Polyurethanes for Enzyme Immobilisation

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A basic introduction to polyurethane technology is given for those unfamiliar with this area, followed by a review of the work published to date on polyurethane ionomers. The latter covers the different approaches to synthesis of ionomers and their reported properties.

A summary of the techniques for forming covalent polymer enzyme bonds is also presented, along with the routes used for enzyme entrapment in gels and a full summary of all techniques involving polyurethanes.

Polyurethane macromonomers, formed from 2-butene-1,4-diol, were unreactive under the mild conditions neccessary for gel entrapment of enzymes. The end capping of polyurethanes with acryloyl chloride was found to be unacceptable as side reactions led to polymer degradation.

Isocyanatoethyl methacrylate was proven to successfully end cap polyurethanes without significant side reactions and the resultant macromonomers readily formed both homo and copolymers, using thermal or photochemical initiation under mild conditions. Use of acrylamide, N-vinyl pyrrolidone or hydroxyethyl methacrylate as comonomers during gel formation gave control over physical properties of the final materials. The key factors responsible for the effects of the comonomers on final morphology were found to be the polarity, ability to hydrogen bond and degree of disorder introduced by the comonomer molecules.

The new chain extender potassium-S-1,2-dihydroxypropyl thiosulphate was synthesised, characterised and successfully used in solution polymerisations to give polyurethane anionomers. Spectroscopic, physical and some solution properties were investigated and all were dominated by inter and intramolecular interactions between ionic groups on the polymer backbone.

The ionic chain extender was shown to be inert during radical polymerisations and a fully water soluble anionomer was formulated and end capped with isocyanatoethyl methacrylate. This macromonomer was used for gel formation in aqueous solutions under mild conditions suitable for enzyme immobilisation. A brief study of the properties of the final materials was carried out and probable causes for their differences from similar materials prepared in organic solutions were presented.

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Abbreviations used in the text.

Abbreviation	Compound Name.
AA	Acrylic Acid
ACl	Acryloyl Chloride
ACM	Acrylamide
ACV	4,4'-azo-bis-cyanopentanoic Acid
AIBN	α-azo-iso-butyronitrile
BD	1,4-Butanediol
BDU	2-Butene-1,4-Diol
BEE	Benzoin Ethyl Ether
CPD	3-Chloro-1,2-propanediol
DCM	Dichloromethane
DMA	N,N-Dimethyl Acetamide
DMF	N,N-Dimethyl Formamide
DMSO	Dimethyl Sulphoxide
EtOH	Ethanol
HEMA	2-Hydroxyethyl Methacrylate
HQ	Hydroquinone
IBMK	4-Methyl Pentan-2-one
IEM	Isocyanatoethyl Methacrylate
IPA	Isopropyl Alcohol
MDI	Diphenylmethane Diisocyanate
MeOH	Methanol
MMA	Methyl Methacrylate
Na_2ACV	Disodium 4,4'-azo-bis-cyanopentanoate
NVP	N-Vinyl pyrrolidone

Abbreviation	Compound Name
PEG	Polyethylene Glycol
TDOL	Potassium-S-1,2-dihydroxypropane thiosulphate
THF	Tetrahydofuran
T-12	Dibutyl Tin Dilaureate

Abbreviation	Meaning
B. Pt.	Boiling Point
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
IR	Infrared Spectroscopy
M. Pt.	Melting Point
NMR	Nuclear Magnetic Resonance Spectroscopy
RI	Refractive Index
Tg	Glass Transition Temperature
UV	Ultra-violet Radiation

1. Introduction to Polyurethanes.

The science of polyurethanes is an area that has been frequently reviewed [1, 2, 3, 4]. Nevertheless, a brief summary of the major points is necessary as an aid to understanding the work presented in this thesis. The areas discussed are the chemical reactions and side reactions involved, the range of monomers available and the formation of elastomeric materials.

1.1 Chemical Reactions and Side Reactions.

1.1.1 Urethane Formation.

The urethane or carbamate unit is one of three closely related groups. These are the carbonate, carbamate and carbamide and they have the same relationship to each other as esters and amides. All three may be considered as derivatives of carbonic acid and all can be prepared by reaction of phosgene with alcohols, amines or both. See equations 1.1 to 1.4

$2\ ROH + ClCOCl \longrightarrow R\text{-}OCOO\text{-}R$ Carbonate....Equation 1.1

$2\ RNH_2 + ClCOCl \longrightarrow R\text{-}NHCONH\text{-}R$ Carbamide....Equation 1.2

$ROH + ClCOCl \longrightarrow R\text{-}OCOCl + RNH_2 \longrightarrow R\text{-}OCONH\text{-}R$

Carbamate via Chloroformate ester....Equation 1.3

$RNH_2 + ClCOCl \longrightarrow RNCO + ROH \longrightarrow R\text{-}NHCOO\text{-}R$

Carbamate via Isocyanate....Equation 1.4

In practice, phosgenation is used only in exceptional circumstances, such as preparation of N,N-disubstituted urethanes from reaction of secondary amines with chloroformate esters.

Equation 1.4 is of special importance as it summarises the normal route for urethane formation, though the phosgenation step is usually avoided by using commercially available isocyanates.

Isocyanates react with the majority of protic compounds and the order of reactivity with the more common compounds is RNH_2 > H_2O > ROH > PhOH > RCO_2H. The stability of the resultant materials is the reverse of this order in most cases. The order is of importance, both when competing groups are present and when protecting groups are used with isocyanates. Isocyanates may be protected or blocked, for example, by reaction with phenol compounds that form a relatively unstable product. This may then be attacked at a later date by more reactive compounds such as aliphatic amines or alcohols, which displace the protecting group to leave a stable urethane or urea,

Such methods of protection are most often used with isocyanate containing polymers during long term storage to prevent side reactions.

The reaction of di or polyfunctional isocyanates and alcohols gives polymers, such polymers first being developed in the 1930's in response to the introduction of polyamides.

Polymerisations were, initially, all carried out in bulk and it was 1960 before the first solution polymerisations were reported [5]. By eliminating the need for melt polymerisations, polymers can be made that do not melt below their decomposition temperature and, in general, thermal decomposition can be avoided.

It should be noted that polyurethanes do not have a high thermal stability. Thermal degradation of urethanes occurs rapidly at temperatures above 200^{o}C and the mechanism has recently been reported to be direct reversal of the urethane

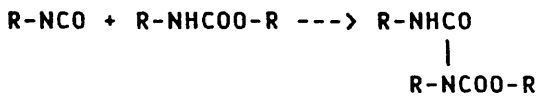
formation reaction [6]. The free isocyanate and alcohol groups liberated may be involved in further reactions upon cooling.

Solution polymerisations have also opened up the field of small scale preparation and development of modified polyurethanes or polymers formed from otherwise immiscible monomers.

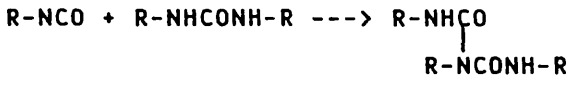
1.1.2 Side Reactions.

There are three important side reactions in polyurethane chemistry, all involving isocyanates. These are hydrolysis of isocyanates and the formation of allophanates and biurets.

Allophanate or biuret formation is the result of reaction of an isocyanate with a urethane or urea group respectively. See equations 1.5 and 1.6. When compared with the rate of reaction of an isocyanate with amines or alcohols, formation of allophanates or biurets is slow. But the process is important when an excess of isocyanate is present. The presence of a base, such as a tertiary amine, activates the urethane or urea by hydrogen bonding with the slightly acidic protons of these groups. During polymer formation, these reactions cause branching and may result in gellation.



Allophanate Formation....Equation 1.5



Biuret Formation....Equation 1.6

Hydrolysis of isocyanates (equation 1.7), which is a vigorous reaction, may or may not be useful depending on the final polymer application.

Presence of traces of water in reagents or solvents upset the ratio of isocyanates to hydroxyls and thus affects the final molecular weight of the polymer. However, one of the products of hydrolysis is carbon dioxide and the deliberate addition of water as a reagent to viscous mixtures in the stages preceeding gellation results in rapid evolution of gas which cannot easily escape. Instead, the reaction mixture forms a foam. The end result, in such cases, is a crosslinked foam. Many variations of these foams are in everyday use.

$$RNCO + H_2O \longrightarrow \underset{\text{Carbamic Acid}}{R\text{-}NHCOOH} \longrightarrow RNH_2 + CO_2$$

Isocyanate Hydrolysis....Equation 1.7

The amine groups produced in the hydrolysis of isocyanates can react to give urea units and this is the source of urea in polyurethanes.

1.1.3 Catalysis.

The formation of urethanes may be catalysed by a variety of tertiary amines and mercury, zinc or tin compounds [7, 8, 9]. The amines activate the alcohols by hydrogen bonding to the alcohol protons and enhance the proton transfer steps. The metal based catalysts form labile complexes with the isocyanates and, in so doing, increase its reactivity[28].

Catalysts allow low temperature reactions with thermally sensitive monomers and give better reaction rates with

isocyanates of low reactivity. The main drawback is that some catalysts also promote allophanate formation.

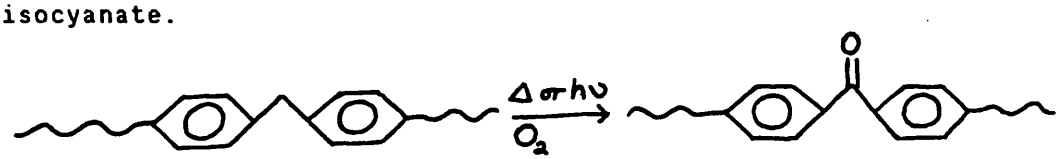
1.2 Monomers.

1.2.1 Isocyanates.

A variety of diisocyanates are in common use, but polyisocyanates are rarely, if ever, used.

Aromatic diisocyanates, such as 2,4-toluene diisocyanate (TDI) and 4,4'-methylene-bis-isocyanate (MDI), are the most popular because of their high reactivity. The latter example is also a non-volatile solid and is, therefore, the safest diisocyanate in use.

Aliphatic diisocyanates give more stable urethane units and are not prone to yellowing, which is caused by oxidation of groups activated by the benzene ring of aromatic isocyanates. See equation 1.8. The disadvantage is that they have low reactivities and often require catalysts. A typical example is 1,6-hexane diisocyanate.



Oxidation of MDI....Equation 1.8

1.2.2 Small Alcohols.

In order to form a polyurethane, a di or polyfunctional alcohol is necessary. In practice, these are usually small di or trialcohol molecules.

Trialcohols such as 1,2,3-propanetriol or 1,2,3-trimethylol propane are used to introduce branch points and create gels.

Dialcohols are chain extenders and many are available. Typical examples are 1,2-ethanediol and 1,6-hexanediol, but by far the most frequently occuring one is 1,4-butanediol. Unusual diols may be used to introduce new functioal groups into polyurethanes.

The synthesis of block copolymer polyurethane elastomers from small diols and hydroxyl terminated prepolymers (see section 1.3) has generated great interest in model polymers based on the diisocyanates TDI and MDI and methods for the synthesis of monomdisperse oligomers have been devised [10, 11].

Polymers prepared from MDI and small diols are hard materials with melting transitions of 180^{o}C and above. Frequently, the decomposition point is reached before a melting transition is found.

There is often a regular arrangement of MDI-diol repeat units in the solid phase and paracrystallinity is often seen, especially with annealed samples.

Numerous X-ray studies of model compounds have led to an understanding of the packing of molecules of these polyurethanes. The two key features are hydrogen bonding between the urethane carbonyls and the urethane protons of neighbouring chains and the regular folding of diol residues and packing of benzene rings of MDI residues.

The reader is referred to the literature [11, 12, 13, 14] for the structure elucidation of MDI-butanediol models and an X-ray study of elastomer hard blocks (see section 1.3), based on several small diols, has been presented by Blackwell and Lee [15].

1.2.3. Hydroxyl Terminated Prepolymers.

An alternative to small dialcohol molecules is the use of hydroxyl terminated prepolymers. Several types of prepolymer have been used, including polyesters such as poly(tetramethylene adipate), polybutadienes, polydimethyl siloxanes, polyacetals [16] and polyethers.

These prepolymers create block copolymers when used as monomers in polyurethane formation. Their properties, such as hydrophilicity and glass transition temperatures (usually below room temperature), dramatically extend the range of characteristics that can be achieved in a final polyurethane. Being polymers in their own right, the properties of any given type of prepolymer may be varied by alteration of molecular weight and, in the case of polyesters, by the choice of monomers used to create the prepolymer.

Polyethers are the most stable prepolymers widely available and the most commonly used. Four types are now available, three commercially. These are polypropylene glycol, polyethylene glycol and polytetramethylene glycol. The fourth is polytrimethylene glycol [17]. Block copolyethers may be synthesised with polyethylene ether and polypropylene ether blocks [18].

The use of prepolymers has thus allowed the development of customised polyurethanes for specific applications and is instrumental in the creation of polyurethane elastomers.

1.3 Elastomers.

Polyurethane elastomers are block copolymers with the two blocks being incompatible. In addition, the glass transition temperature (Tg) of one of the blocks must be well below normal operating temperature.

These conditions can be met by using both a small diol (see section 1.2.2) amd a hydroxyl terminated prepolymer (see section 1.2.3) in the formation of the polyurethane. The block formed from diisocyanate and small diol forms the block with a high Tg, known as a hard block, and the prepolymer forms the low Tg block, known as the soft block.

The incompatibility of these blocks results in phase separation of the blocks into domains. Usually, small domains of the hard blocks form and are randomly distributed in a continuous amorphous phase formed from the soft blocks.

Each hard domain contains blocks from many chains, which are believed to be packed in the same manner as simple urethanes (section 1.2.2). Any given chain will have hard blocks in more than one domain. These domains therefore act as crosslink sites and are joined by the soft blocks of polymer chains.

The soft phase is usually amorphous and made up of chain segments well above their Tg and which are also extensively coiled.

If a polymer sample is stretched, the soft chain segments are sufficiently free to uncoil, allowing the sample to lengthen. The hard domains, however, prevent the polymer chains from sliding past each other. When the sample is relaxed, the soft blocks coil up again causing the sample to contract. Thus the polymer displays elastomeric behaviour.

In addition, the hard domains also act as filler particles, increasing the elastic modulus of the material above that for the pure soft prepolymer.

Each individual prepolymer has its own set of properties and these affect the degree of phase separation that occurs.

In general, phase separation is almost complete for polybutadienes [19, 20] and polydimethyl siloxanes [21, 22].

Polyethers do not phase separate to such a high degree [23], probably due to hydrogen bonding between some of the urethane protons and the ether oxygens of the polyether. The phase separation of polytetramethylene glycol segments has been studied by neutron scattering [25] as well as more common techniques such as differential scanning calorimetry [24] and has been found first to decrease, and then, to increase with increasing temperature. This polyether is also the only commonly used prepolymer to sometimes form a crystalline soft phase.

Poyester soft blocks are the slowest to separate [26] as they have the polar carbonyls of the ester groups with which to form strong hydrogen bonds to urethane protons. The effects of ageing and annealing on phase separation of such soft blocks has also been studied [27].

