP-100-Th/BD in Butler's study from which he further proposed that a minimum ion concentration was required for the formation of such an ordered structure. The absence of such exotherms in the lower ionic content polymers may be due to the different co-chain extender used in Butler's study. The present series of ionomers which utilise BD as co-chain extender, in contrast to CPD used by Butler, should give a slightly more ordered domain structure and thus require a lower

ionic content for hard segment rearrangement (crystallisation) to occur.

The second reason for the occurrence of this exotherm is related to the stability of the thiosulphate group as discussed in Section 4.5. The thiosulphate group in Bunte salts is rather unstable to heat and starts to decompose at around 100°C to yield disulphide linkages resulting in chemical crosslinking(147). The presence of chemical crosslinking greatly reduced the mobility of the hard segments, consequently the hard segment transition disappeared in the re-run thermograms. The absence of this exotherm in the re-run thermograms also suggests that such decomposition is very rapid.

The DSC results for the PP-X-S/BD series of ionomers are presented in Fig. 4.30 and Table 4.13, respectively. The general features of these thermograms resemble those observed in the PP-X-Th/BD ionomers except that the exotherm observed in PP-X-Th/BD is absent in these systems. The overall results can be explained using the same interpretation discussed for the PP-X-Th/BD ionomers. The sulphonate ionomers, however seem to be more effective in improving the degree of phase separation than the thiosulphate ionomers. This is demonstrated by the greater difference between the two segment transitions and the their presence in the lower ionic content polymers. The absence of the exotherm at around 140°C in the PP-X-S/BD ionomers suggests that the

Fig.4.30 DSC thermograms of PP-X-S/BD series



origin of the exotherm in PP-XTh/BD is unlikely to be due to structual ordering, as both series of ionomers contain a similar ion content. On the other hand, the low thermal stability of TDOL suggests that this exotherm is most likely caused by the decomposition of the thiosulphate group in the PP-X-Th/BD ionomers.

Table 4.13 DSC data for PP-X-S/BD series

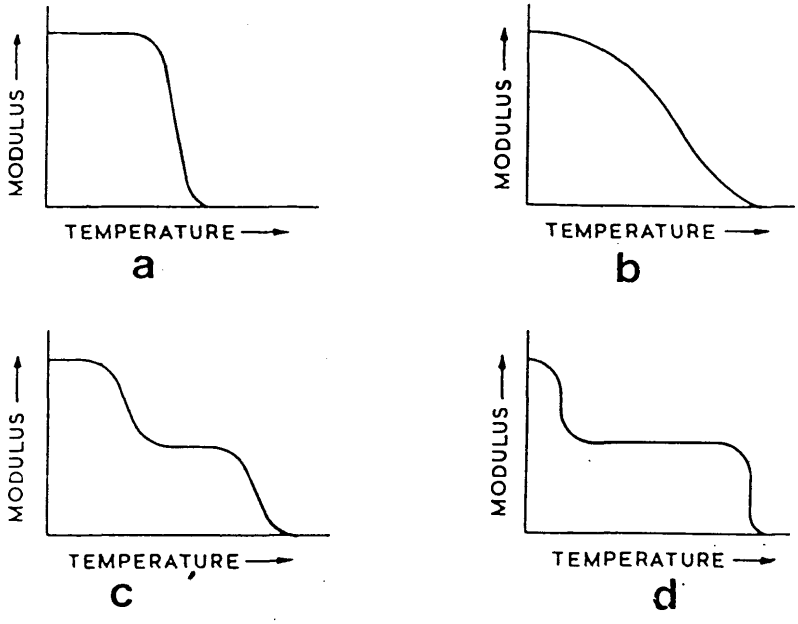
Polymer code	Glass transition	
	T_g (°C)	Width of transition(°C)
PP-0	-11	23
PP-25-S/BD	-7	24
PP-50-S/BD	-5,30	37,20
PP-75-S/BD	-17,48	35,18
PP-100-S/BD	-17,53	23,20

4.13. Dynamic Mechanical Thermal Analysis of Polyurethane Ionomers

DMTA has been utilised to characterise the phase transitions and degree of phase separation of the polyurethane ionomers. This technique basically follows the change in dynamic moduli of the polymers with temperature. The distinct change in dynamic moduli at any particular transition can be taken as a measure of the phase transition temperature. The phase morphology can also be interpreted qualitatively from the position and

the shape of the transition peaks in these segmented block copolymers. Depending on the degree of phase separation in the copolymer, the shape of the modulus curves can differ widely as shown in Fig. 4.31.

Fig. 4.31 Typical modulus-temperature curves for block copolymers with various degrees of phase separation



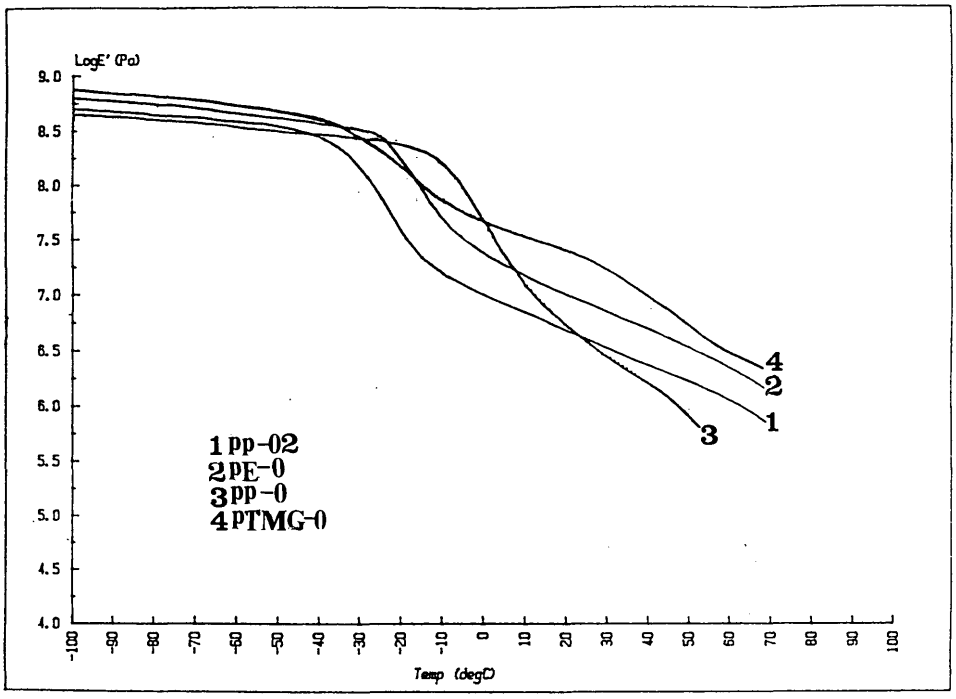
Curve (a) is a typical plot of an amorphous block copolymer containing compatible segments in which a single transition temperature close to that of a random copolymer of the same copolymer composition is observed. In the other extreme, a block copolymer with complete phase separation will have a trace similar to curve (d) with sharp boundaries between domains and the matrix. In practice, however, partial phase mixing occurs, which

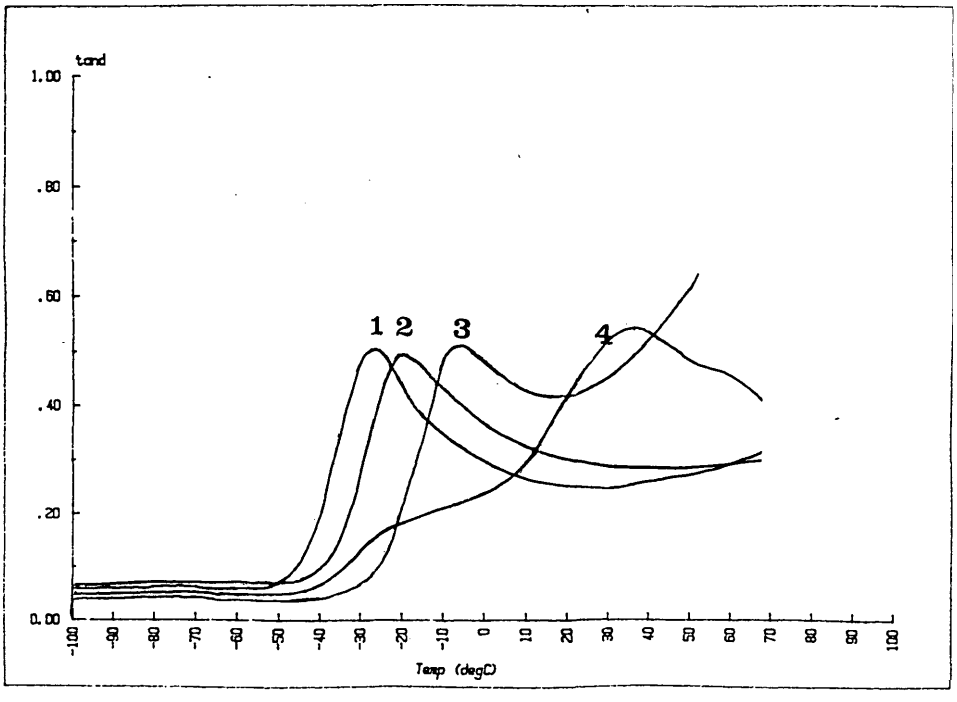
causes diffuse boundaries between the two phases. In such cases, the plateau will either exist over a narrow temperature range, as shown in curve (c), or the plateau may not be well defined, with a gradual decrease in modulus over a wide temperature range as in Curve (b).