2 Polyurethane Ionomers.

2.1 Introduction.

Ionic polymers have been available for many years for uses such as ion exchange [29]. Typical examples are sulphonated polystyrenes, sulphonated phenol-formaldehyde resins and polymers bearing quaternary ammonium groups.

Relatively few polyurethane ionomers have been reported, though the classes of cationomer, anionomer and zwitterionomer are all represented.

The main areas of application for urethane ionomers being investigated are wound dressings [30], dialysis membranes [31, 32], hydrophilic and water soluble materials[33] for the coatings industry and prosthetic implants. Work on the latter application has progressed as far as in vivo studies with animals[34].

2.2 Synthetic Routes.

Three general routes have been used to prepare polyurethane ionomers. These are:-

One - Direct introduction of ionic groups using an ion containing monomer during polymerisation.

Two - Introduction of a group, on a monomer, which may be converted to an ionic group after polymerisation.

Three - Use of the urethane link to introduce or create an ionic centre. (For polyurethane-ureas, the urea link may be similarly used.)

All the reported examples of polyurethane ionomers fall into one of these categories.

2.2.1 Ionic Monomers.

In theory, the simplest route to an ionomer is to take an

ionic monomer and use it in the polymer forming reaction. In practice, however, numerous problems may arise, such as solubility in reaction media or melting points for bulk polymerisation and compatibility with other monomers. Nevertheless, several authors have prepared ionomers by this route.

In a review of research work carried out at Bayer Chemicals [33], the synthesis of polyurethane-ureas using diamino-carboxylate salts was reported. The work, dating back to 1957, began with the synthesis of water soluble polyureas from potassium-2,5-diamino benzoate. The method was then extended to the preparation of polyurethane-ureas. These materials were segmented polymers with polyether or polyester soft segments.

Other chain extenders used for this method were 2,6-diamino benzoate salts (often referred to as lysine salts) and N-(2-aminoethyl)-3-propanoate salts. Sulphonate salts were introduced by use of sodium N-(2-aminoethyl)-3-aminopropane sulphonate in a similar manner.

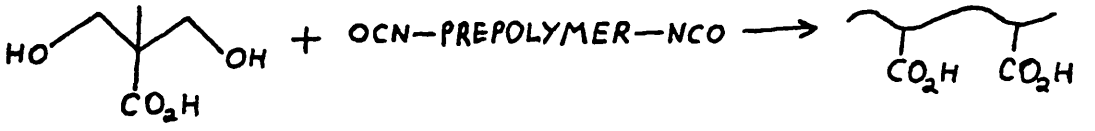
The sodium or potassium salts were generally used, rather than the free acid, to avoid any possible reaction between the acid and the isocyanate used in the polymerisation. Although the reaction conditions were not specified in the review, the authors reported that no abnormal viscosity increases were observed during polymerisation. This was attributed to hydration of the ionic groups preventing aggregation of the ionomer chains. However, no mention was made of the likely hydrolysis of some of the isocyanate present by the water of hydration and the

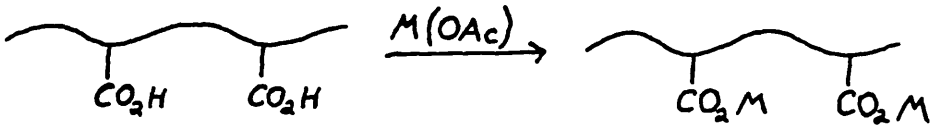
resultant reduction in molecular weight that would follow. This factor, also, could nullify any viscosity increase that might otherwise have been detected.

Much more recently, the use of 2,2-dimethylolpropanoic acid as a chain extender to prepare anionic polyurethanes has been reported by Al-Salah et al. [35]. See also equation 2.1.

Following synthesis of a segmented polyurethane by bulk polymerisation using the free carboxylic acid, the polymer was dissolved in DMF and the acid groups converted to the desired metal-carboxylate salts by cation exchange with the appropriate metal acetate. A variety of mono and divalent metal cations were used successfully, including alkali metal, alkali earth and transition metal ions. The effect of cation size and charge were studied (see section 2.3.3).

The synthesis of polyurethane anionomers from potassium-S-2,3-dihydroxypropyl thiosulphate [30] is discussed in section 8 and, therefore, is not dealt with at this stage.

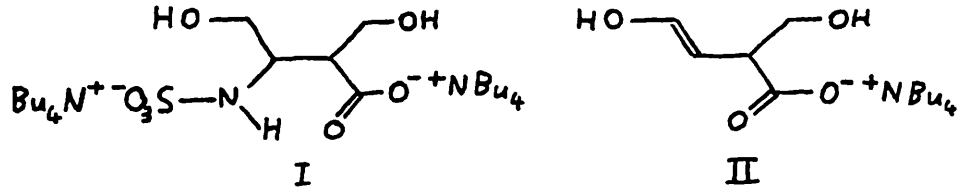




Ionomer synthesis using 2,2-dimethylol propanoic acid...Equation 2.1

One further method involving ionic chain extenders has been reported [31, 32]. In a three step synthesis, Egboh et al prepared a mixture of products, the predominant species of which were

believed to be compounds I and II (see equation 2.2) in a ratio of approximately 7:3. The workers suggested some further unidentified products were also present. This mixture was then used in the chain extension step of a polyurethane synthesis. The extent of the success of this approach is not clear, though these workers did observe some alterations in both soft segment Tg and equilibrium water uptake of the final polymers.



Products of chlorosulphonation of 2-butene-1,4-diol...Equation 2.2

All the literature examples of ionic monomers for polyurethane synthesis so far reported give rise to anionomers. In principle, there is no bar to the introduction of cationic groups by this technique.

2.2.2 Functional Group Modification.

The second main approach to the creation of urethane ionomers is the introduction of a functional group and its subsequent reaction to generate an ionomer. This philosophy has led to cationomers, anionomers and zwitterionomers.

2.2.2.1 Cationomers.

Two forms of cationomers have been prepared, both being reported by Dieterich et al[33].

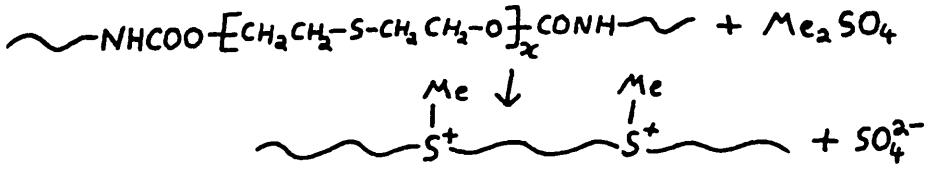
The first is prepared by the synthesis of a segmented polyurethane-urea, using either polyether or polyester soft segments, with N,N-bis-(2-aminoethyl)-amine used as a chain extender to introduce secondary amine groups into the backbone.

The secondary amines will be predominantly untouched by the chain extension step due to its lower reactivity with isocyanates relative to the two primary amine groups.

The residual secondary amine groups are then quaternised to form the cationomer, alkylating agents such as alkyl iodides or dialkyl sulphates being used for this step.

A similar reagent, N-methyl-N,N-(2-hydroxyethyl)-amine has also been used to form polyurethane cationomers with no urea groups and a combination of quaternisation and crosslinking was achieved by Nierzwicki et al [36] using triethanolamine as chain extender and 1,6-dibromohexane as alkylating agent.

An analagous use has been made of polythioethers incorporated in a polyurethane to form sulphonium cations by alkylation (see equation 2.3) has also been reported [33].

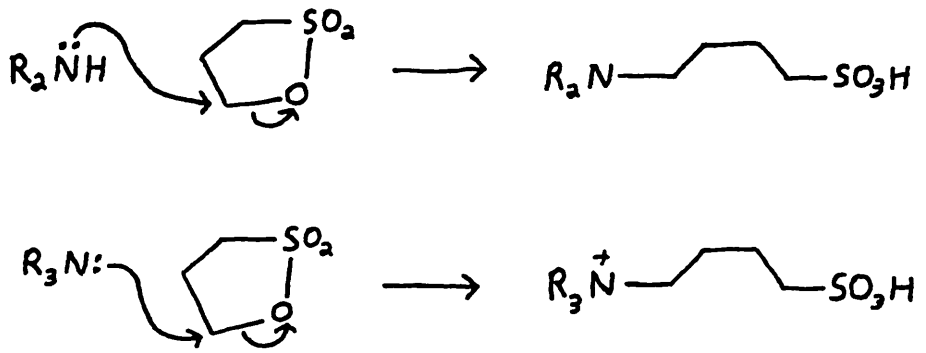


Methylation of Thioethers....Equation 2.3

2.2.2.2 Zwitterionomers.

The reported syntheses of zwitterionomers depend upon the nucleophilicity of amino groups in or attached to a polurethane backbone and the preparation proceeds by a pathway almost identical to quaternisation with dialkyl sulphates.

γ-propane sultone, a cyclic sulphonate ester undergoes S_N2 attack by primary, secondary or tertiary amines resulting in ring opening. For primary and secondary amines, a proton transfer occurs from nitrogen to sulphur to give the sulphonic acid, but for tertiary amines, a zwitterion is formed. See equation 2.4.



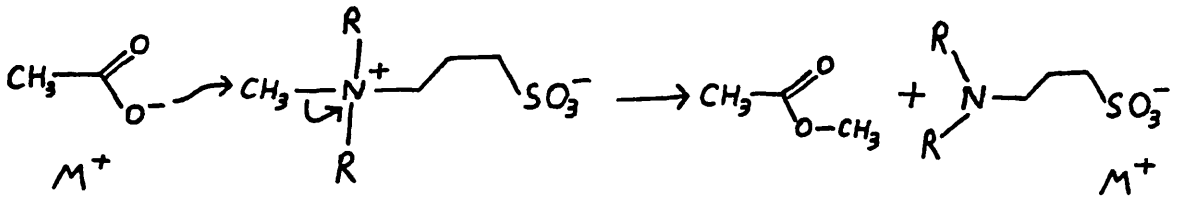
Amine attack on γ-propane sultone....Equation 2.4

Hwang et al prepared a polyurethane using N-methyl-N,N-diethanolamine as a chain extender to introduce tertiary amino groups into a polyurethane as part of the backbone. These were then reacted as described above to yield a zwitterionomer with quaternary cations in the backbone and sulphonate anions on short side chains [37]. This method has since been used with segmented polyurethanes with widely varied soft blocks [34, 38, 39, 40, 44].

2.2.2.3 Anionomers.

Two closely related methods have been used to generate anionomers by modification of a specifically introduced group. Both are dependent on the reaction described in section 2.2.2.2 for γ-propane sultone.

The first approach, taken by Cooper et al, is to prepare a zwitterionomer as previously described and then to attack it with a metal acetate in DMF solution [40]. The least hindered group of the quaternised amine undergoes S_N2 attack to leave an anionomer as shown in equation 2.5.



Zwitterionomer to anionomer conversion.....Equation 2.5

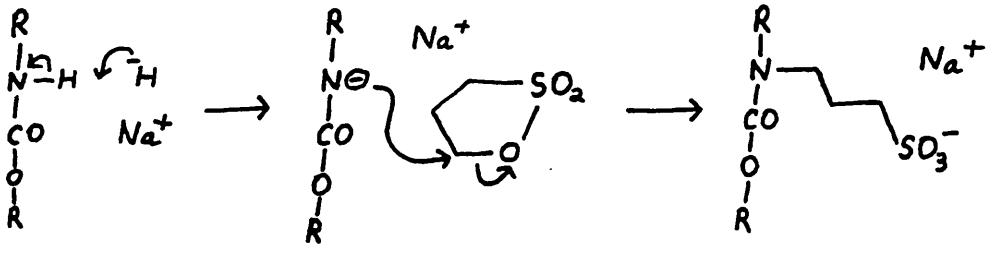
The second approach is the use of N,N-bis-(2-aminoethyl)-amine to form a segmented polyurethane-urea with secondary amine groups in the backbone [33]. Subsequent treatment with γ-propane sultone yields a sulphonate anionomer (see equation 2.4).

2.2.3 Derivatisation of the Urethane Group.

Use of the urethane group may be regarded as a special case of reaction of an introduced group as described in section 2.2. However, it is a special case since, by definition, all polyurethanes contain urethane groups and utilisation of these groups can, in theory, be applied to any polyurethane. For these reasons, this mode of attack is given a separate section.

The urethane proton is labile and its removal provides a means of enhancing the reactivity of this group. Adibi et al used sodium hydride to remove the urethane proton, leaving a metallated urethane which was used to initiate anionic graft polymerisation [41]. The metallated polymer is an anionomer in its own right, but was found to be increasingly unstable with time, temperature and degree of metallation. Its use is therefore limited to that of a temporary precursor to further reactions.

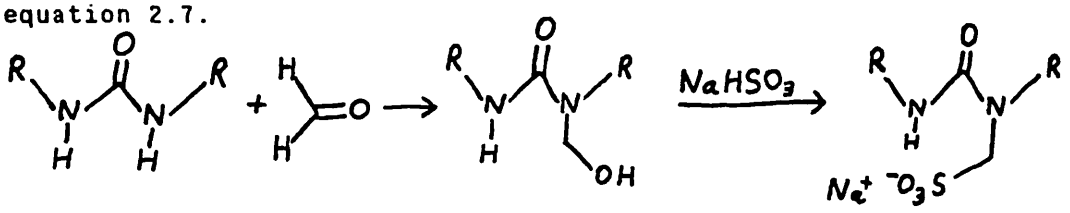
It was put to just such a use by Cooper et al to form stable anionomers [42, 43]. The urethane anions were used to attack γ-propane sultone to form sulphonate anions attached to the urethane nitrogen by a short side chain (see equation2.6).



Anionomers via urethane metallation....Equation 2.6

An analogous approach using a trialkyl amine to remove a proton from the more reactive urea group has also been reported[33].

The greater reactivity of the urea of the urea group, present in polyurethane-ureas, allows a further synthetic approach. The urea group is reacted with formaldehyde in the presence of sodium hydrogen sulphite and undergoes the initial step involved in the urea-formaldehyde condensation polymerisation. But the sulphite ion prevents the condensation step, displacing the hydroxyl group of the newly formed metylol group by S_N2 displacement. The result is a suphonate group attached to the urea unit by a methylene group [33]. See equation 2.7.



Urea-formaldehyde ionomer synthesis....Equation 2.7

2.3 Physical Properties of Ionic Polyurethanes.

2.3.1 Introduction.

The underlying reason for interest in introducing ionic groups into polyurethanes is the search for improved mechanical properties. The inclusion of ionic centres introduces electrostatic forces between groups in molecules and alters the polarity of specific segments of the polymer molecule, usually the hard segment. Hence they have a significant effect on the properties and morphology of the final polyurethane.

Several methods are commonly used for the study of these effects. The usual techniques are infrared spectroscopy for study

of hydrogen bonding, differential scanning calorimetry (DSC) for glass transition temperatures, dynamic mechanical analysis (DMA) for glass transitions and morphological information and tensile testing for Youngs modulus, ultimate tensile strength and elongation at break. A recent but little used technique for study of polymer morphology is pulsed nuclear magnetic resonance[36]. In this technique, the protons are excited and their rate of relaxation is recorded. The relaxation time reflects the rigidity of the environment of the protons, being faster for more rigid environments. Computer analysis of the relaxation curve allows an estimation of the proportion of protons on the different environments present in the solid polymer.