From the DMTA trace, the relationship between the three dynamic parameters, storage modulus (E'), loss modulus (E") and tan δ is apparent if the curves are superimposed. The maximum loss modulus peak coincides with the onset of the fall off of the storage modulus, while the tan δ peak occurs at a temperature where the storage modulus is about half its original value. If the temperature of the maximum loss modulus peak represents the beginning of the movement of the major segments in the main chains and the tan δ peak represents the mid point of the transition, then it would more appropriate to consider the temperature at which the tan δ is at its maximum as the T_g of the polymer.

The DMTA thermograms and values of transitions of the non-ionic polyurethanes are shown in Fig. 4.32 and Table 4.14 respectively. The results obtained from this method generally show the same pattern as those obtained by DSC. However, there is some disparity between the values obtained from the two methods. DMTA values are in most cases higher than those obtained from DSC, perhaps the former is more associated with the fall off in modulus than with the damping peak. The broad transitions of the

Fig.4.32 DMTA thermograms for non-ionic polyurethanes





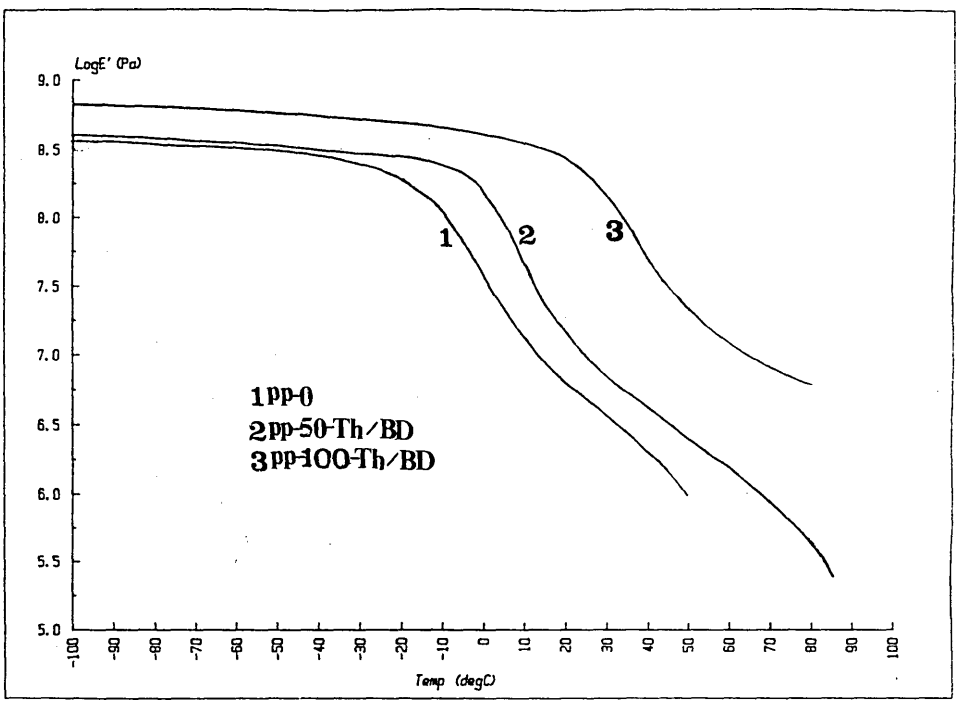
storage modulus curves of all four polymers are an indication of high degree of phase mixing. The fact that the storage modulus of all the materials does not fall sharply after the transition temperature shows that these polymers are not completely homogeneous. The presence of two transitions in the PTMG-0 system suggests that this polymer has the best phase separation among the four non-ionic polymers as demonstrated in the DSC results.

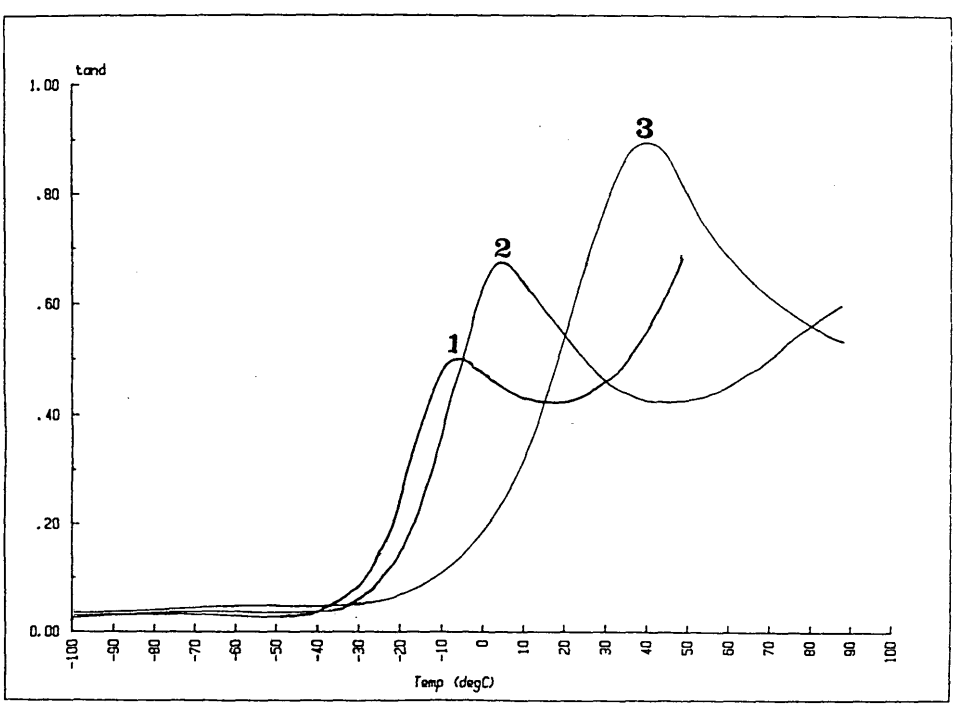
Table 4.14 DMTA data for non-ionic polyurethanes

Polymer code	Glass transition (taken at max tan δ) T_g (°C)
PP-0	-5
PP-02	-26
PTMG-0	-24,38
PE-0	-20

The results for the PP-X-Th/BD series of ionomers are shown in Fig.4.33 and Table 4.15. The transition temperatures observed in this series correlate well with the DSC results except that the soft segment transition observed by DSC for PP-100-Th/BD is not visible in the tan δ peak. Perhaps secondary transitions in polymers are more associated with change in specific heat capacity than dynamic properties. The storage modulus curve indicates that the level of modulus retained after the transition increases gradually with increasing ionic

Fig.4.33 DMTA thermograms for PP-X-Th/BD series





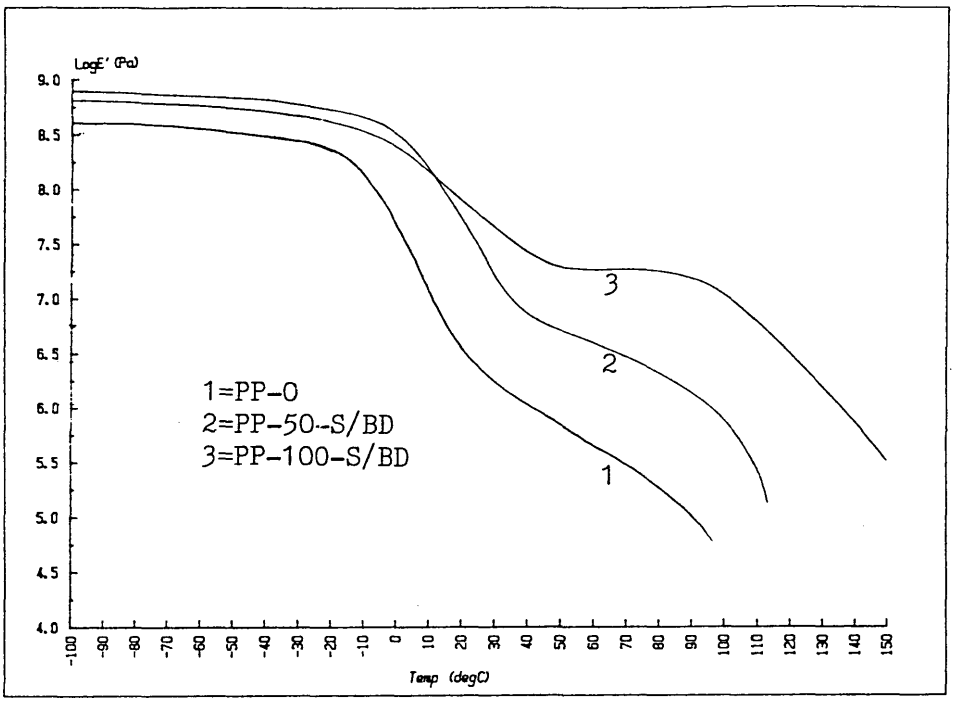
content which demonstrates an increase in phase separation and an enhancement of the physical crosslinking and filler effects.

Table 4.15 DMTA data for PP-X-Th/BD series

Polymer code	Glass transition (taken at max tan δ) T_g (°C)
PP-0	-5
PP-50-Th/BD	7
PP-100-Th/BD	39

Fig. 4.34 and Table 4.16 illustrate the results for the PP-X-S/BD series of ionomers. The results again show the same trend of behaviour as those observed from DSC. A more distinct increase in the rubbery plateau modulus with increasing ionic content is clearly seen in this series of ionomers compared to the PP-X-Th/BD series which suggests that the sulphite ion is more effective in enhancing the physical crosslinking and filler effects than the thiosulphate ion. The increasing modulus retained by the ionomers with increasing ionic content at high temperatures is attributed to the improved hard segment domain cohesion. Similar increase in T_g and rubbery modulus with increasing ionic content are also demonstrated in the PE-X-S/BD series of ionomers shown in Fig. 4.35 and Table 4.17.