2.3.2 Zwitterionomers.

The most extensive investigation of an ionised polyurethane system was carried out by Cooper et al on their series of zwitterionomers [37, 38, 39, 40, 44]. See section 2.2.2.2 for the synthesis of these polymers. These workers have studied materials with a selection of polyether soft segments, namely polytetramethylene glycol (PTMO), polyethylene oxide (PEO) and polypropylene oxide (PPO). Hydroxyl terminated polybutadiene (PBD) was also used as a soft segment.

An infrared investigation of the polymers based on PTMO and PBD gave an early indication of the effects of ionic content. The non-ionic PTMO material showed an even quantity of carbonyls involved in hydrogen bonding and those not hydrogen bonded. Since almost all the urethane protons were involved in hydrogen bonding, as indicated by the N-H stretching frequency, the extra

hydrogen bonding of the N-H groups was believed to be due to phase mixing and hydrogen bonding to the polyether oxygen atoms. For the non ionic PBD material, almost all the carbonyls were involved in hydrogen bonding. The latter material is very well phase separated due to the incompatibility of PBD with the polar urethane groups.

Upon inclusion of ionic groups, the strength of the hydrogen bonds was increased, the N-H stretching frequency showing a corresponding fall in the N-H bond strength. The quantity of hydrogen bonded carbonyls fell for both materials. These observations were attributed to hydrogen bonding between the urethane protons and the sulphonate groups, replacing hydrogen bonding to the carbonyl groups.

Examination of glass transition temperatures and the change in heat capacity, ΔCp, of the transition gave further information. ΔCp is larger for larger increases in freedom of motion as the transition is passed through. This, in turn, reflects the morphology of the polymer.

The polybutadiene based polymer showed no change in soft phase glass transition temperature, ΔCp or transition width with ionic content.

The PTMO and PPO based polyurethanes both displayed decreasing soft phase Tg's, a narrowing of the transition width and a fall in ΔCp relative to the control materials.

The PEO containing material, which is completely phase mixed when non ionic due to the higher compatibility of the polar urethane and PEO segments, showed a falling soft phase Tg and ΔCp with increasing ionic content but a broadening of the transition.

From these observations, it was concluded that the addition of ionic groups increased the degree of phase separation by increasing the polarity of the hard segments and making them less compatible with the polyether segments. The fall on soft phase Tg reflects the increasing purity of the soft phase and the fall in ΔCp indicated increasing cohesiveness of the hard domains due to electrostatic interactions within the domain. The PEO material showed a broadening of the transition zone as it moved from a single phase to a phase separated morphology and developed a region of phase mixing of varying composition at the interface between the two phases. For PTMO and PPO materials, which were already partially phase separated, a reduction in transition zone width reflected a reduction of the quantity of material in the interfacial region.

The PBD material was phase separated to a very high degree before ionisation and thus showed no further changes.

Analysis of the mechanical properties of these ionomers further clarified the effects of ionic content.

A rubbery plateau appeared in the storage modulus versus temperature curve (obtained by DMA) for the PBD containing polymer and as ionic content was raised, it showed increasing magnitude and temperature independence over a broader temperature range. Increases in Youngs modulus and tensile strength were also apparent.

All the polyether containing materials showed a similar rubbery plateau. However, the changes in the plateau modulus with ionic content were much greater. Similarly, Youngs moduli and

tensile strengths also increased rapidly with increasing ionic content. A decrease in flexibility was reflected in a decrease in elongation at break.

These changes all reflect alterations in polymer morphology and the forces acting within the domains. The PBD based polyurethane shows an improvement in properties as the thermal stability and cohesion of the hard domains is enhanced by increasing electrostatic interactions.

The polyether systems also show this behaviour. In addition, ionic content greatly improves phase separation in the materials and an interconnecting hard domain is formed. This latter effect explains the greater magnitude of changes with ionic content seen for these systems. Improved cohesion and stability in such a system have a much greater effect than in a corresponding system of isolated discrete hard domains, such as the PBD based system.

2.3.3 Anionomers.

No anionomer system has been studied as systematically as the zwitterionomers, but studies of three different types of anionomer all come to the same general conclusions, which are in turn, very similar to those of the study on zwitterionomers.

The properties of anionomers derived from zwitterionomers (see section 2.2.2.3) has been briefly investigated using PTMO containing materials [42].

As was seen for zwitterionomers, increasing ionic content lowers the soft phase Tg and increases in Youngs modulus and tensile strength are observed.

A new factor is present in these anionomers, namely the nature of the metal counter ion.

Cooper et al did not observe any visible effect of counter ion type on the soft phase Tg, which is not suprising as the majority of ionic groups reside in the hard domain and PTMO is not particulary effective at complexing ions, unlike PEO. However, Cooper did observe an increase in rubbery plateau modulus with increasing charge on the counter ion. Corresponding increases in Youngs modulus and tensile strength were also noted. Since the breadth of the soft phase glass transition was unchanged, these effects are not due to any changes in overall morphology. The explanation lies in the number of sulphonate groups associated with the counter ion. The greater the number of sulphonate groups associated with a counter ion, the higher the density of the ionic crosslinks in the hard domain and hence the greater the cohesion of the hard domain. Thus, Cooper observed the magnitude of the effect on the mechanical properties of three metal counter ions to fall in the order $Na^{+} < Zn^{2+} < Fe^{3+}$.

Interestingly, the precursor zwitterionomers, from which these anionomers were prepared, possessed better mechanical properties than any of the anionomers. This can be attributed to the extra space occupied by the counter ion reducing the degree of ordering and cohesion in the hard domain relative to that of the hard domains in the zwitterionomer. The latter has the counter ions present on the backbone and they do not require any extra volume.

A study by Al-Salah et al [35] was specifically targetted at elucidating counter ion effects.

A series of carboxylate containing anionomers differing only

in the nature of the counter ion were studied.

Hard phase Tg was found to be linearly dependent on the charge to radius ratio for monom and divalent counter ions. Divalent transition metal ions affected the hard domain glass transition in a similar manner.

The relationship between counter ion and changes in mechanical properties was less clear. For mono and divalent non transition metals, Youngs modulus and tensile strength increased in the same order as the charge to radius ratio increased. However, no such relationship was visible for the divalent transition metals.

For the relatively large changes in ionic potential seen for the mono and divalent non transition elements, the increasing strength of the ionic crosslinks visibly improves the stability of the hard phase. The smaller changes seen with the transition metal ions, all of which came from the same row of the periodic table, result in such small changes in crosslink strength that the effects are obscured by other factors such as chain configurations. Thus, no relationship has yet been established for transition metal counter ions.

Anionomers synthesised via urethane metallation [43] (see section 2.2.3) have been found to show exactly the same behaviour as the other ionomer systems that have been discussed above.

Once again, improved phase separation results in large changes in mechanical properties as the cohesion and thermal stability of the hard domains is enhanced. An additional influence can be seen in ionomers prepared using chain extenders such as 1,4-butanediol. Polyurethanes based on these chain

extenders show good phase separation and possess highly ordered hard domains. The introduction of a small quantity of ionic groups into these domains results in disruption of the ordering. The loss of cohesion due to reduced ordering and the presence of ionic crosslinks approximately counterbalance each other and little effect for low ionic content can be seen.

Higher ionic contents do give the expected changes in properties as the density of ionic crosslinking in the hard domains rise.

2.3.4 Cationomers.

There has been little recent work on polyurethane cationomers and information on their properties is somewhat limited. However, Dieterich's review of research at Bayer [33] reveals that their behaviour is exactly the same as that of anionomers and zwitterionomers.

Increasing ionic content raises Youngs modulus and tensile strength and introduces a rubbery plateau, the latter being seen in dynamic mechanical studies. Also, increases in the strength of hydrogen bonding were noted, the urethane proton interacting with the halide counter ions rather than carbonyl croups.

A recent study of chemical crosslinking coupled with quaternisation of a polyurethane [36] has provided a new source of evidence for the improvement of phase separation with ionic content. Pulsed NMR studies on a cationomer have yielded information on the morphological changes occurring on ionisation. A decrease in phase mixing was apparent along with a reduction in the quantity of material present in the interfacial regions

between the phases. The rigidity of the hard domains was greatly increased, as expected from the concentration of ionic interactions in these regions.

However, this new technique was unable to identify the cause of an increase in the soft phase Tg of the samples prepared by these workers. The polymer system was more complicated than most, involving chemical crosslinking agents as well as ionic groups and the authors report that further investigations are under way.

In conclusion, it can be seen from the literature, that polyurethane ionomers show the same general trends of behaviour irrespective of the type of ionomer and that, in almost all cases, the dominant effect is the inclusion of highly polar ionic groups in the hard segments of the polymer molecules.

3 Enzyme Immobilisation.

3.1 Introduction.

The field of enzyme immobilisation is currently an area of great interest and rapid expansion in both academic and industrial environments.

There are three major reasons for this interest [45].

Enzymes are efficient catalysts with a high degree of substrate specificity that makes them ideal for many industrial processes, such as conversion of glucose to fructose [P.53 of 48] and conversion of lactose to glucose [P.17 of 48]. However, an enzyme used in an industrial process must not be allowed to contaminate the product. It is also an expensive item and recovery is enconomically justified. If it is attached to an insoluble support, it may be easily recovered. Furthermore, insoluble supports open up the possibility of flow through as opposed to single batch processes giving further economies in the production process.

Enzymes may be immobilised in close proximity to electrodes using membranes. If the electrode is used to determine the concentration of a reaction product such as O_2 or a pH change, then it is possible to determine the concentration of the substrate that the enzyme reacts with [45, 46, 52, 53, 54]. The specificity of the enzyme allows determination of only one component in quite complex mixtures.

The final area of interest is in the preparation of models for biological systems. In natural systems, enzymes are frequently attached to membranes. Therefore, it is to be expected that enzymes attached to polymers will provide better models for

these systems than enzymes floating free in solution.

The quantity of literature in these fields is vast and the scope of this review has been necessarily limited to methods of covalently coupling enzymes to polymers and entrapping enzymes in crosslinked polymer networks (gels). The techniques of adsorption, use of inorganic support and coupling agents, microencapsulation, entrapment during fibre formation or use of semipermeable membranes in ultrafiltration systems are not covered, nor are the effects of immobilisation on enzymes or applications of the immobilised systems.

The primary sources of information were text books [45-50] and the reader is referred to these for information on areas not covered and for references to the original literature. References 45, 46 and 47 are especially useful and comprehensive.

3.2 Covalent Polymer-Enzyme Coupling.

3.2.1 Introduction.

One method of immobilising an enzyme is to form a covalent bond or bonds between the enzyme and the support. This requires functional groups on both enzyme and polymer capable of reacting under the mild conditions needed to avoid denaturing the enzyme. Frequently, the polymer is pre-treated to render it more reactive.

In the following review, the methods of attachment are arranged according to the functional group available on the polymer.

3.2.2 Common Reactive Groups available in Enzymes.

Enzymes are polypeptide (polyamide) chains built from amino

acids of general formula $X\text{-}CH(NH_2)CO_2H$. The group X varies widely for different amino acids. It is the functional group on the residues of these amino acids that may undergo chemical reactions. These reactions form the basis of methods of chemical immobilisation. The residues present at the active site of the enzyme are responsible for the catalystic activity of the enzyme.

Table 3.1 lists the amino acids whose residues are most commonly used as sites for covalent attachment. A more complete list of amino acids is given in reference 51.

Amino Acid	Residue
Serine	RCH_2OH
Threonine	$RCH(OH)CH_3$
Tyrosine	$RCH_2C_6H_4OH$
Lycine	$R(CH_2)_4NH_2$
Cysteine	RCH_2SH
Methionine	$R(CH_2)_2SH$
Aspartic Acid	RCH_2CO_2H
Glutamic Acid	$R(CH_2)_2CO_2H$
Asaragine	RCH_2CONH_2
Glutamine	$R(CH_2)_2CONH_2$
Cystine	$RCH_2\text{-}S\text{-}S\text{-}CH_2R$

$R = CHNH_2CO_2H$ in all cases.

Note that cystine is the disulphide dimer of cysteine.

Table 3.1 Common amino acids with useful residual functionality.

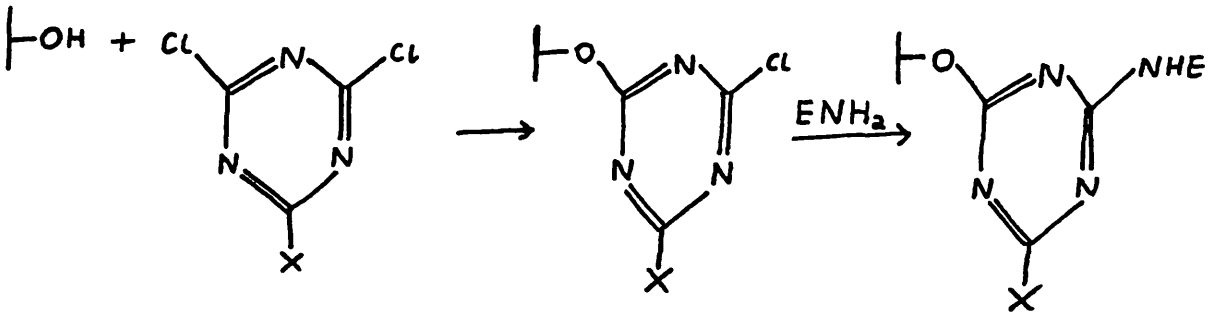
3.2.3 Reactions of Polymers containing amino, hydroxyl, thiol or alkyl halide Groups.

3.2.3.1 Hydroxyl Groups.

One of the most common points of attachment of new units to a polymer is the hydroxyl group. These are present in many polymers popular as enzyme supports, such as cellulose, agarose and copolymers of polyvinyl alcohol. As a result, many methods of exploiting these groups have been investigated. They are almost always reacted with difunctional agents that introduce a new centre of reactivity that can then couple directly to an enzyme.

3.2.3.1.1 Cyanuric Chloride (s-Triazine) Derivatives.

The general reaction of a cyanuric chloride derivative with an alcohol and its subsequent coupling to an enzyme is given in equation 3.1. This is a common method and it is usual to use dichloro-s-triazinyl derivatives such as 2-amino-4,6-dichloro-s-triazine so that one bond is formed to the polymer and one to the enzyme. If required, the trichloro derivative may be used to give a further reactive site, which allows either formation of a polymer-polymer crosslink or a second polymer-enzyme link.