Fig.4.34 DMTA thermograms of PP-X-S/BD series



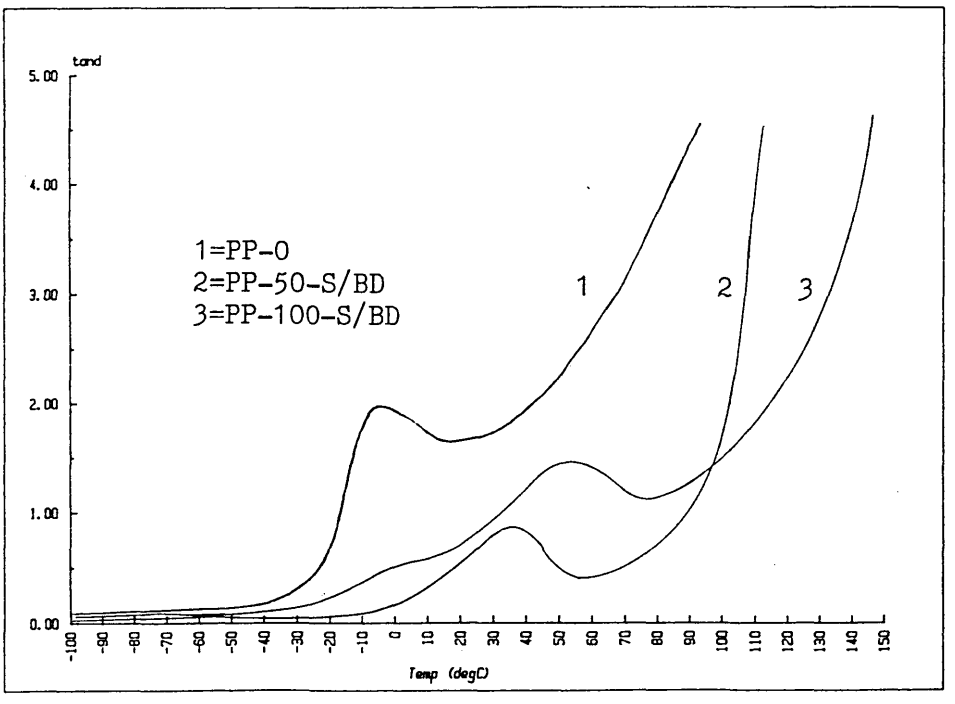
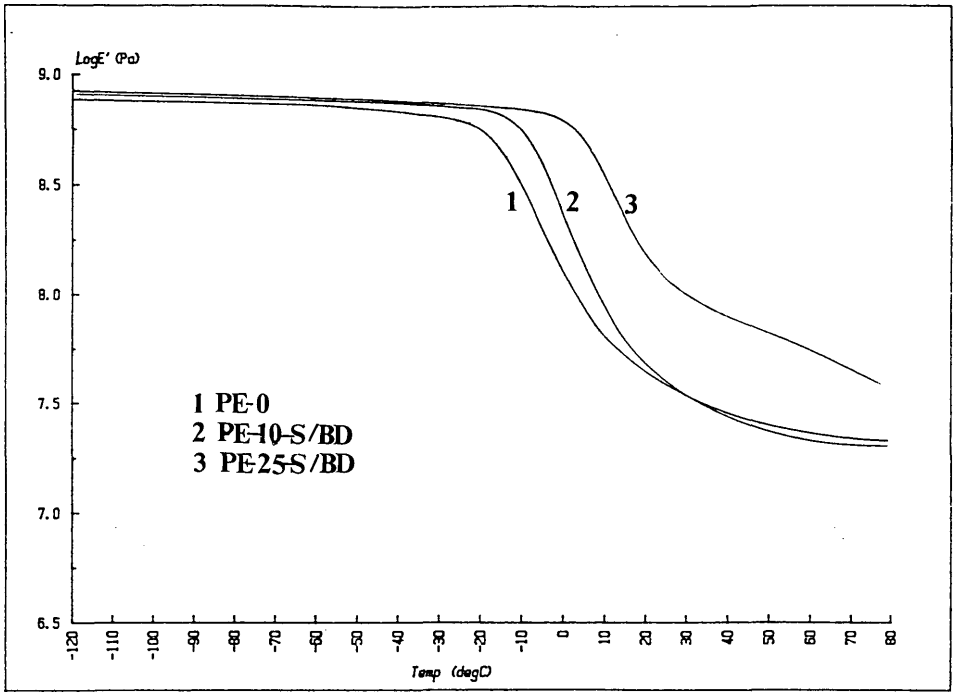


Fig.4.35 DMTA thermograms of PE-S/BD series



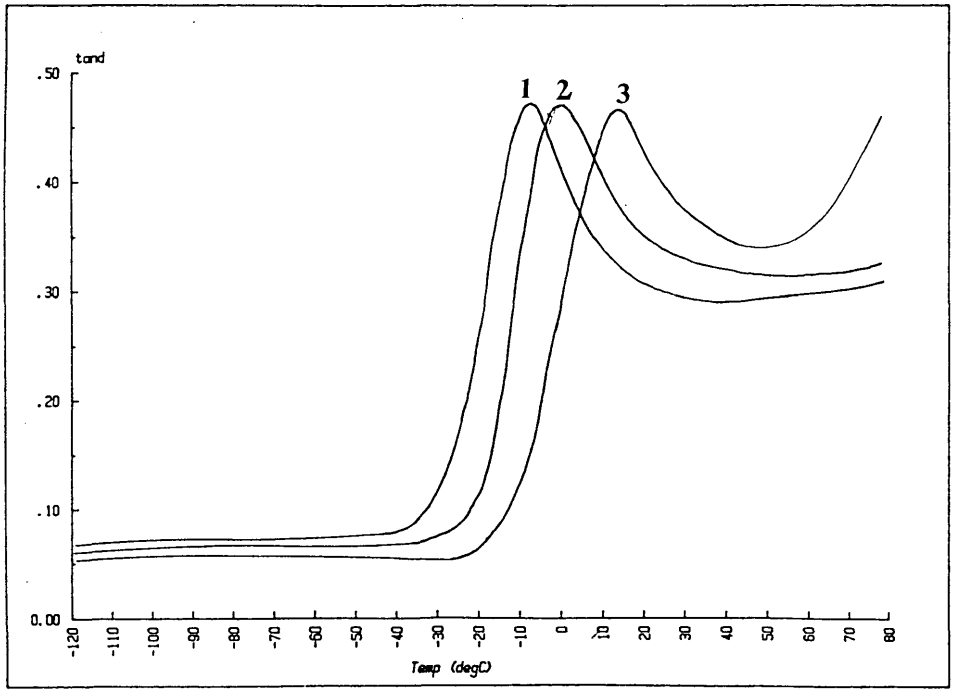


Table 4.16 DMTA data for PP-X-S/BD series

Polymer code	Glass transition (taken at max tan δ) T_g (°C)
PP-0	-5
PP-50-S/BD	35
PP-100-S/BD	-5,55

Table 4.17 DMTA data for PE-X-S/BD series

Polymer code	Glass transition (taken at max tan δ) T_g (°C)
PE-0	-10
PE-10-S/BD	-3
PE-25-S/BD	11

On the whole, the results obtained from this method are consistent with results published by other workers that ion incorporation improves the degree of phase separation and room temperature modulus (34-37,160).

4.14 Stress-Strain Analysis of Polyurethane Ionomers

Stress-strain measurements have been used to examine the mechanical properties of several series of polyurethane ionomers having various compositions and thermal histories. Fig. 4.36 and Fig. 4.37 show the stress-strain curves of the PP-X-Th/BD series of ionomers

Fig.4.36 Stress-strain curves of PP-X-Th/BD series

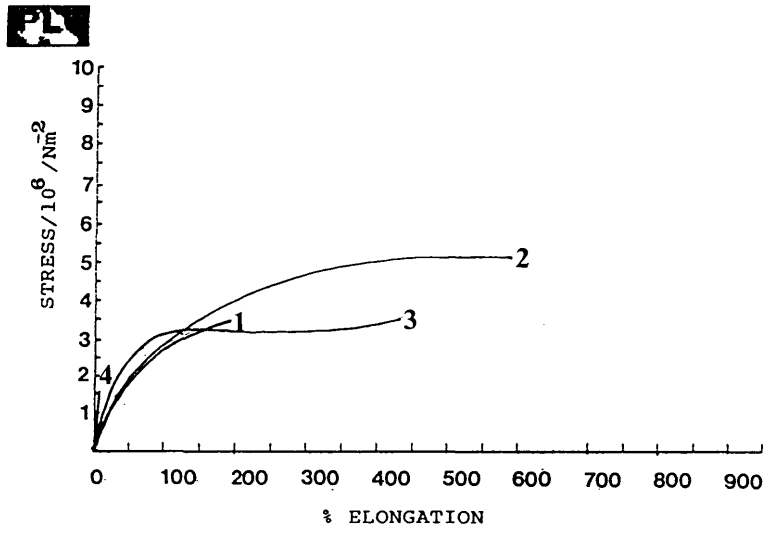


Fig.4.37 Stress-strain curves of PP-X-Th/BD series (samples treated at 120°C for 24 hours)