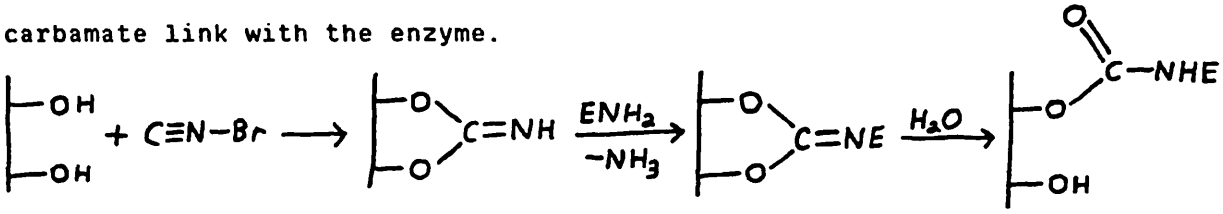
Cyanuric chloride coupling.....Equation 3.1

The enzyme reacts most readily via its amino groups, but coupling with its thiols or hydroxyls is also possible.

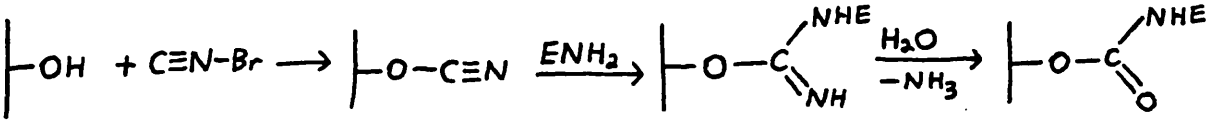
3.2.3.1.2 Cyanogen Bromide.

Polymers such as cellulose, that contaion 1,2-diol units or those that contain 1,3-diol units may be activated with cyanogen bromide to give a reactive cyclic imidocarbonate. This ia then reacted with free amino groups on the enzyme to complete the coupling process. When complete, the enzyme is attached to the polymer via a carbamate (urethane) linkage. See equation 3.2.

Widely spaced hydroxyls may either form intermolecular imidocarbonates, which behave in the same way as their cyclic counterparts or they may follow the reaction pathway shown in equation 3.3. In either case, the end result is to form a carbamate link with the enzyme.



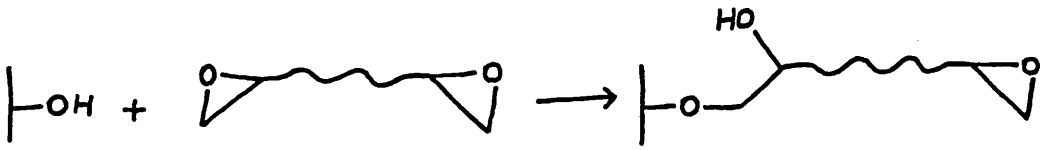
Cyanogen brimide coupling via 1,2 or 1,3 diols...Equation 3.2



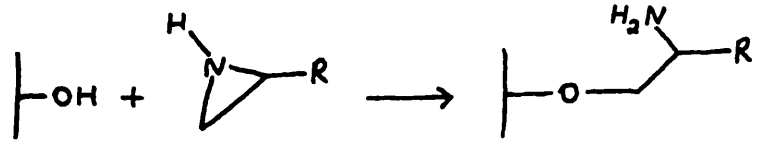
Cyanogen bromide coupling via single hydroxyls...Equation 3.3

3.2.3.1.3 Oxiranes, Thiiranes and Aziridines.

Oxiranes, thiiranes and aziridines are 3 member rings and therefore are strained systems. Under acid or base conditions the ring may be attacked and opened by a hydroxyl group. See equations 3.4 and 3.5. The result is an ether linkage between the polymer molecule and the molecule bearing the ring. In the case of oxiranes, it is usual to use a dioxirane or a molecule such as 2-(chloromethyl)-oxirane to leave a new functional group on the polymer that can react with an enzyme.



Oxirane-hydroxyl coupling.....Equation 3.4



Aziridine-hydroxyl coupling.....Equation 3.5

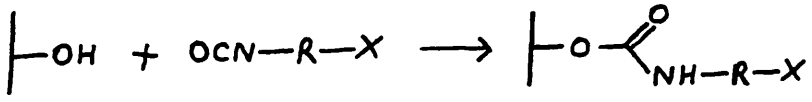
For aziridines, a primary amino group is generated in the ring opening reaction and this may be utilised as described in section 3.2.3.2.

Thiiranes are the sulphur analogues of oxiranes and leave a thiol after ring opening which can then undergo the coupling reactions described in section 3.2.3.3.

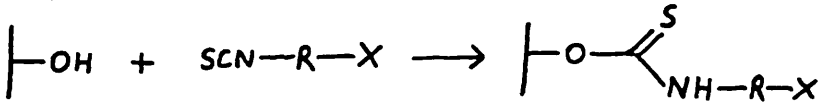
3.2.3.1.4 Isocyanates and thioisocyanates.

Isocyanates and thioisocyanates react readily with alcohol groups to form carbamate (urethane) or thiocarbamate (thiourethane) links respectively. See equations 3.6 and 3.7.

Frequently a diisocyanate may be used, with the second isocyanate coupling directly to the enzyme. Alternatively, some other functional group may be present on the isocyanate molecule.



Isocyanate-hydroxyl coupling.....Equation 3.6

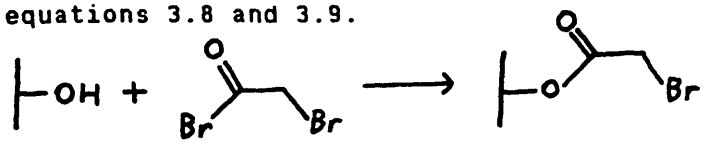


Thioisocyanate-hydroxyl coupling.....Equation 3.7

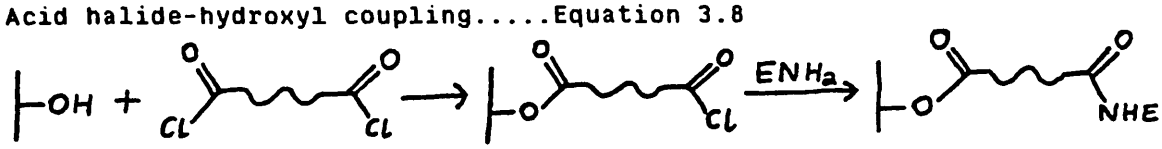
3.2.3.1.5 Acid Halides.

Acid halides and hydroxyls form ester linkages readily. Thus, acid halides may be used to attach molecules bearing new

functional groups to a hydroxyl containing polymer as shown in equations 3.8 and 3.9.



Acid halide-hydroxyl coupling.....Equation 3.8

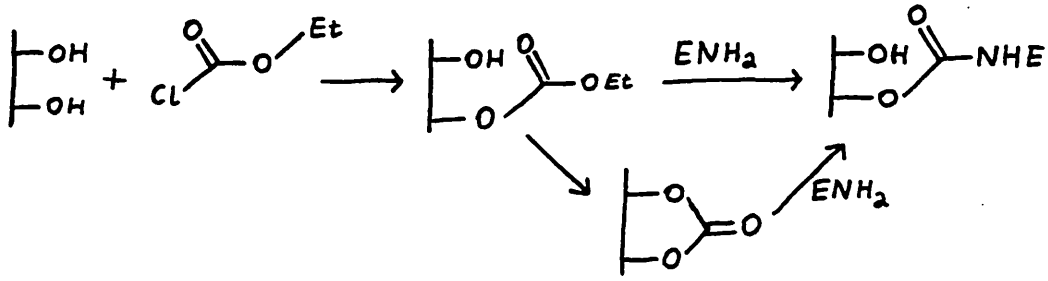


Acid halide coupling via polymer-enzyme bridging....Equation 3.9

If a diacid halide is used, then hydrolysis of the second acid halide group creates a carboxylic acid attached to the polymer. See section 3.2.8.1 for reactions of carboxylic acids. The second group may alternatively be used to couple directly to the enzyme (equation 3.9) or to crosslink the polymer.

3.2.3.1.6 Chloroformate Esters.

Chloroformate esters may be reacted with alcohols to yield carbonates (equation 3.10). The carbonate formed may be cyclic or a crosslink between 2 polymer chains. The carbonate is then attacked by amines on the enzyme, forming a carbamate link between the polymer and the enzyme.



Chloroformate ester coupling.....Equation 3.10

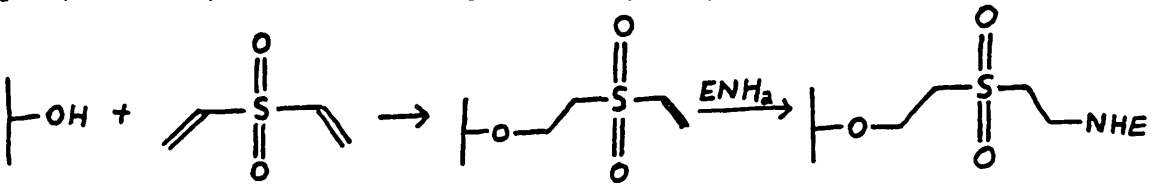
3.2.3.1.7 Activated Carbon-Carbon Double Bonds.

Two types of activated C=C bond have been reported and both undergo 1,4 addition reactions with hydroxyls.

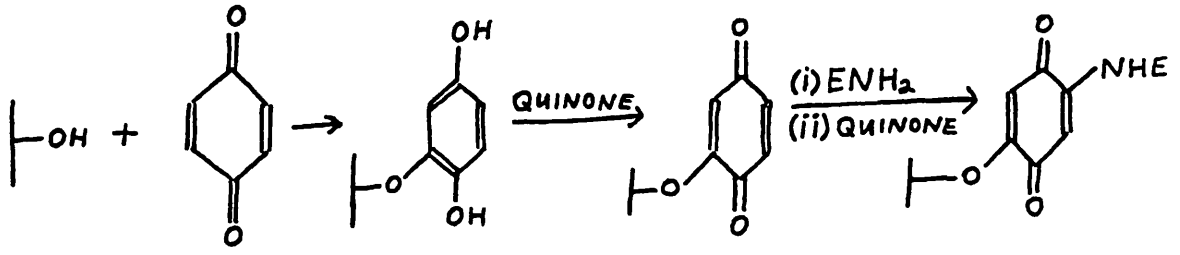
In the first type, the bond is activated by a sulphonyl group, as in diethenyl sulphone. The sulphonyl polarises the

double bond, enhancing the electrophilicity of the 4 position. This position is then attacked by nucleophiles such as a hydroxyl group (equation 3.11).

Vinyl ketones are the second type of compound containing activated double bonds that have been used for enzyme immobilisation. The double bond is polarised by the ketone. However, the polarising power of the ketone is less than that of the sulphone and simple vinyl ketones such as 1-butene-3-one are not sufficiently polarised to undergo attack from a hydroxyl group. More complex molecules such as quinones with 2 carbonyl groups are capable of reacting with a hydroxyl. See equation 3.12



Diethenyl sulphone coupling....Equation 3.11



Quinone coupling.....Equation 3.12

Both examples shown in equations 3.11 and 3.12 have 2 activated double bonds, the second bond either crosslinking the polymer or reacting with nucleophilic groups on the enzyme.

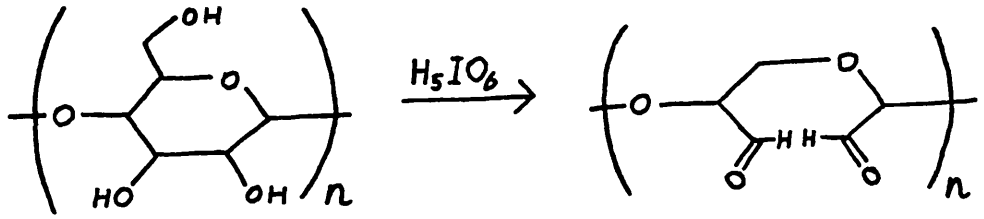
3.2.3.1.8 Oxidation.

Alcohols can be oxidised to aldehydes or acids, both groups of use in coupling to enzymes. However, it is important not to sever the polymer backbone and other methods exist for

introducing these groups into polymers.

One example of oxidation of a carbohydrate has been reported. Some of the 1,2 diol groups on the carbohydrate section of a glycoenzyme were oxidised with periodic acid to give two aldehyde groups which could then be coupled to amino groups on a support by imine formation.

In principle, the same method could be applied to a support polymer such as cellulose which contains similar 1,2 diol units. Scission of the carbon carbon bond between the 2 hydroxyls does not sever the polymer chain in carbohydrates. See equation 3.13.

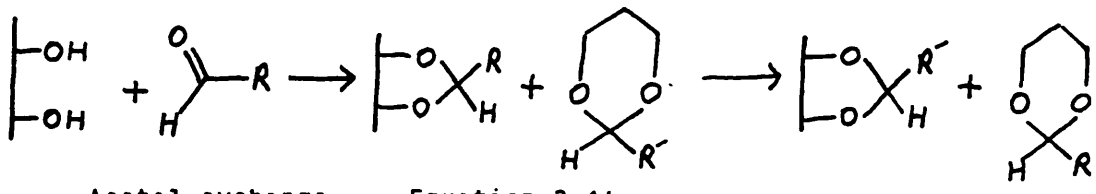


Oxidative coupling with carbohydrates....Equation 3.13

3.2.3.1.9 Acetals (Ketals) and Aldehydes.

Polymers with closely spaced hydroxyls, such as polyvinyl alcohol may have new functional groups introduced by means of acetal formation.

The hydroxyls are reacted with an aldehyde containing compound and form an acetal. The new functional group may be present on the aldehyde, or it may be attached by displacing the existing acetal and attaching a new one. See equation 3.14. Crosslinks may be created by using a dialdehyde.



Acetal exchange.....Equation 3.14

3.2.3.2 Amine Groups.

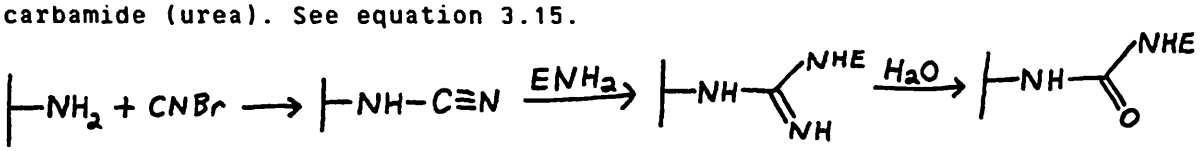
Amine groups undergo similar reactions to hydroxyl groups, but are more nucleophilic. The following section outlines reactions that proceed differently or do not occur with hydroxyls. The reactions of aromatic as well as aliphatic amines are covered.

Amine groups are frequently added to polymers bearing less reactive groups such as hydroxyls and are the most common point of attachment on enzymes that are covalently immobilised.

The reacions of cyanuric chloride, activated C=C's, acid halides, oxiranes and their analogues and isocyanates are all almost identical to the corresponding reaction for the hydroxyl group.

3.2.3.2.1 Cyanogen Bromide.

Amines react with cyanogen bromide in a simiar but not identical manner to the reaction of hydroxyls. The final polymer-enzyme link is an imidocarbamide which can hydrolise to a carbamide (urea). See equation 3.15.



Cyanogen bromide-amine coupling.....Equation 3.15

3.2.3.2.2 Phosgenation.

Unlike alcohols, which react to give chloroformate esters and, subsequently, carbonates when treated with phosgene, primary amines form isocyanates. Use of thiophosgene yields isothiocyanates. See equations 3.16 and 3.17 respectively.

$R\text{-}NH_2$ + ClCOCl ---> R-NCO (+ 2HCl)

Phosgenation.....Equation 3.16

$R\text{-}NH_2$ + ClCSCl ---> R-NCS (+ 2HCl)

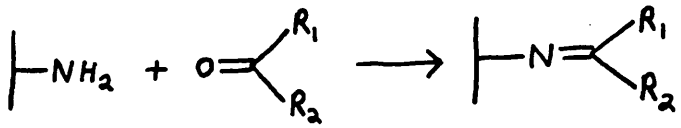
Thiophosgenation.....Equation 3.17

This method converts the amine into a group which may couple directly to an amine or hydroxyl on an enzyme. It is applicable to both aliphatic and aromatic amines, but is more commonly used with aromatic amines as these yield the most reactive isocyanates.

3.2.3.2.3 Aldehydes and Ketones.

Aldehydes and ketones react with primary amines to form N-substituted imines (Shiff's bases), see equation 3.18. By far the most popular aldehyde in use is glutaraldehyde, a dialdehyde. It is used to attach an amine containing polymer to an enzyme via the amino groups on the enzyme. However, the chemistry of glutaraldehyde is more complicated than that of simple aldehydes and is dealt with in section 3.2.7.1.

Other aldehydes or ketones may be attached and can bring other functional groups with them. Aldehydes may be created in the crabohydrate sections of some enzymes by oxidation (section 3.2.3.1.8) and can then react with amino groups on a polymer backbone.



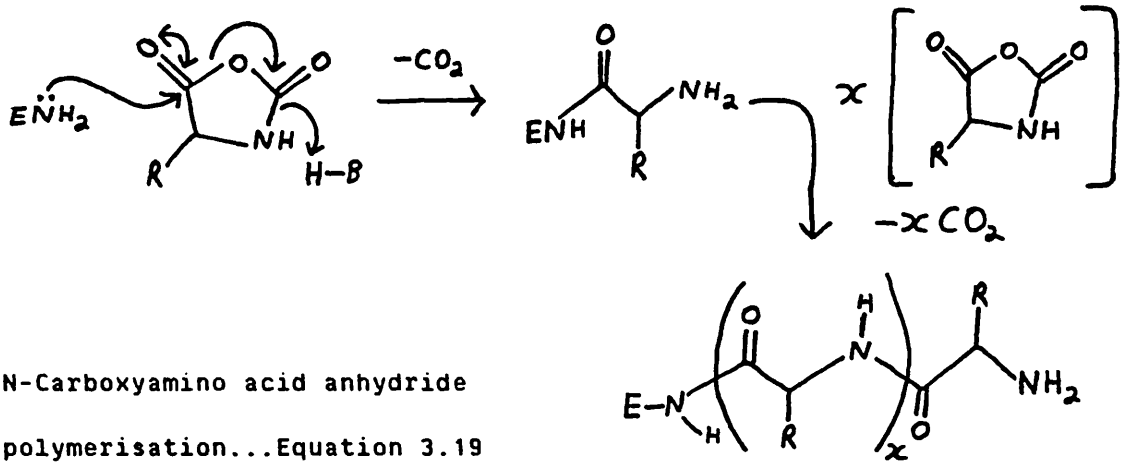
Aldehyde-amine coupling (Shiff's base formation) Equation 3.18

3.2.3.2.4 N-Carboxyamino Acid Anhydrides.

Polymerisation of N-carboxyamino acid anhydrides to form polyamides is initiated by amino groups (equation 3.19). Thus, if an enzyme is used as the source of amine groups, polymer chains

may be grown directly from these sites and render the enzyme insoluble.

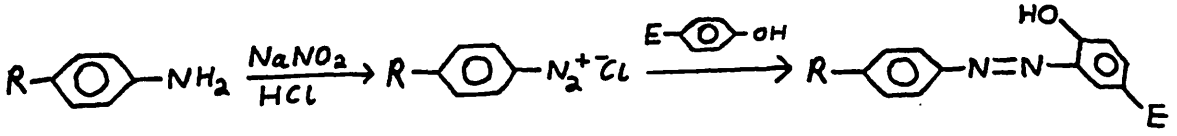
The main problem encountered with this method is the finding of monomers insoluble in water. The anhydride derivatives of amino acids such as glycine, valine, phenylalanine and some esters of glutamic acids have all been found to give polymers of very low water solubility.



N-Carboxyamino acid anhydride polymerisation...Equation 3.19

3.2.3.2.5 Diazotisation and Azidobenzene Formation.

Primary aromatic amines may be converted to diazo salts by reaction with a nitrite salt under strongly acidic conditions. This will then couple with other benzene rings that are activated for electrophilic substitution, such as the phenol group present on the tyrosyl residues in an enzyme (equation 3.20). This is a popular method of coupling enzymes to polymers and aromatic amines are one of the groups most often introduced into polymers of otherwise low reactivity.

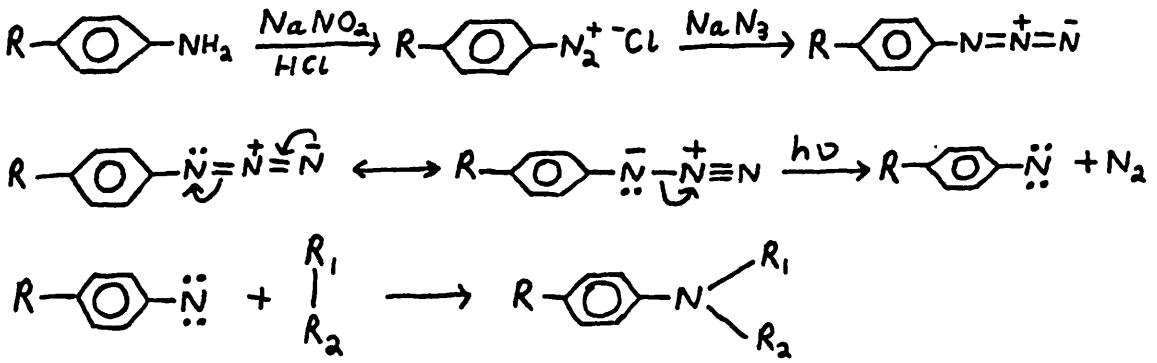


Diazo-coupling.....Equation 3.20

An unusual reaction of diazo salts is their conversion to aryl azides by reaction with an azide anion. Azidobenzene compounds are reasonably stable thermally, but decompose rapidly in the presence of visible light, losing a dinitrogen molecule and forming a nitrene. The highly reactive nitrene will insert into a wide variety of bonds, even carbun hydrogen bonds. See equation 3.21. This lack of specificity is both advantageous and disadvantageous. The advantage is that it does not depend on any particular group being on an enzyme and shows no preference for attack on the more reactive groups of the enzyme's catalytic site. The chances of reaction in this vital area are dependent on the proportion of the enzyme's total surface area taken up by the site.

The disadvantage is that other molecules such as the polymer support or organic solvent molecules are also attacked, reducing the number of polymer enzyme bonds formed.

In practice, a small molecule with both the photochemically reactive azide and a thermally reactive group, such as fluoro-2-nitro-4-azidobenzene, is used. The experimentor then has the choice of using either group to couple to the enzyme or can perform the thermal and photochemical steps in any order.



Azidobenzene coupling.....Equation 3.21

3.2.3.2.6 The Ugi Reaction (Isocyanide Method).

The ugi reaction is a 2 step process and involves 4 different components. These are a primary amine, an aldehyde, an isocyanide and a carboxylic acid.

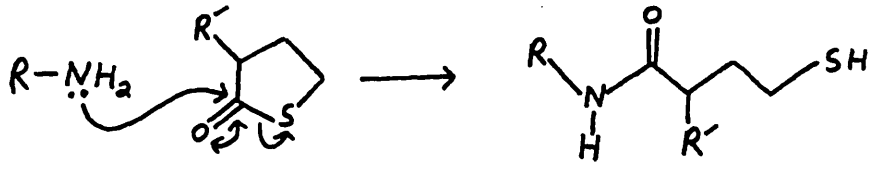
Details of this reaction are given in section 3.2.8 on reactions of cyanides and isocyanides.

3.2.3.2.7 Thiolactones.

One of the groups sometimes used in enzyme immobilisation is the thiol or sulphhydryl group (section 3.2.3.3), but there are relatively few of these present in enzymes. Also, an experimentor may have reasons for choosing a polymer support that has few, if any, thiols while wishing, still, to use a thiol coupling reaction. In both cases, a method of adding new thiols is necessary.

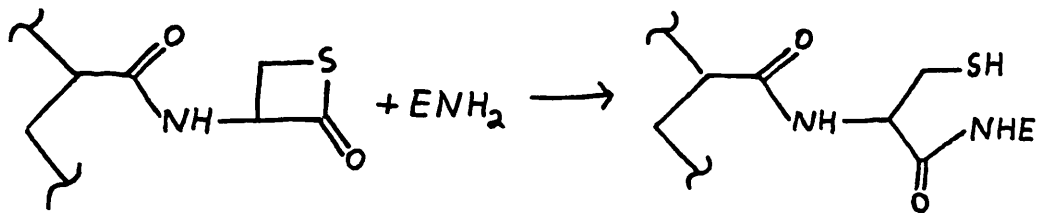
The reaction of thiolactones with amines provides one means of enriching the thiol content of a material and is equally applicable to both enzymes and polymers with many free amino groups.

Thiolactones are less stable than amides and undergo attack from free amino groups. The reaction results in formation of an amide and breakage of the thiolactone ring, leaving a thiol (equation 3.22). This thiol may then be used in coupling reactions.



Thiolactone-amine coupling.....Equation 3.22

Enzacryl thiolactone, a commercial copolymer of acrylamide, methylene-bis-acrylamide and N-acryloyl-4-carboxymethyl-2,2-dimethyl thiazoline, may be used to directly immobilise enzymes. The amino groups of the enzyme break open the thiolactone rings of the polymer and form amide linkages (equation 3.23).



Enzyme coupling with commercial Enzacryl thiolactone polymer.
Equation 3.23

3.2.3.3 Thiol Groups.

Thiols are the sulphur analogues of hydroxyls and behave in the same way with the majority of reagents. Coupling reactions that proceed by mechanisms that are almost identical to the analagous hydroxyl mechanism are not discussed here.

Thiols are more nucleophilic than hydroxyls because of the larger orbitals of sulphur and give faster rates in reactions such as nucleophilic substitutions. However, the carbon-sulphur bond is weaker than the carbon-oxygen bond. This results in many organosulphur compounds being less stable than their oxygen counterparts. For example, Thioesters and thioethers are more labile than ordinary esters and ethers.

Sulphur-sulphur bonds are more stable than oxygen-oxygen bonds and the chemistry of these forms the basis of the coupling methods described below.

3.2.3.3.1 Oxidative Coupling.

Thiols on a support may be coupled with thiols on an enzyme to give a disulphide link. Occasionally, this reaction can occur spontaneously, but it is usually performed utilising potassium ferricyanide as an oxidant. See equation 3.24.

$$\vdash SH + HS-E \xrightarrow{K_3Fe(CN)_6} \vdash S-S-E$$

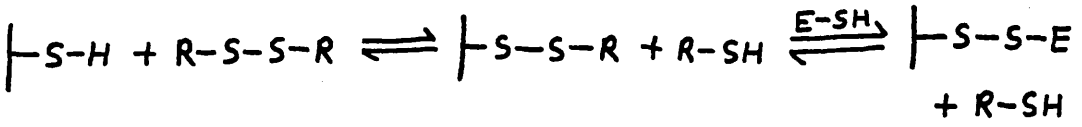
Oxidative thiol-thiol coupling.....Equation 3.24

An advantage of this technique is that the dissociation of the polymer-enzyme link may be induced by addition of a simple thiol which regenerates the original support by thiol-disulphide interchange (section 3.2.3.3.2). This allows the removal and replacement of denatured enzyme in a reactor system without the need to replace the support material.

3.2.3.3.2 Thiol-Disulphide Interchange.

An alternative to oxidative coupling with potassium ferricyanide is available. This is the thiol-disulphide interchange method and can be applied in two ways.

The simplest is to treat the thiol containing polymer with a labile disulphide which reacts to form a disulphide link with the polymer and liberate a thiol. This new disulphide then undergoes a second interchange with thiols on an enzyme, forming an enzyme-polymer disulphide link. See equation 3.25. The most critical factor is the choice of labile disulphide. In the ideal situation, both steps would completely favour the forward reactions. 2,2'-dipyridine disulphide has been used with some success.



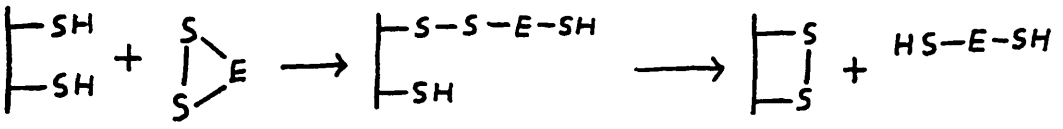
Thiol-disulphide interchange.....Equation 3.25

It should be noted that all steps are reversible and it is thus possible to decouple the enzyme by addition of an appropriate thiol. Denatured enzyme may be flushed from the support and subsequently replaced by a fresh batch without a corresponding change in support.

The second way of employing this reaction involves an extra step as follows.

The enzyme is partially reduced by being passed through a thiol containing packed bed or column reactor. This step breaks disulphide linkages in the enzyme to generate thiols. At the same time, disulphide links between the thiols in the reactor are formed. See equation 3.26. Thus, enzymes rich in disulphides but poor in thiols have their thiol content increased immediately prior to immobilisation.

The second phase of the process is to pass the enzyme into the support material, which has been pretreated with a disulphide. A thiol is liberated and enzyme-polymer disulphide links formed. This second phase is identical to the approach described in equation 3.25



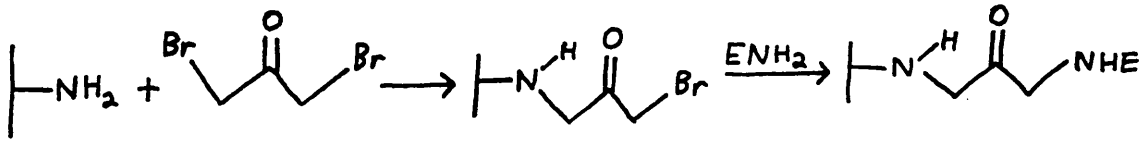
Thiol-disulphide enrichment of enzymes.....Equation 3.26

3.2.3.4 Alkyl Halides.

Primary alkyl halides undergo S_N2 displacement and are rendered more reactive when the neighbouring group increases the polarisation of the carbon centre. For example, neighbouring carbonyls, hydroxyls and carboxylates act in this way to varying degrees.

The nucleophiles present in enzymes are amines, hydroxyls, thiols and carboxylates. They can, in theory, all be used to displace a halide and form a polymer-enzyme bond. Most commonly, amino groups are favoured as they produce the most stable bonds. Carboxylates are not generally used, thiols give thiethers which are somewhat labile and hydroxyls are not very reactive.