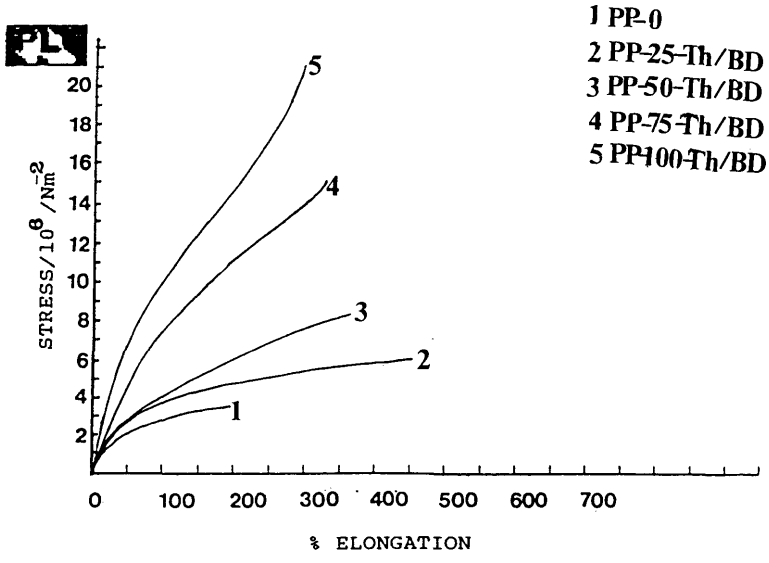
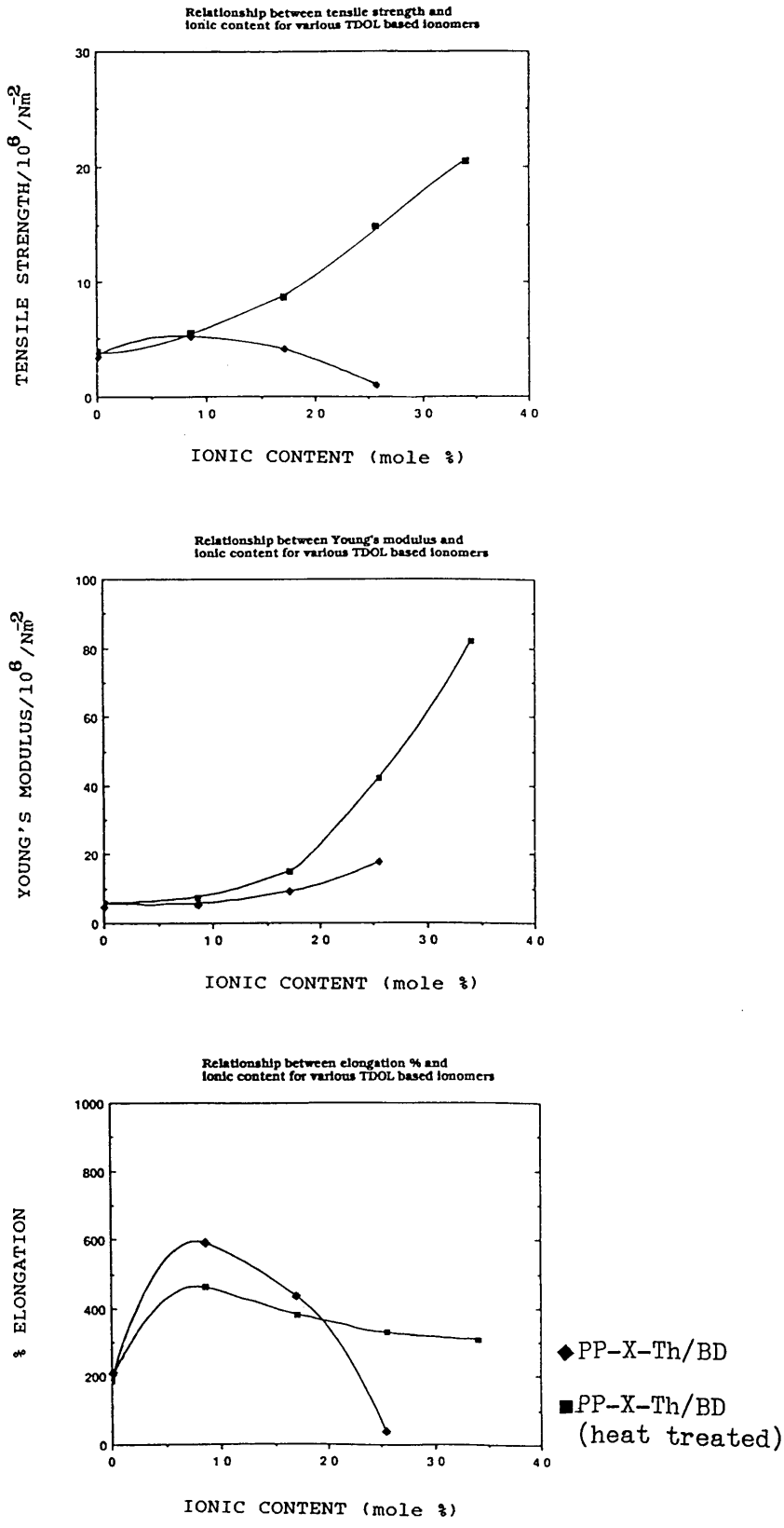


Fig.4.38 Relationship between various tensile properties and ionic content for PP-X-Th/BD series with different thermal histories



and the same series after heat treatment at 120°C for 24 hours, respectively. The relationships between the various tensile properties and ionic content are illustrated in Fig.4.38.

The results show that for the non-treated series, the presence of low levels of ions as in PP-25-Th/BD causes a marked increase in the ultimate elongation and a slight improvement in tensile strength of the material, while the Young's modulus is not significantly affected. Increasing the concentration of ionic groups leads to an increase in modulus while at the same time reduces the tensile strength and ultimate elongation. At high levels of ionic content, the material becomes brittle as shown by the very high modulus and low ultimate elongation and tensile strength for PP-75-Th/BD. Data for PP-100-Th/BD could not be obtained as this polymer was too brittle for this test.

These results appear to be slightly different from those reported by Kwang et al(114) where ion incorporation caused a decrease in ultimate elongation even at levels lower than the present system due to the greater phase cohesion of the hard domains and their reduced ability to deform. On the other hand, Miller et al(113) observed an increase in ultimate elongation upon ionisation of polyether polyurethanes based on PTMG-2000 molecular weight soft segment. This was attributed to the stress-induced crystallisation of the soft segment which

prevented premature failure. However, this is unlikely to be the reason for the high ultimate elongation in the present system as polypropylene glycol does not exhibit crystallinity due to its atactic structure and would not be expected to crystallise even during deformation. The main reason for the large increase in ultimate elongation compared to the non-ionic material may be associated with the one phase structure and low molecular weight nature of the non-ionic polymer. Introducing a small amount of ionic groups simply improves the very weak strength of the material through coloumbic interactions between short polymer chains. At higher ionic contents, the polarity difference between the two segments becomes larger and the tendency for phase separation increases. The presence of more ionic groups improves the hard segment cohesion and enhances the crosslink and filler effects, and thus leads to a large increase in modulus and lower values of ultimate elongation. The reduced tensile strength at high ionic contents is again due to the low molecular weight nature of the polymer. For polymers with higher molecular weight, both the modulus and tensile strength are expected to be higher.

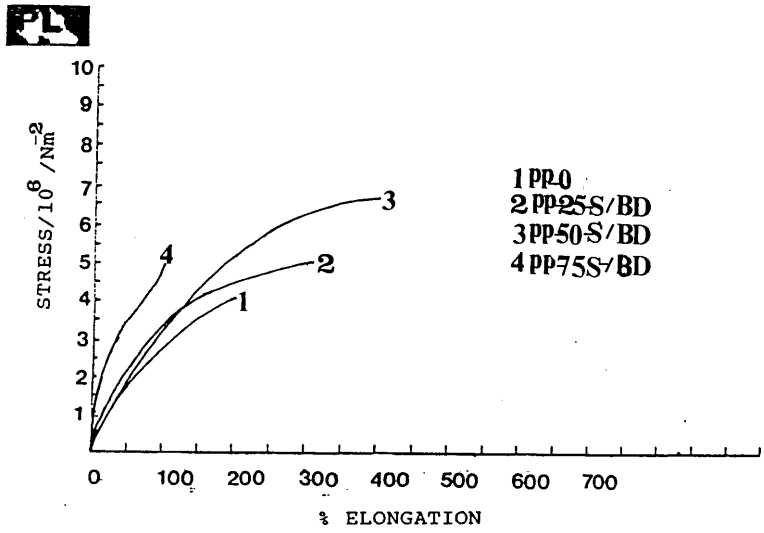
The results for the ionomers after heat treatment show a large difference in tensile behaviour from the untreated materials. At low levels of ionic content, both series of polymers exhibit similar behaviour, except a lower tensile strength is observed for the heat treated

sample. This is due to the unstable thiosulphate groups in the polymer which break down to give chemical crosslinking through disulphide linkages. The presence of small amounts of chemical crosslinks reduces the stiffness of the polymer slightly, as more force is required to break the chemical bonds. This is shown by a slight increase in modulus and decrease in ultimate elongation. At higher ionic contents, more chemical crosslinks are created as a result of decomposition of the thiosulphate groups. Thus both PP-75-Th/BD and PP-100-Th/BD ionomers exhibit a much larger increase in both modulus and tensile strength typical of polymers with chemical crosslinking. The slight decrease in ultimate elongation even at high levels of crosslinking is attributed to the presence of soft segment which is able to retain the viscous property of the polymer.

The stress-strain results for both the PP-X-S/BD and PP-X-S/BD2 series of ionomers are presented in Fig. 4.39. The relationships between the various tensile properties and ionic content for these and another two series of ionomers are shown in Fig. 4.40. The tensile properties of the PP-X-S/BD ionomers are generally better than those of the PP-X-Th/BD series, which is consistent with the DSC and DMTA results. This is due to the slightly better phase separation possessed by the SDOL-based ionomers. The effect of increasing the soft segment molecular weight can be seen in the results of the PP-X-S/BD2

Fig.4.39 Stress-strain curves of PP-X-S/BD and PP-X-S/BD2 series

PP-X-S/BD series



PP-X-S/BD2 series

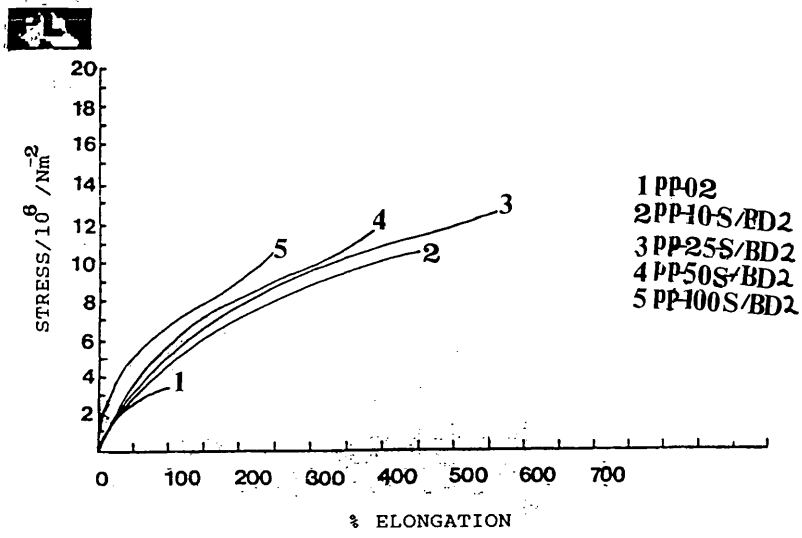
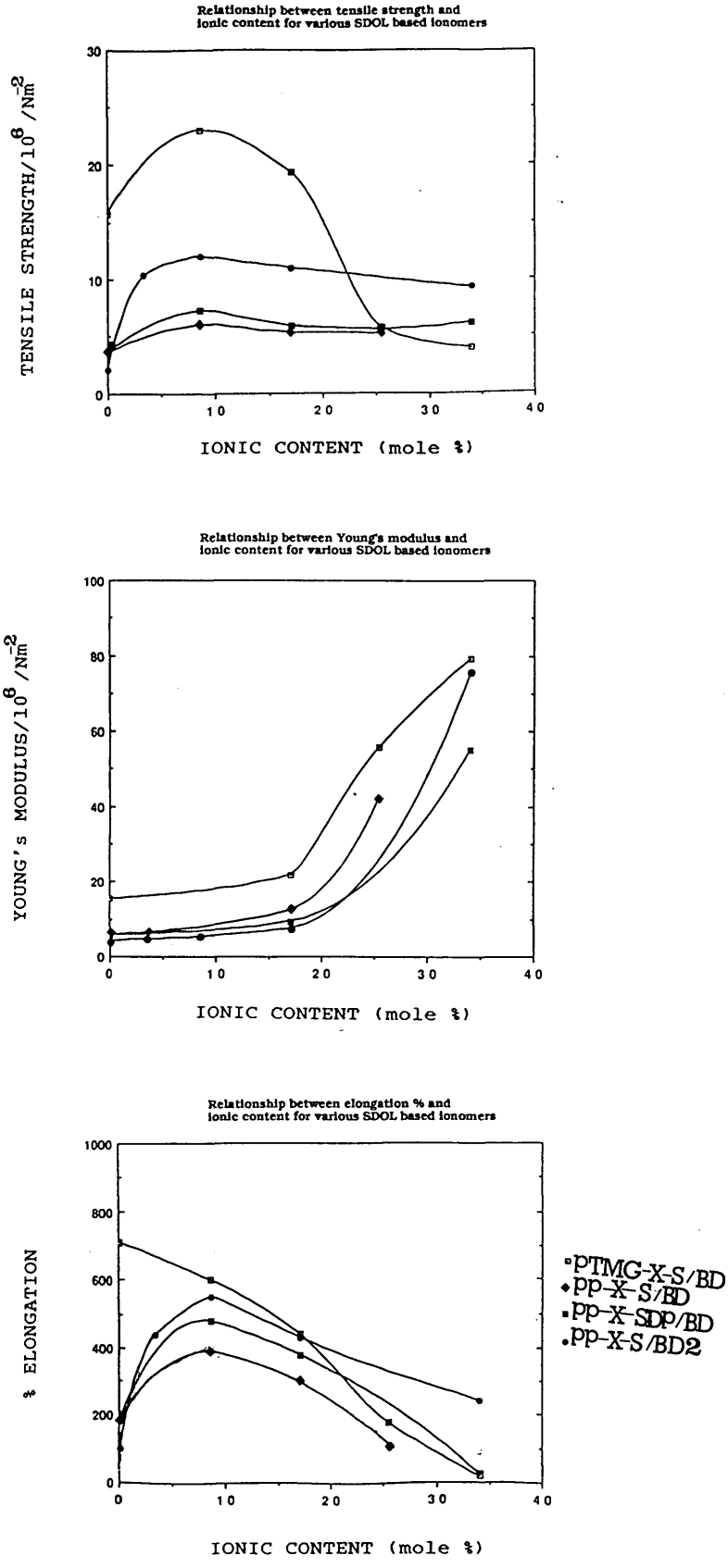


Fig.4.40 Relationship between various tensile properties and ionic content for different series of SDOL-based ionomers



series of ionomers. The slightly lower tensile strength of PP-02 compared to PP-0 may be due to the slightly lower hard segment content of the PP-02 polymer. It must also be recalled that PP-02 has the lowest molecular weight among the four non-ionic polymers which may also affect its mechanical strength. Upon ionisation, however, the PP-X-S/BD2 series show better overall properties than the PP-X-S/BD series. This suggests that the introduction of ionic groups is able to overcome the effects of molecular weight and hard segment content on the tensile behaviour. Thus the increase in modulus and tensile strength can be attributed to the improved degree of phase separation in the PP-X-S/BD2 polymers.

Fig. 4.41 and Fig. 4.42 present the stress-strain results for the PP-X-SDP/BD and PTMG-X-S/BD series of ionomers. Both series of ionomers show the same trend of behaviour as all the other series. The PTMG-based polymers possess the best tensile properties compared to all the other series. This is because of the good phase separation exhibited by the PTMG-0 polymer as shown by the high modulus and tensile strength and good ultimate elongation values. Introducing ionic groups further improves the properties of this polymer. However, at high ionic contents the material also shows brittle behaviour similar to the other high ionic content polymers. This simply demonstrates the significance of the molecular

Fig.4.41 Stress-strain curves of PP-X-SDP/BD series

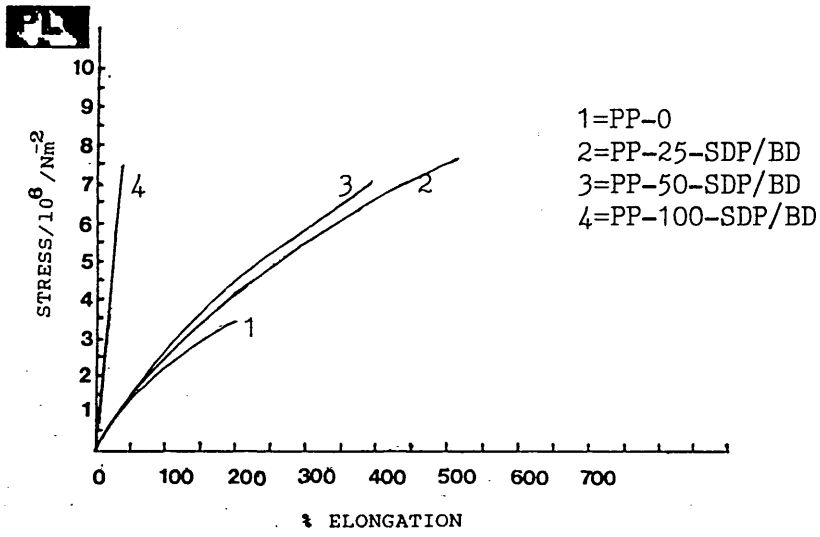
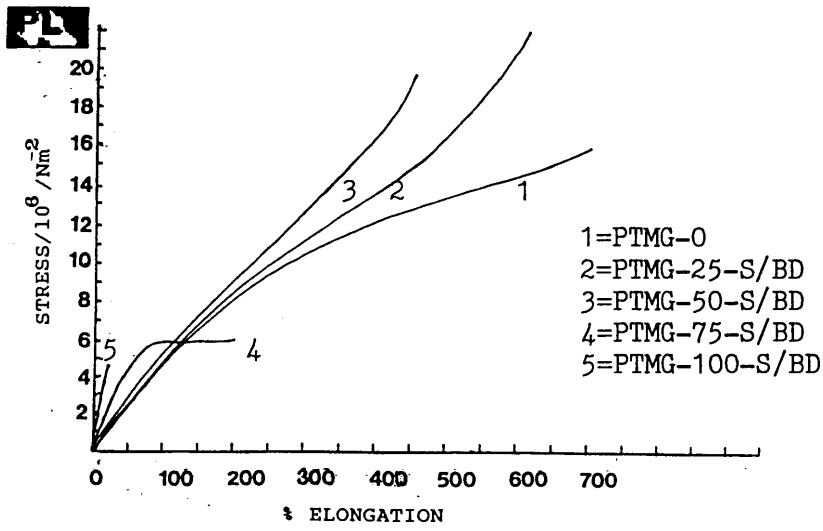


Fig.4.42 Stress-strain curves of PTMG-X-S/BD series



weight effect on the mechanical properties of the polymer.