Small difunctional reagents such as 1,3-dibromopropane or 2-bromoacetyl bromide are often utilised as bridging molecules between nucleophilic groups on the support and the enzyme. See equation 3.27.



Alkyl halide coupling.....Equation 3.27

3.2.4 Oxiranes and their analogues.

As discussed in section 3.2.3.1.3, oxiranes, aziridines and thiiranes are 3 member strained rings that can be opened by nucleophiles. The former two types have been used most successfully, generating hydroxyl or amino groups. See equations 3.4 and 3.5.

The nucleophilic groups most commonly employed are, in order of reactivity, thiol, amine and, under stronger conditions,

alcohols. The amino group is the more popular group due to its abundancy in enzymes, high reactivity and the low stability of thioether links.

3.2.5 Activated Carbon Carbon Double Bonds.

Section 3.2.3.1.7 dealt with alkene groups activated by ketones and sulphones and the attack of hydroxyls upon them (equation 3.11).

Other nucleophiles, such as amines and thiols show similar behaviour with these compounds. Amines and thiols, being more nucleophilic, may also react with simple vinyl ketones in contrast to hydroxyls, which require strongly activated systems. As for oxiranes, the order of reactivity for attack is RSH > RNH_2 > ROH and amines are once again the nucleophilic group of choice.

Radical polymerisation of carbon-carbon double bonds as a means of enzyme immobilisation is dealt with in section 3.3.

3.2.6 Isocyanates and Isothiocyanates.

Amino groups may be phosgenated or thiophosgenated (see section 3.2.3.2.2 and equations 3.16 and 3.17) to give isocyanates or isothiocyanates. These react with amines to form carbamides (ureas), equation 3.28, and with hydroxyls to give carbamates (urethanes), equation 3.29. Thiols behave like hydroxyls but are rarely, if ever, used. It is popular to use a diisocyanate as a bridging molecule, one end reacting with the support, the other with the enzyme.

If desired, isocyanates may be reacted with phenols to form a relatively unstable carbamate which, at a later date, may be attacked by amines or primary alcohols to give the desired

carbamate or carbamide. This is known as blocking an isocyanate and is a method of protecting it from any intermediate reactions. The use of polycarbamates (polyurethanes) for enzyme immobilisation is covered in section 3.4

R-NCO + R'-NH_2 ---> R-NHCONH-R'

Isocyanate-amine coupling.....Equation 3.28

R-NCO + R'-OH ---> R-NHCOO-R'

Isocyanate-hydroxyl coupling..Equation 3.29

3.2.7 Aldehydes, Ketones and their Derivatives.

This section is concerned with the reactions of aldehydes and ketones that are of use in enzyme immobilisation, along with reported uses of acetal and ketal derivatives.

The aldehyde group is, by far, the more common of the two in immobilisation procedures. It is present either on the support or on a small molecule that acts as a bridge. There are no aldehydes and few ketones in enzymes, except when artificially introduced. See section 3.2.3.1.8.

The reaction of simple aldehydes with amines has already been covered in section 3.2.3.2.3 and their reaction with alcohols mentioned in section 3.2.3.1.9. Their involvement in the Ugi reaction is discussed in section 3.2.9

3.2.7.1 Reactions of Acetals .

The use of acetals to attach new functional groups to a hydroxyl containing polymer has already been explained in section 3.2.3.1.9. and a different approach to the use of acetals is presented here.

An acetal may be easily hydrolised to give an aldehyde under acid conditions and can be regarded as a form of protected

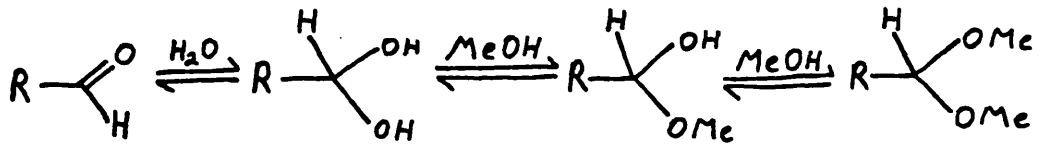
aldehyde. Thus, aldehydes may be generated immediately prior to use, avoiding severe problems with side reactions such as aldol condensations.

Two monomers have been used to introduce acetal groups into acrylate copolymers. These are acryloyl-N-(2,2-dimethoxyethyl)-amine, as used in the commercial polymer Enzacryl Polyacetal, and acryloyl-N,N-bis-(2,2-dimethoxyethyl)-amine.

Copolymers of either of these monomers undergo partial hydrolysis when swollen with water, giving a variety of species. See equation 3.30. The aldehyde groups will give either an imine or an azomethine attachment to an enzyme. See equation 3.31.

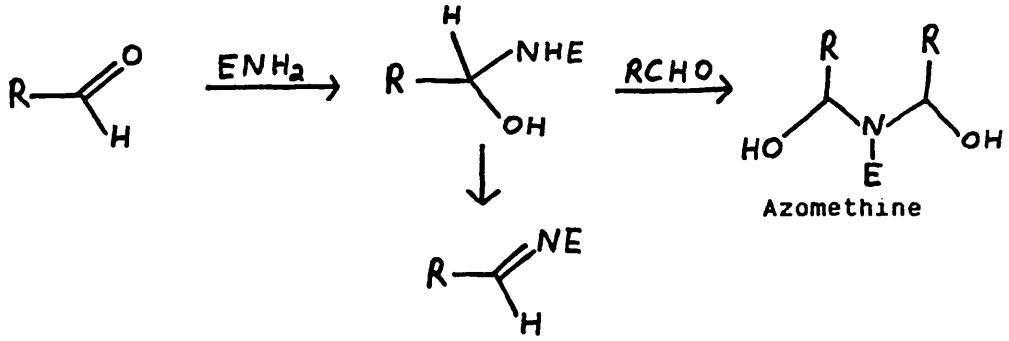
For polymers containing acryloyl-N,N-bis-(2,2-dimethoxyethyl) -amine, the close proximity of the acetals can, on hydrolysis, give rise to a 6 membered pyranose-bis-hemiacetal like ring in addition to all the other possibilities. See equation 3.32. Many of these species are normally unstable, but are present due to the high local concentration of aldehydes in the polymer.

The hydrolised polymers from both monomers may be reacted with a diacid hydrazide, unreacted hydrazides converted to azides and these used to immobilise an enzyme. See section 3.2.8.3.2

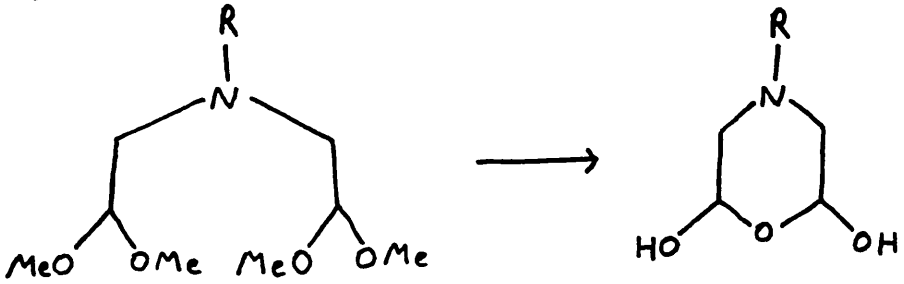


Aldehyde Aldehydrol Hemiacetal Acetal

Aldehyde acetal equilibria.....Equation 3.30



Aldehyde conversion to imine or azomethine...Equation 3.31



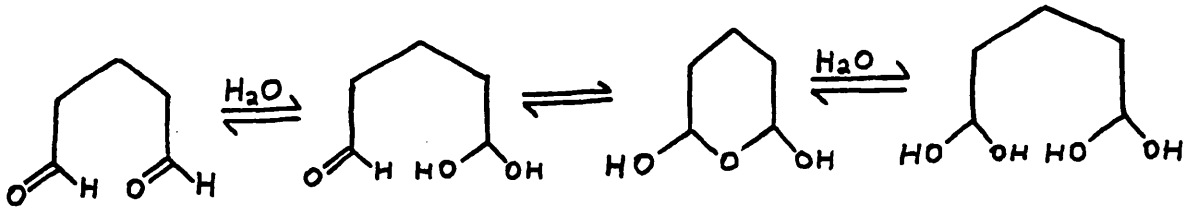
Acetal hydrolysis to pyranose like rings.....Equation 3.32

3.2.7.2 Glutaraldehyde.

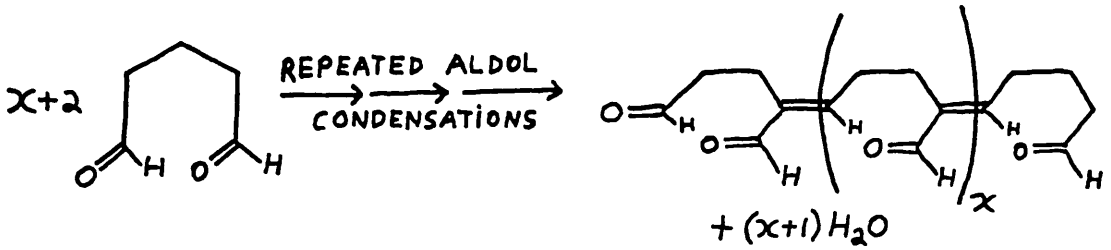
Glutaraldehyde is the most popular aldehyde used in immobilisation. It is a dialdehyde and forms bridges between amine containing polymers and enzymes. Usually, it is assumed to behave like a simple aldehyde, but NMR studies of its aqueous solutions have revealed its behaviour to be far from simple. It hydrolises to a variety of species (equation 3.33) and, except at neutral pH, it rapidly undergoes aldol condensations to form oligomers. See equation 3.34.

In neutral conditions, pure glutaraldehyde does behave as a simple dialdehyde and forms imines as expected. However, the oligomers contain carbon-carbon double bonds activated by the aldehydes. These are believed to be sufficiently reactive to undergo 1,4 additions with primary amines present in enzymes to form a secondary amine. See section 3.2.5 for reactions of

activated alkenes.



Glutaraldehyde hydrolysis.....Equation 3.33

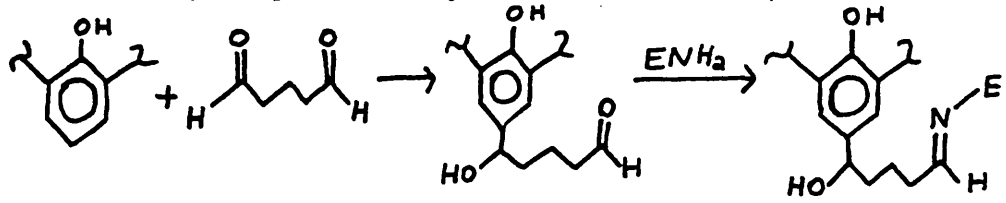


Glutaraldehyde self polymerisation.....Equation 3.34

3.2.7.3 Phenol-Formaldehyde Resins.

An ingenious method for the modification of phenol-formaldehyde resins to act as enzyme supports has been developed.

After polymerisation of the polymer, some of the remaining reactive positions on the phenol rings are used to attack one end of a glutaraldehyde molecule. The other end is then reacted with an enzyme to form an imine link. See equation 3.35. It should be noted that pure glutaraldehyde is used in this procedure.



Coupling to phenol-formaldehyde resins.....Equation 3.35

Enzymes may also be attached to phenolic resins by oxidation of residual methylol groups to aldehydes, followed by imine formation as usual.

3.2.7.4 Oxidation or Reduction.

If desired, aldehydes may be oxidised to acids or reduced to alcohols (for example, polyacrolein can be reduced to polyallyl alcohol) and these groups utilised in immobilisation methods.

3.2.8 Carboxylic Acids and their Derivatives.

Carboxylic acids or their common derivatives are some of the most readily available reactive moieties on polymers.

The usual approach is to form a reactive derivative that forms an amide link to the enzyme under mild conditions. The carboxylate group is usually present on the polymer and the amine on the enzyme, though the reverse arrangement may be used.

3.2.8.1 Carboxylic Acids.

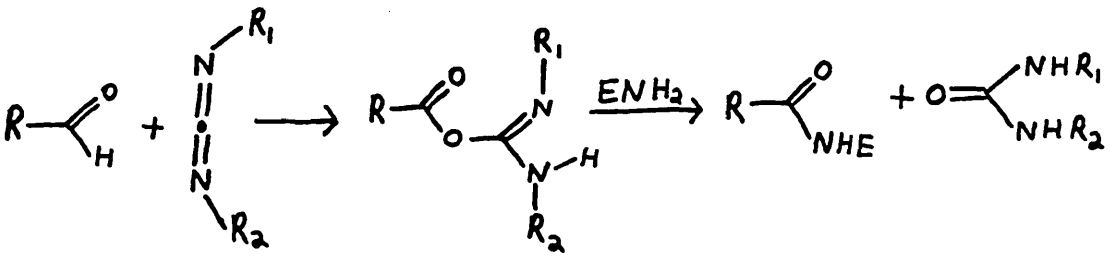
Free carboxylic acids are usually converted to relatively unstable amides or esters which are subsequently attacked by the amine groups on an enzyme to form a more stable amide link to the polymer.

Typical examples are esters of phenols or amides derived from succinimide.

The reactions of two popular reagents used for producing labile carboxylate derivatives, that react with amines under mild conditions, are given below. Both were originally developed for the synthesis of polypeptides.

3.2.8.1.1 Reaction with Carbodiimides.

Carbodiimides have a carbon centre polarised by the two nitrogen atoms attached to it and reacts with carboxylate anions as shown in equation 3.36. The resultant intermediate is attacked by amines to form an amide and a carbamide.

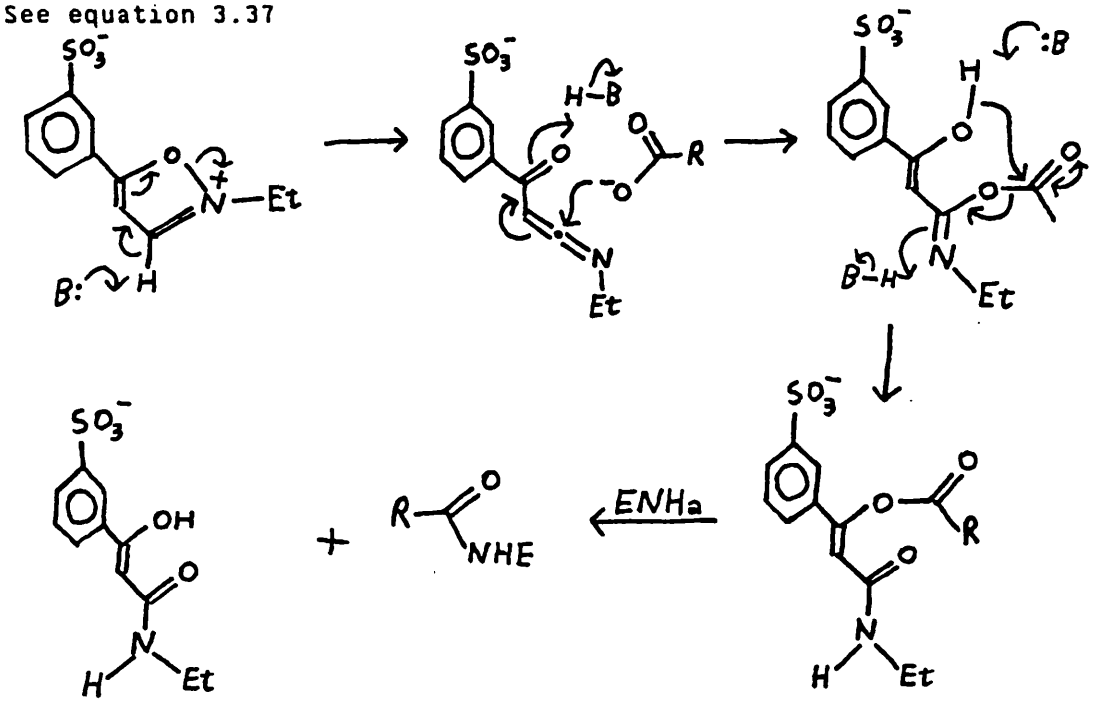


Carboxylic acid-carbodiimide coupling.....Equation 3.36

3.2.8.1.2 Reaction with Woodward's Reagent K.

The second approach is the reaction of carboxylates with N-ethyl-5-phenylisoxazolium-3-sulphonate, often referred to as Woodward's reagent K [55, 56], which rearranges in the presence of a base, such as a carboxylate anion, to form an α-keto-ketenimine. This is promptly attacked by a carboxylate in a manner similar to that of the attack on a carbodiimide. Intramolecular rearrangement takes place to give a labile ester. This undergoes aminolysis with the amines of an enzyme to form the final polymer-enzyme bond.