4.15 Thermogravimetric Analysis of Polyurethane Ionomers

As results from other measurements showed that heat treatment of the PP-X-Th/BD series of ionomers led to several types of unusual behaviour. Thus there was an extremely high water uptake, unusually good tensile properties for the given molecular weight and the presence of an exotherm at around 140°C in the DSC thermograms. It is of interest to compare the relative thermal stability of the two series of ionomers, PP-X-Th/BD and PP-X-S/BD, because the latter series did not show any abnormal properties.

The thermogravimetric analysis results for both PP-X-Th/BD and PP-X-S/BD series of ionomers are shown in Fig. 4.43 and Fig. 4.44, respectively. The temperatures at 5% weight loss were taken as the relative thermal stability of all the polymers and the values are tabulated in Table 4.18. The main aim of this experiment was to compare the thermal stability of the two different ionic groups in the polymers. Therefore it was not intented to study the mechanism of the degradation of the polyurethanes. The results nevertheless show clearly that the degradation of the non-ionic polyurethane at least,

Fig.4.43 TGA thermograms of PP-X-Th/BD series

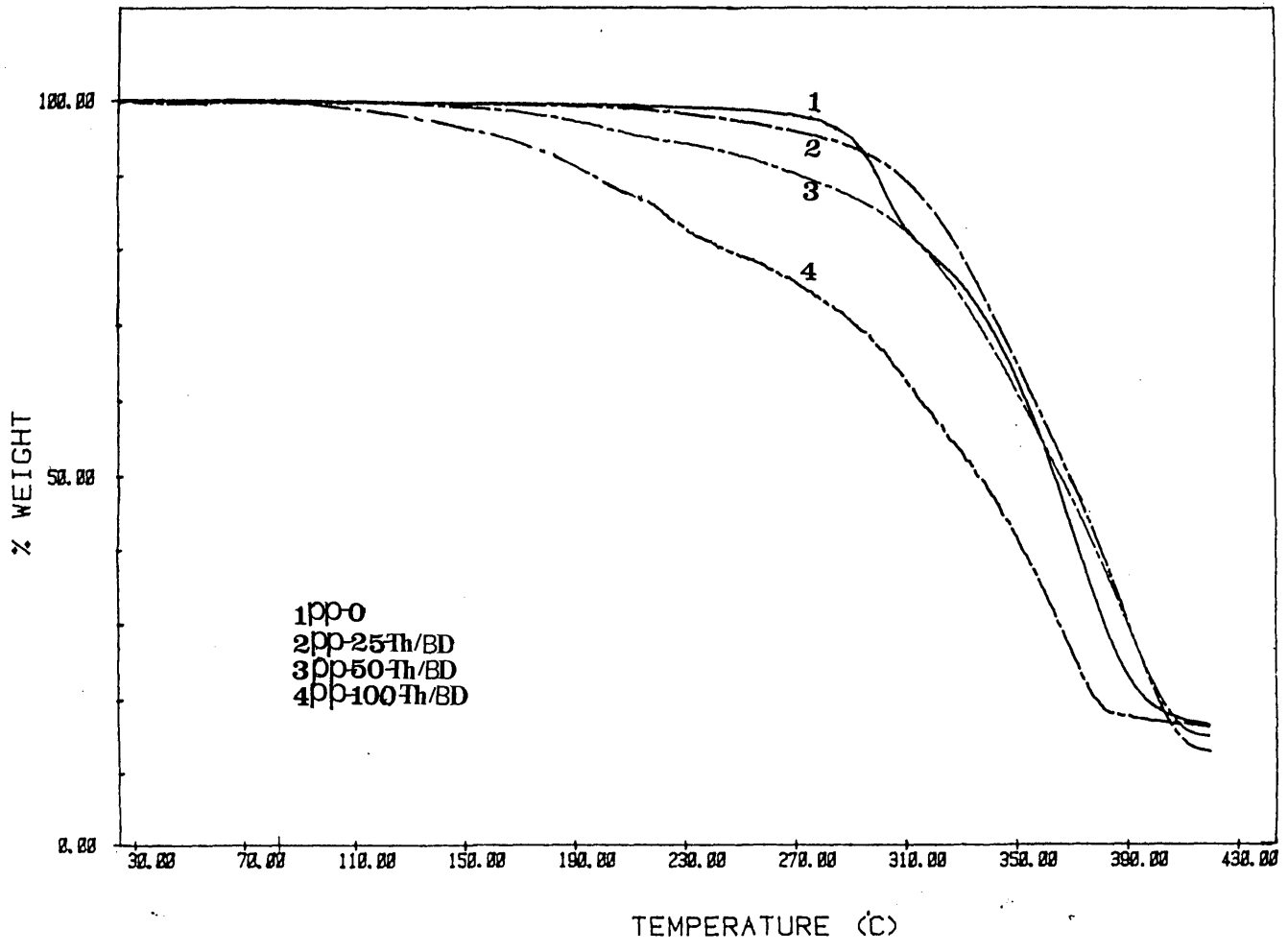
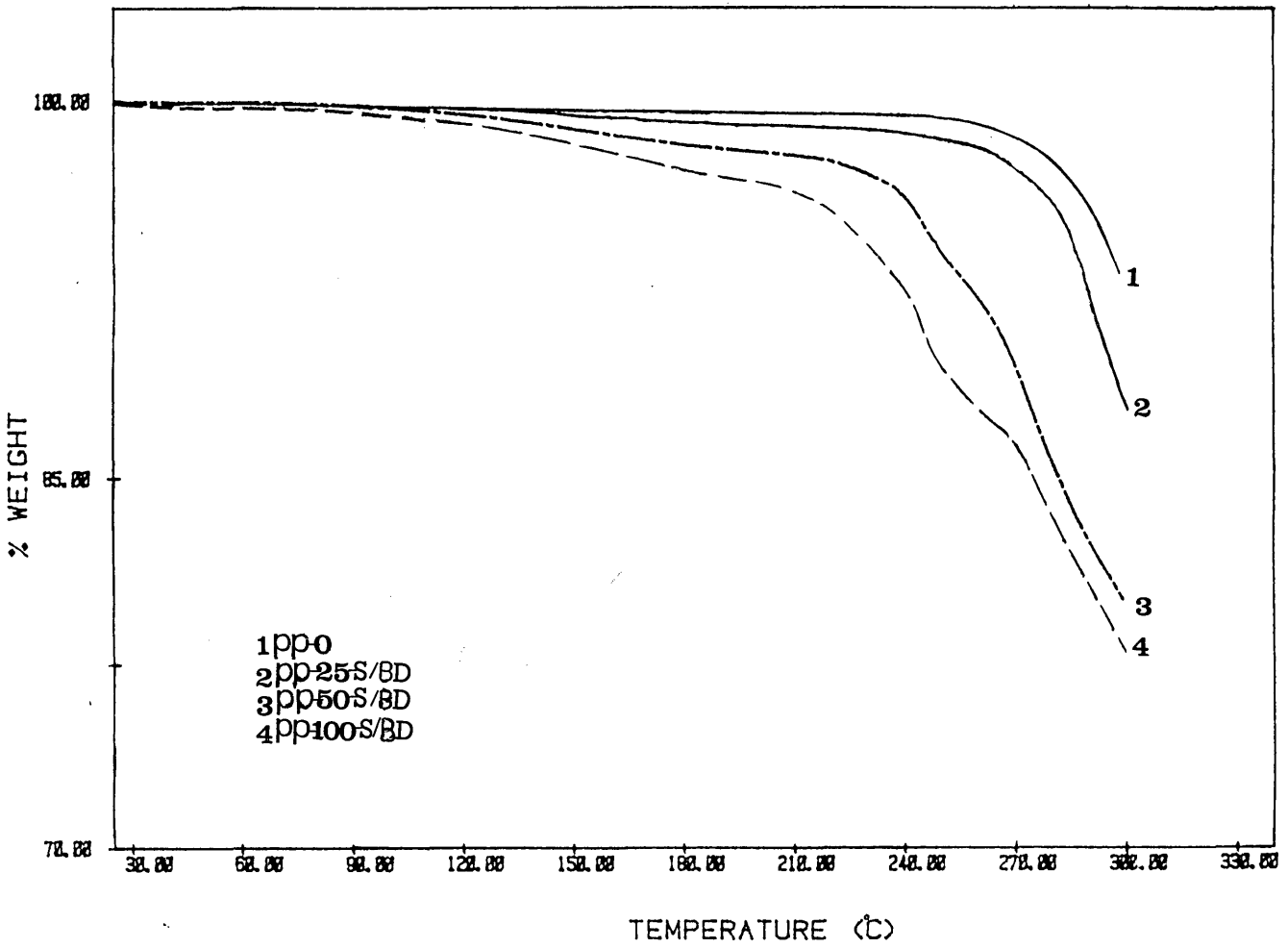


Fig.4.44 TGA thermograms of PP-X-S/BD series



occurs in two steps which is consistent with results obtained by other workers(161).

Table 4.18 Thermal Stability data for PP-X-Th/BD and PP-X-S/BD Ionomers

Polymer Code	Temperature at 5% Weight Loss (°C)
PP-0	296
PP-25-Th/BD	285
PP-50-Th/BD	225
PP-100-Th/BD	160
PP-25-S/BD	286
PP-50-S/BD	244
PP-100-S/BD	228

The values for the two series of ionomers indicate that the thermal stability of the PP-X-Th/BD ionomers is lower than that of the PP-X-S/BD ionomers. The difference becomes larger as the ionic content of the polymer increases. These results support the suggestion made in other sections that the abnormal properties of the PP-X-Th/BD ionomers after heat treatment were caused by thermal degradation of the thiosulphate groups.

4.16 Scanning and Transmission Electron Microscopy of Polyurethane Ionomers

Electron microscopy provides the most direct evidence for the domain structure of segmented polyurethanes. Both the scanning and trans mission techniques have been applied in an attempt to elucidate the microstructure of the PP-X-Th/BD series of ionomers.

Fig. 4.45 and Fig. 4.46 show respectively the scanning electron micrograph of PP-0, PP-25-Th/BD, PP-50-Th/BD and PP-100-Th/BD. The surface morphologies of the non-ionic polyurethane and the two low ionic content ionomers generally look alike in that snake-like surface structures of 1-3 μm in width are observed. Similar surface structures have been reported by Butler(19). However, no definite assignment was given to this morphology. The scanning electron micrograph of PP-100-Th/BD, on the other hand, reveals a rather characterless surface texture. No improvement could be obtained by increasing the magnification.

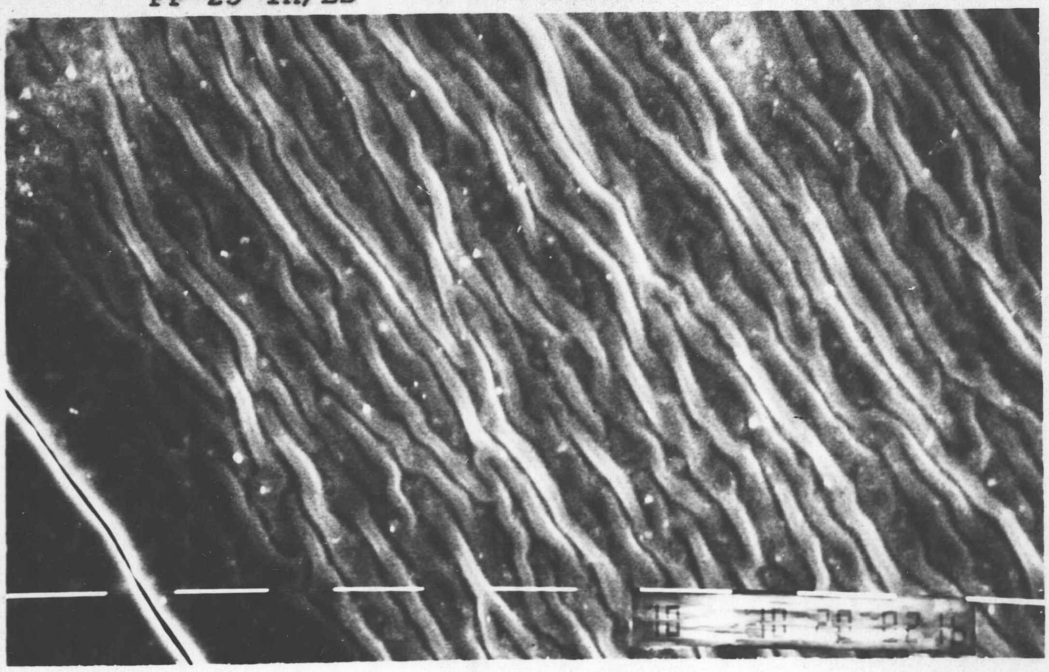
The SEM results appear to contradict with most observations that phase separation was attained only in the PP-100-Th/BD system. The size of the snake-like morphology seems to be much larger than those reported for the microdomain structure of segmented polyurethanes which usually range from 0.003-0.05 μm(83,162). Although superstructures of the order of several microns in size

have been observed in polyurethanes, these were in the form of spherulites caused by crystallisation of the hard segments(163). No evidence of such crystallisation has been noticed in the present systems. The interpretation given for the snake-like superstructures is that these are just surface artifacts induced as the casting solvent evaporated. The morphology of segmented block copolymers has been shown to depend strongly on the choice of casting solvent(164,165). Micrographs of the fracture surfaces of the polymers should confirm this postulation. However, these are not available due to the shortage of available time. The two phase morphology of PP-100-Th/BD did not show up in the scanning electron micrograph due to resolution limit of the machine.

The application of transmission electron microscopy to the same series of ionomers, however, yields very different types of micrographs as illustrated in Fig.4.47. The transmission electron micrograph of PP-0 is typical of homopolymers with a one phase amorphous structure, i.e., all regions of the micrograph are of similar electron densities. The micrograph of PP-50-Th/BD, on the other hand, shows a granule-type of structure. Finally, the result of PP-100-Th/BD indicates a two phase microstructure with dark spherical regions of 0.1-0.3 μm in diameter, believed to be the hard segment domains. It is interesting to note that the size of the domains is approximately an order of magnitude larger

than those observed by other workers(83). The difference may be attributed to the presence of ionic groups within the hard segments which are capable of forming aggregates of much larger dimensions.

Fig. 4.45 Scanning Electron Micrographs of PP-0 and PP-25-Th/BD



PP-0 ——— 10 μm

PP-25-Th/BD ——— 10 μm

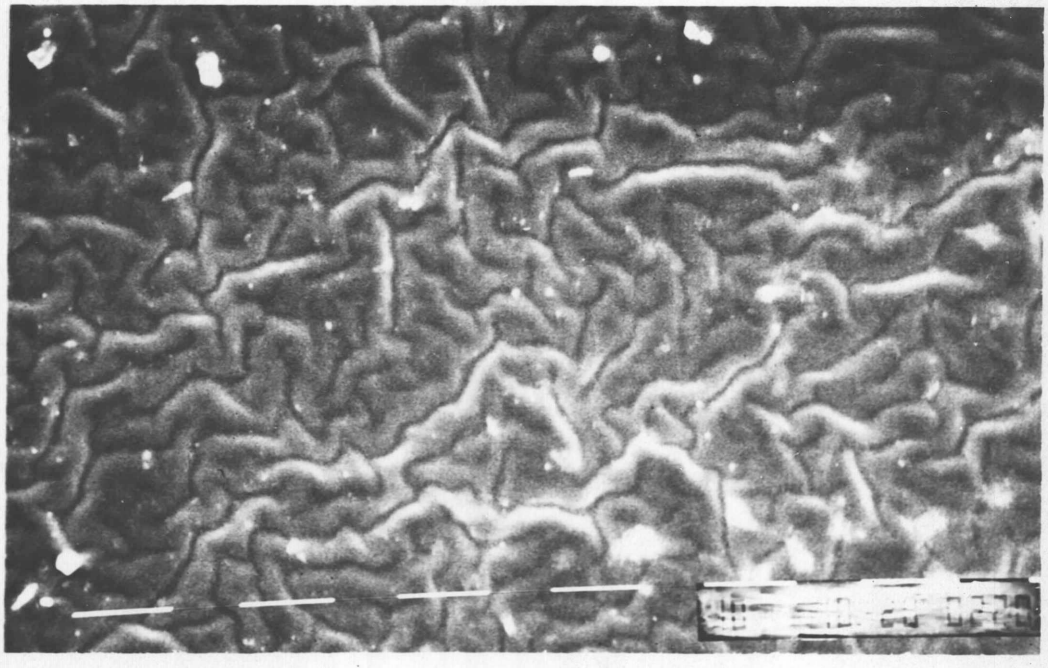
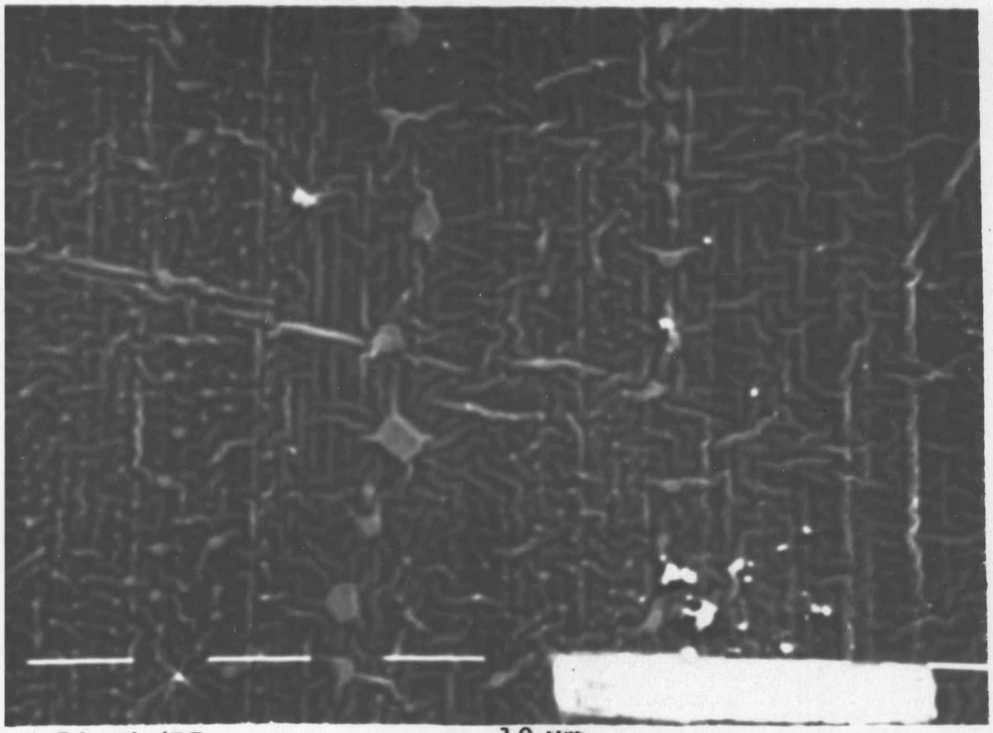