See equation 3.37



Immobilisation of enzymes via Woodwards reagent K. Equation 3.37

3.2.8.2 Acid Halides and Acid Anhydrides.

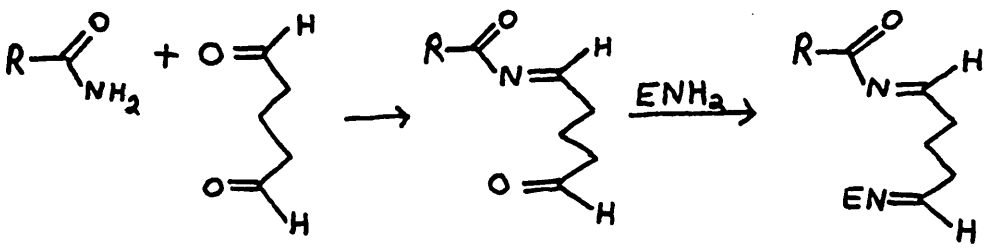
Both acid halides and acid anhydrides react much more readily than the parent acids under mild conditions. Acid halides give esters or amides when reacted with alcohols or amines. Anhydrides give esters or amides as well, but also form a free carboxylate group in addition. If the anhydride was a 5 or 6 member ring, for example maleic anhydride, then reaction with a primary amine may result in formation of a cyclic imide. Both anhydrides and halides are readily hydrolised to form free carboxylates.

3.2.8.3 Amides, Hydrazides and Azides.

The reaction of labile amides has been mentioned, but is only one of the methods of immobilisation based on amides. Other important systems are described below.

3.2.8.3.1 Reaction with Glutaraldehyde.

Glutaraldehyde can react with a primary amide as shown in equation 3.38, the unreacted aldehyde being left to bind an enzyme. Note that glutaraldehyde is assumed to behave as a simple dialdehyde in equation 3.38. See section 3.2.7.2 on glutaraldehyde chemistry.



Amide-glutaraldehyde coupling

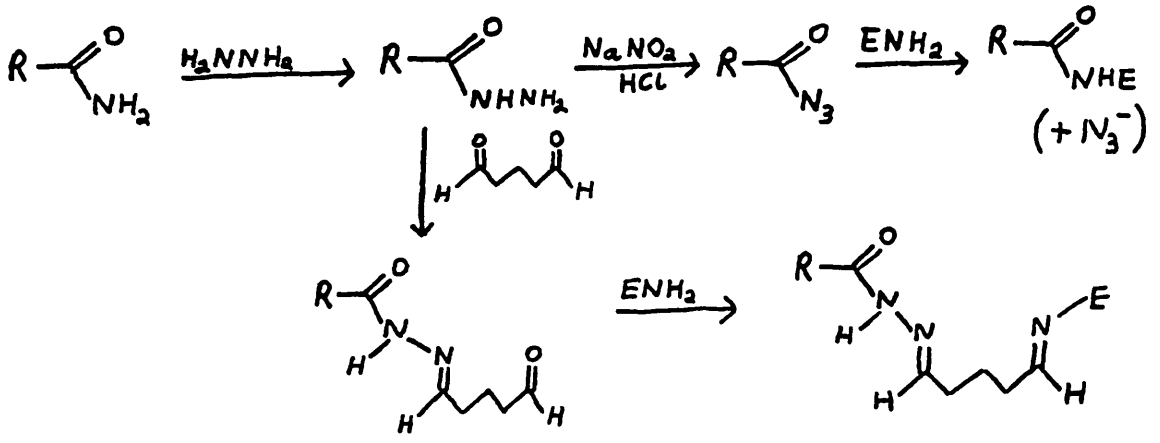
Equation 3.38

3.2.8.3.2 Hydrazides and Azides.

Amides may be converted to hydrazides by treatment with hydrazine. These new derivatives will in turn couple to aldehydes such as glutaraldehyde providing one route to immobilisation.

A second route is treatment of the hydrazide with nitrite in acid solution. which yields the acid azide. The azide ion is then easily displaced by an amino group on an enzyme.

Both pathways are shown in equation 3.39.



Coupling via hydrazides and azides.....Equation 3.39

Diacid hydrazides may be used as bridging agents, either by being linked to an aldehyde group on a polymer at one end, followed by conversion of the remaining free acid hydrazide group to the acid azide which can then form an amide link to the enzyme, or by being converted to the diacid azide and linking an amine containing polymer and an enzyme by reacting with an amine group on each.

3.2.8.3.3 O-Alkylation of Amides (Imido Esters).

The secondary amide links of a polyamide may be used as an attachment point by 2 methods.

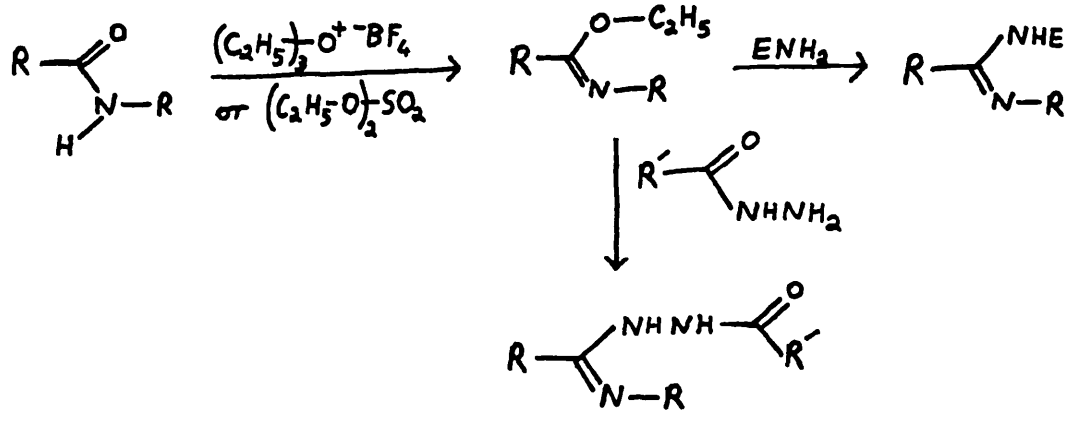
The first of these is hydrolysis to give an amine and a

carboxylate and the use of these two groups in the Ugi reaction. This method ammounts to N-alkylation and is covered in section 3.2.9

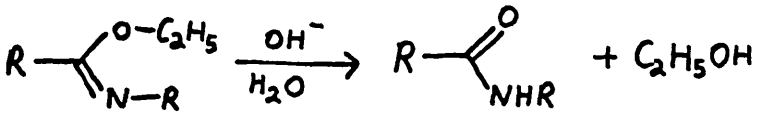
O-alkylation of the amide is the second method.

The amide is alkylated on the oxygen with strong alkylating agents such as dimethyl sulphate or triethyloxonium-tetrafluoroborate to yield an imido ester or the protonated imidate salt, dependent on pH. This will react with amino groups or acid hydrazides to give amidines or amidrazones respectively. An enzyme may be directly attached at this stage or a bridge molecule used to increase the distance between the enzyme and the polymer backbone. See equation 3.40.

It should be noted that the enzyme may be reversibly displaced by ammonia, offering a means of removing denatured enzyme and replacing it with a fresh batch. However, high pH in aqueous solutions can ultimately lead to regeneration of the original amide, accompanied by the liberation of an alcohol molecule (equation 3.41). The site must then be re-alkylated if it is to be of further use.



O-alkylation of amides and subsequent coupling.....Equation 3.40



Alkaline hydrolysis of imido esters.....Equation 3.41

An alternative route to imido esters is given in section 3.2.9.1.

3.2.9 Nitriles and Isonitriles.

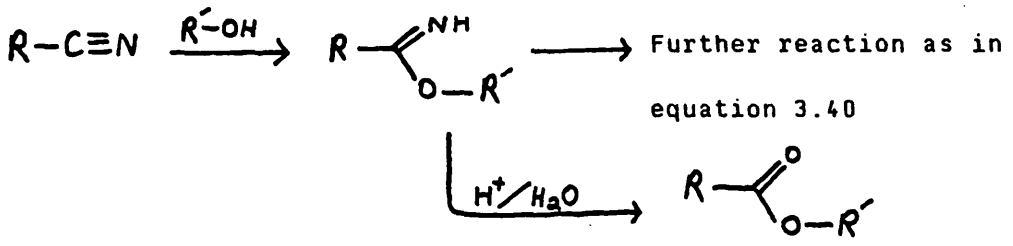
3.2.9.1 Nitriles.

Nitriles are of use in two ways.

Firstly, they may be reduced to amines and reacted as described in section 3.2.3.2.

Secondly, they will form imido esters with alcohols under acid conditions. These may then be reacted with amines as described in section 3.2.8.3.3 and equation 3.40.

If a primary amide, rather than a secondary amide, is involved, acid conditions can lead to hydrolysis of the imido ester to leave an ester group. See equation 3.42.



Nitrile to imido ester conversion.....Equation 3.42

3.2.9.2 Isonitriles.

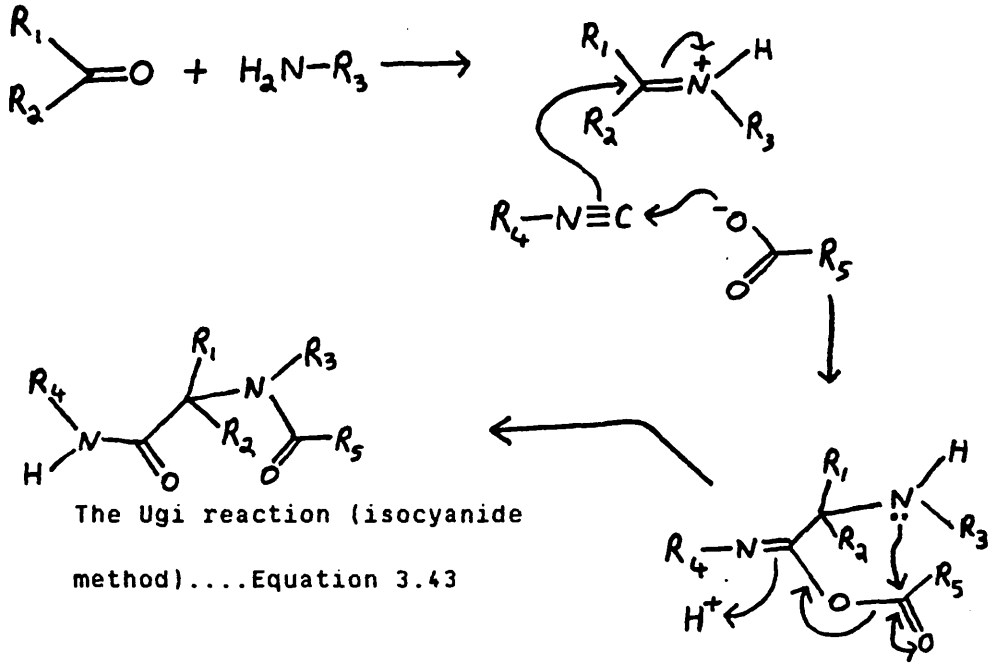
Isonitriles, also called isocyanides, are of use in one very important reaction, namely the Ugi reaction.

This is a reaction involving 4 components and 2 steps. The components are a carboxylate, a primary amine, an isonitrile and

a carbonyl containing molecule. Either an aldehyde or a ketone is suitable.

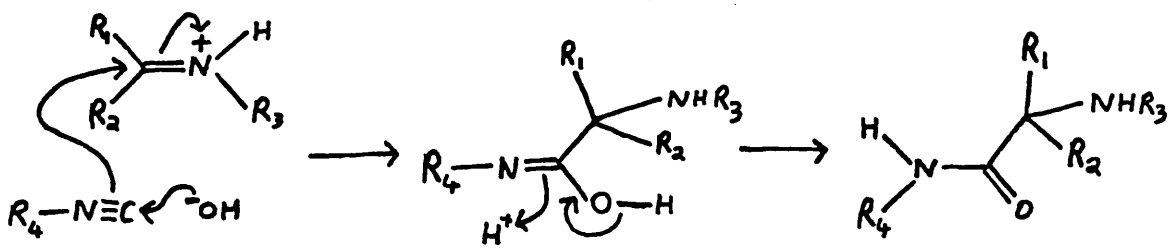
The first step is formation of an imine from the amine and the carbonyl containing molecule.

The second step involves the isonitrile, cacrboxylate and imine. The carboxylate attacks the isonitrile, which in turn attacks the imine. The resultant unstable intermediate then undergoes an intramolecular rearrangement to give the final diamide. See equation 3.43.



The Ugi reaction (isocyanide method)....Equation 3.43

Note that if the isonitrile is attacked by a hydroxide rather than a carboxylate anion, then there is no rearrangement, just a proton transfer to give the product which contains no amide and one secondary amine group. See equation 3.44



The Ugi reaction with hydroxide rather than carboxylate.

Equation 3.44

If the isonitrile carries another functional group, it is left hanging from the polymer backbone as a pendant group and can be used in further reactions. Thus, the Ugi reaction provides a method of placing new functional groups along the backbone of any polyamide. For example, polyisonitrile nylons are prepared using 1,6-hexane diisonitrile and have pendant isonitrile groups on the backbone.

3.3 Enzyme Entrapment in Gels.

3.3.1 Introduction.

A gel is a three dimensional crosslinked polymer network. It is insoluble but may be swollen by solvents that would be considered as good for a similar uncrosslinked polymer.