Fig. 4.46 Scanning Electron Micrographs of PP-50-Th/BD and PP-100-Th/BD



PP-50-Th/BD —— 10 μm

PP-100-Th/BD —— 10 μm

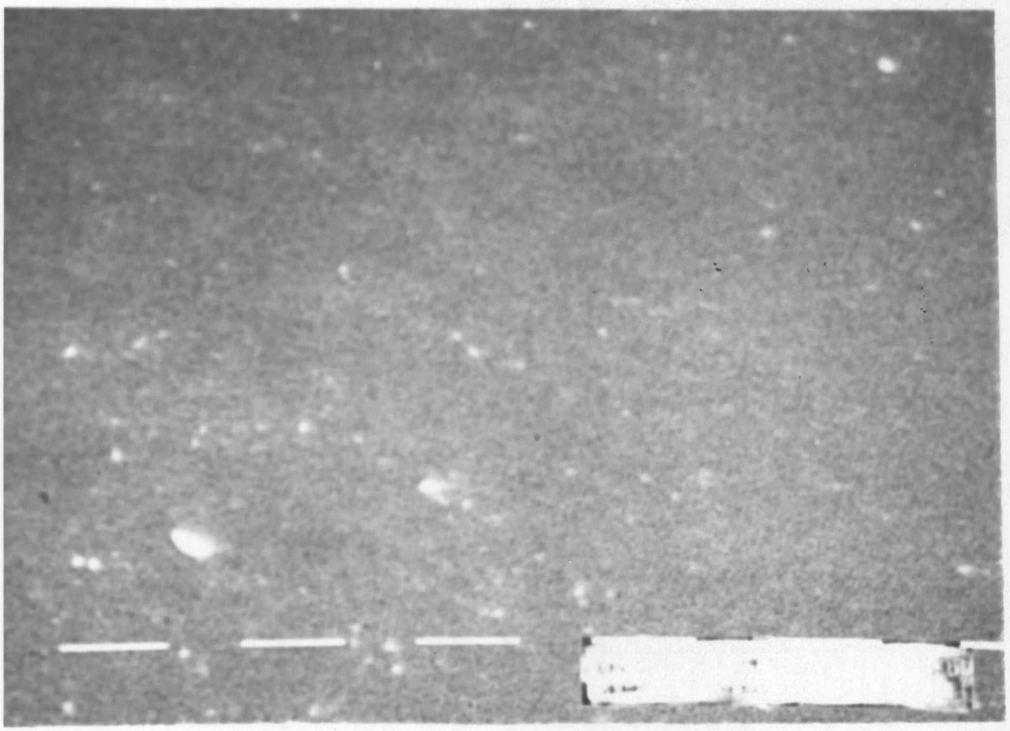
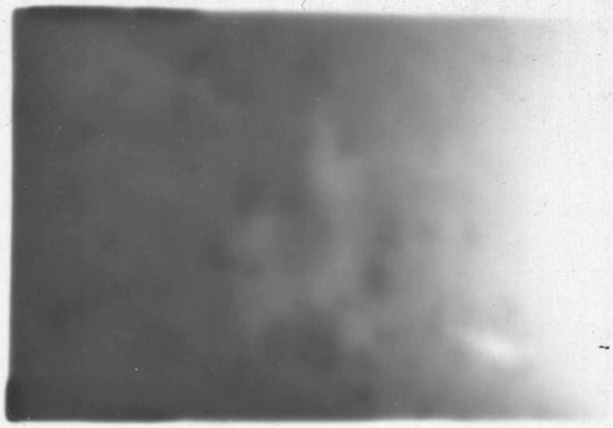


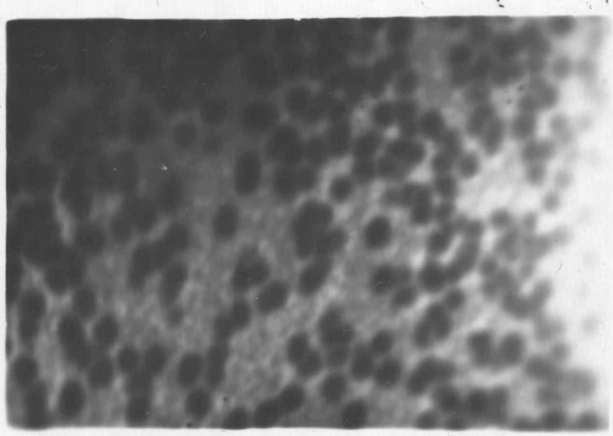
Fig. 4.47 Transmission Electron Micrographs of PP-X-Th/BD



PP-o ——— 1 μm



PP-50-Th/BD ——— 1 μm



PP-100-Th/BD ——— 1 μm

CHAPTER FIVE CONCLUSIONS AND PROPOSALS FOR FURTHER WORK

5.1. CONCLUSIONS

In the course of this study in seeking new routes for the synthesis of polyurethane ionomers, two new ionic diols, potassium-S-1,2-dihydroxypropyl thiosulphate and potassium-S-1,2-dihydroxypropyl sulphonate, have been successfully synthesised and incorporated into the hard block of several segmented polyurethanes.

In addition, several series of ionomers based on various soft segments and different ionic contents have been prepared and characterised using a variety of techniques. The conclusions to be drawn from the results are as follows:

Of the two methods used for the synthesis of TDOL, only the nucleophilic substitution reaction involving 3-chloro-propane-1,2-diol has been proved to be viable. The nucleophilic attack of thiosulphate ions on the epoxy ring of glycidol is considered as a unsatisfactory method due to the presence of a number of side reactions which led to product degradation and contamination of impurities.

With regard to the solubility and thermal stability of the two ionic diols, TDOL has been shown to have higher

solubility in common polar aprotic solvents than SDOL. This may be due to the slightly less ionic character of the former diol. The thermal stability of TDOL, on the other hand, has been found to be much lower than that of SDOL. Nevertheless, both ionic diols seemed to be sufficiently stable for use as chain extenders in the synthesis of polyurethane ionomers.

The various predetermined levels of ionic groups have been proved to be successfully introduced into the polyurethanes by IR and ^{1}H NMR spectroscopy and further confirmed by solubility studies.

The ionomers have been found to have a high tendency for residual solvent retention, especially for the high ionic content ionomers. This is attributed to the large solvation energy between the ionic groups and the polar solvents used in the synthesis and casting. The retention of solvents has been shown to disrupt the degree of H-bonding within the hard blocks and causes phase mixing.

GPC analysis of the various non-ionic polyurethanes has proved that all the polymers synthesised had relatively low molecular weight which is believed to be the key to the low mechanical strength of the ionomers. The GPC results of the the ionomers, on the other hand, has been shown to exhibit abnormal behaviour which is typical of polymers containing ionic functionalities. These include chain expansion and ionic aggregation in solution,

depending on the concentration and ionic strength of the polymer solution. The peculiar behaviour of the ionomers in dilute solution has also been demonstrated by the results of viscosity measurements.

The gradual increase in water uptake values with increasing ionic content reflects the increasing ionic character of the polyurethanes. Furthermore, the effect of ether content in the polyols has been shown to be significant in controlling the amount of water absorbed by the polyurethanes.

The unusually high equilibrium water uptake values and mechanical strength of the PP-X-Th/BD series of ionomers after thermal treatment are thought to be caused by thermal degradation of the thiosulphate group to give disulphide linkages which resulted in chemical crosslinking.

Apart from the PTMG-0 polymer, all the non-ionic polyurethanes have been found to exhibit a high degree of phase mixing, shown by DSC and DMTA analysis. This has been attributed to the low molecular weight nature of the polymers and possibly to the retention of residual solvents. The requirement of a minimum molecular weight for phase separation has been proposd. The high degree of phase mixing has led in most cases to deterioration in mechanical properties.

On the whole, the results have demonstrated that incorporation of ionic groups increases the degree of phase separation and consequently yields materials with improved mechanical properties.

5.2. Proposals for Further Work

The results of extensive investigation on the synthesis and properties of several series of new polyurethane ionomers has contributed to a much better understanding of the properties of these new ionic polymers. However, a number of the postulations made are still in need of verification.

1. Although TGA results suggested that both TDOL and SDOL are sufficiently stable for use as chain extenders for ionomer synthesis, similar Bunte salts have been reported to decompose at around 100°C in the solid state. Therefore an isothermal study of TDOL at around 100°C should give a much clearer picture of the thermal stability of this diol. A similar study of the ionomers based on TDOL is also needed. This should confirm the assignment of the DSC exotherm, the high water uptake and mechanical strength after heat treatment, which have been attributed to the thermal degradation of the thiosulphate groups. The thermal stability of TDOL and related ionomers should also be examined by spectroscopic techniques, such as infrared and mass spectroscopies.

2. It will be interesting to apply the Flory-Huggins theory of thermodynamics of polymer mixtures to segmented polyurethanes which involves finding the solubility parameters of the two individual segments. To the author's best knowledge, such data has not been reported in the literature. The results of such experiments should throw some light on the minimum molecular weight required for phase separation in these segmented copolymers. However, precautions must be taken to allow for the effects of H-bonding, as well as possible crystallisation of the segments.

3. Further studies involving electron microscopy are required in order to obtain more knowledge of the microdomain structure of the ionomers. In particular, the effect of molecular weight and different casting solvents on the morphology should prove to be interesting.

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