Gels may be created by most polymerisation methods and form when growing polymer chains continually branch. The branches on different molecules then link together in the polymerisation reaction, forming the network. Usually this process is achieved by addition of tri or polyfunctional monomers to the monomer mixture. For example, 1,2,3-propane triol in polyesterification or N,N-nethylene-bis-acrylamide in radical polymerisation.

If an enzyme is present as the three dimensional network

forms in the surrounding solution, it may become trapped within a cage of polymer chains. Its ability to escape will depend on the distance between the crosslink points joining the chains together. Generally, the greater the distance between the crosslink points, the more easily the enzyme can diffuse out. It is possible to prevent diffusion of the enzyme by reducing this distance. In practice, a compromise must be reached between the prevention of diffusion of the enzyme out and allowing the diffusion in of the substrate. It is important to note that high molecular weight substrates may not be able to penetrate the gel and gel entrapment is, therefore, not suitable for systems with large substrate molecules.

The two approaches to the entrapment of an enzyme are, firstly, the crosslinking of polymer molecules by addition of a crosslinking agent to join the chains together and, secondly, the reaction of crosslinking agent and monomers to form both crosslinks and polymer chains at the same time. In both cases, the enzyme is present in the reaction solution and is incorporated randomly as the network forms.

It is possible to use the enzyme as one of the monomers in the second approach, in which case, it becomes covalently attached to the polymer network.

Enzymes may be immobilised in gels that have been preformed, possibly under conditions that would rapidly denature the enzyme. In this approach, the gel is extensively swollen and an electric potential applied across it. The enzyme is then drawn into the gel by the potential gradient. The method is known as electrophoresis and is used extensively in enzyme purification.

It will not be further discussed here.

Crosslinks between chains of polymers may be either chemical or physical and are discussed in the following sections.

3.3.2 Physical Crosslinking:- Coarctation and Polymer-Polymer Complexes.

Coarctation is the formation of a gel by interaction of a polyelectrolyte with a polyvalent ion. The gel is held together by ionic polymer-ion-polymer bridges and the degree of crosslinking is dependent on the concentration of both polymer and small ion.

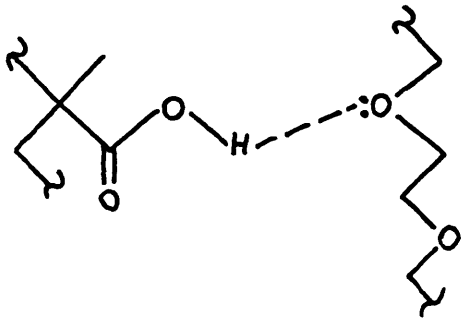
An example is a copolymer of maleic anhydride. The anhydride ring may be hydrolised to generate free carboxylate groups. Polymer-ion-polymer links are then formed with calcium ions in an aqueous solution of the enzyme. The degree of crosslinkling can be controlled by variation of the calcium concentration.

A similar process to coarctation is polymer-polymer complexation. This may be ionic in nature or due to hydrogen bonding between different polymer molecules.

A typical example of the latter is the formation of a gel between polymethacrylic acid and either polymethylene glycol, poly(N-vinyl-pyrrolidone) or poly(ethyleneimine). The nature of the interaction has been described both qualitatively [58] and quantitatively [59]. The interaction between polyethylene glycol and polymethacrylic acid is illustrated in equation 3.45 and the use of this system to immobilise Inverase has been reported [57].

Both coarctation and polymer-polymer complexation provide very mild methods of entrapment and are likely to be investigated

much more in the future as attempts are made to immobilise increasingly delicate enzymes.



Polyether-polymethacrylic acid complexation by hydrogen bonding.....Equation 3.45.

3.3.3 Chemical Crosslinking.

The creation of chemically crosslinked gels can be broadly divided in to two sections. The first is the crosslinking of existing polymer chains and the second is the polymerisation of monomers and crosslinking agent simultaneously.

3.3.3.1 Crosslinking of Polymer Chains.

Most of the methods described for covalently attaching enzymes to polymers can also be used to form crosslinks between polymer molecules to give gels. In many cases, these methods simultaneously result in formation of polymer-enzyme links as well as gellation.

Formation of gels by radical polymerisation is an alternative. This is usually achieved by incorporating radically reactive double bonds in the polymer and then initiating the polymerisation of these bonds in solution. Polymer molecules with this sort of reactivity are frequently referred to as macromonomers.

Crosslinks have also been formed by creation of radicals on polymer chains, which then couple to form crosslinks. This

approach has been fairly successful using electron beam irradiation, but irradiation with γ-rays has been found to cause damage to the enzyme resulting in almost complete denaturing of the enzyme.

3.3.3.2 Gel Formation from Monomers.

Gel formation from monomers in the presence of an enzyme almost always requires the use of radical polymerisation if the enzyme is not to be chemically included in the polymer chains.

Most work has been done using polyacrylamide gels as these were already in use in electrophoresis systems when interest in gel entrapment began to grow. However, any radically reactive monomer that is water soluble may be used. Examples which have been used are acrylic acid, 2-hydroxyethyl methacrylate and N-vinyl pyrrolidone. Copolymers may be formed from any desired combination of the avaiable monomers. The usual crosslinking agents are the difunctional monomers N,N-methylen-bis-acrylamide and ethylene glycol dimethacrylate.

Gel formation may be allowed to take place in a large volume solution polymerisation or in a suspension polymerisation.

Solution polymerisation gives rise to sheets or blocks of gel that are then cut to the size and shape required. Lumps of gel can also be dried and ground to a fine powder for use in column reactors. This latter process gives rise to rather unevenly sized particles of odd shapes.

More evenly sized spherical particles, sometimes called enzyme beads, are prepared by formation of a suspension of the monomer enzyme solution. The solution forms evenly sized droplets

in a bulk oil phase and polymerisation takes place in each droplet to give crosslinked spheres of gel. The size of the droplets can be accurately controlled by use of constant stirring rates for the formation and maintenance of the suspension. Equipment for the continuous production of these particles has been developed. The even size and shape of enzyme beads makes them ideal for column reactors, as does their high surface area to volume ratio.

3.3.3.3 Interpenetrating Networks.

A method that falls between the crosslinking of polymers and polymerisation of monomers to give a gel is the formation of an interpenetrating network.

An insoluble gel with a low crosslink density is prepared and then swollen with a solution of an enzyme and fresh monomers. The new monomers are then polymerised while inside the existing network of polmyer chains and form a new crosslinked network. The chains of the two networks are not necessarily joined at any point but are completely entangled with each other. The enzyme, which was able to diffuse into the first network, is unable to diffuse out after the second network is formed, as the chains of the second network block the large gaps in the first network. Small substrate molecules are still able to diffuse through the gaps between the chains of both networks.

3.3.3.4 Radical Copolymerisation of Enzymes.

It is popular to use gels formed from radical monomers with fairly low crosslink densities to allow diffusion of larger substrate molecules into the gel. In such cases, leaching out of the enzyme becomes a problem. The answer is to form a covalent

bond between the enzyme and the polymer network, either by one of the methods described in section 3.2 or by chemically including the enzyme in the gel as it is formed.

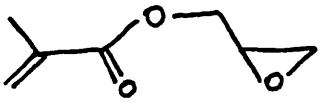
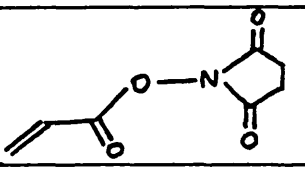
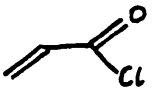
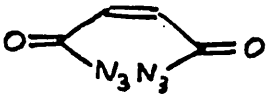
Monomer	
Glycidyl Methacrylate	
Acrylic acid-O-Succinimide ester	
Acryloyl Chloride	
Maleic Anhydride	
Maleic Acid Azide	
3,4-Epoxybutene	
3-Bromopropane	

Table 3.2 Monomers for rendering enzymes radically reactive.

The latter can be achieved by attaching a radically reactive compound to the surface of the enzyme. This is done using one of the many methods described previously in section 3.2 for coupling molecules to enzymes. Some typical compounds are shown in table 3.2. The enzyme then behaves as a monomer and, therefore, is included directly in the growing chains as the polymerisation proceeds. This approach is normally used in gel formations from monomer solutions, but can be used in formation of

interpenetrating networks or crosslinking of radically reactive macromonomers.

3.4 Polyurethanes in Enzyme Immobilisation.

3.4.1 Introduction.

The use of polyurethanes for the immobilisation of enzymes has been an area of study for approximately 10 years. However, only a few workers have been active in this area and much of this work is reported only in industrial patents.

The work to date can be divided into three sections according to the immobilisation method used. These are electrophorese, chemical attachment via isocyanate groups and formation of gels.

3.4.2 Chemical Immobilisation.

This approach to enzyme immobilisation is the most common and is basically a variation on the use of small diisocyanate molecules to attach enzymes to polymers (see also section 3.2.6). It was also the first method used with polyurethanes.

A diisocyanate and a dialcohol, either short chain or polyether, are reacted to give a polyurethane. Use of excess diisocyanate results in a polymer with free isocyanate groups at each end.

Hartdegen and Wood have published numerous patents over the years and have prepared a variety of materials. Generally, their approach has been to form a prepolymer from toluene diisocyanate and a diol such as ethane diol [60] or polymethylene glycol [61]. They also include a trialcohol such as glycerol or trimethylol propane to give crosslinking centres. Having formed the

prepolymer, they then react it with an enzyme in aqueous solution to form covalent polymer-enzyme links. The water of the solution hydrolises much of the isocyanate content, liberating carbon dioxide and forming a foam. This final foam is washed, dried and ground prior to use in packed bed or column reactors.

A similar approach has been patented by the Mitsubishi Petrochemical Company, with the added step of blocking the unreacted isocyanates [62, 63]. This involves reacting the excess isocyanate groups of the prepolymer with an imidazole or phenol compound to form a relatively unstable carbamide or carbamate. Since this company used only polyethylene glycol as diol in the prepolymer formation, the prepolymer was water soluble. It was used in two ways.

Firstly, it could be dissolved in an enzyme solution. The amino groups of the enzyme then attack the unstable carbamides and carbamates, forming a stable polymer-enzyme carbamide link. The large number of amino groups attached to an enzyme result in it acting as a centre for crosslinking and a gel is formed [62]. The use of blocked isocyanates prevents reaction of isocyanates with water and, therefore, there is no foam formation.

The second use is in membrane formation. A solution of polyvinyl chloride was spread onto a glass plate covered by a polyester cloth and immersed in water to give a PVC reinforced polyester material. This was then cut into disks, allowed to soak in an aqueous solution of the polyurethane prepolymer and dried. The film which, by then, consisted of polyester cloth, PVC reinforcement and a polyurethane coating with numerous blocked isocyanates, was placed in an enzyme solution. The enzyme reacted

with the blocked isocyanates to crosslink the polyurethane coating and was,in the process, immobilised [63].

These examples are typical of the work performed with polyurethanes and most of the available literature contains variations on this approach. The exceptions are discussed in sections 3.4.3.and 3.4.4

3.4.3 Polyurethane Macromonomers for Gel Formation.

The second approach that has received attention is the formation of radically reactive polyurethane macromonomers.

Following on from their work in end-capping polyethers with methacrylate groups by ester exchange with methyl methacrylate [64] and their use of a polyether end-capped with toluene diisocyanate[65] in the fashion described in section 3.4.2, Fukui et al used isophorone diisocyanate to end cap apolyether molecule, leaving terminal isocyanate groups. These were then reacted with 2-hydroxyethyl methacrylate to form a macromonomer. Being capped at both ends with a methacrylate, it was also a gellation agent [66].

A solution of the macromonomer and the enzyme was prepared and crosslinking initiated photochemically to form a gel.

The distance between crosslinks was altered by variation of the molecular weight of the polyether molecule and this parameter thus allows control over the diffusion of large substrates in the final material.

The degree of swellability of the gel was controlled by forming copolymers from hydrophilic and hydrophobic macromonomers, detergents being used to mix them in aqueous

solution where necessary. The copolymerisation is random as the hydrophilic and hydrophobic monomers differ only in that the latter were based on a polypropylene glycol molecule. A review of the work of these authors is available [67].

A combination of both covalent attachment and gel formation by radical reaction has been developed by Kumakura and Kaetsu [68, 69, 70].

These workers reacted toluene diisocyanate and hydroxyethyl methacrylate in a 1:1 ratio to get a radically reactive isocyanate compound. To this liquid prepolymer was added an aqueous enzyme solution and the resultant mixture was vigorously agitated. A suspension of the prepolymer formed and reacted rapidly with both enzyme and water to give small agglomerates of material. These were then gelled by initiation of radical polymerisation with high energy radiation. The gel particles were then collected.

This method was extended in later work [70], where 1,5-pentanediol was used to form true polyurethane chains. These were then reacted with the enzyme and crosslinked. The particle size in this later work was controlled by the enzyme concentration and the concentration of the monomers.

3.4.4 Electrophoresis.

A single report of the use of electrophoresis with polyurethanes has been published [71].

A membrane of porous PTFE, approximately 0.5 mm thick, was coated with a thin (approximately 0.01 mm thick) film of polyurethane and placed between two electrolyte solutions. An electropotential was then applied and the enzyme in the

solutions, which was positively charged at the pH used, was drawn towards the cathode. The membrane was positioned so that enzyme molecules would have to migrate across it from the uncoated to the coated side, if they were to reach the electrolyte solution in contact with the cathode.

Approximately one third of the enzyme in the solution became immobilised in the membrane. Application of a reverse potential released all the immobilised enzyme.

The membrane was washed after the immobilisation process was complete and once again placed between two electrolyte solutions, this time containing the substrate. A potential was again applied, in the same direction as used during immobilisation. This was essential to prevent the enzyme diffusing back out through the porous uncoated side of the membrane.

The substrate was found to react almost entirely on the uncoated side of the membrane, as diffusion of the substrate through the porous PTFE was much faster than through the polyurethane.

In summary, this method uses a fine coating of polyurethane on porous PTFE to create an asymetric ultrafiltration membrane. The enzyme is drawn through the pores, but its exit from the membranes is blocked by the non-porous polyurethane coating. When the driving force (I.E. the electropotential) is removed, or reversed, the enzyme respectively diffuses, or is driven, back out through the porous side of the membrane.

This type of membrane is probably equally useful in systems where the driving force is a pump pushing a solution through the membrane, although this application was not investigated.

4 Experimental Procedures.

4.1.1 Purification of Solvents.

Dimethyl sulphoxide (Aldrich Chemical Co. Ltd) was dried over calcium hydride for 1 week, distilled and stored over molecular sieves.

4-methyl-pentan-2-one (BDH Ltd) and N,N-dimethyl formamide were dried over barium oxide powder for 1 week, distilled and stored over molecular sieves.

Tetrahydrofuran (Aldrich Chemical Co. Ltd) was distilled and stored over molecular sieves prior to use.

Water and dichloromethane (BDH Ltd) were distilled immediately prior to use.

N,N-dimethyl acetamide (BDH LTd), methanol (May & Baker), ethanol (James Borough Ltd), toluene (May & Baker), isopropyl alcohol (BDH Ltd) and acetone (May & Baker) were all used as supplied.

4.1.2 Purification of Reagents.

Butane-1,4-diol and 2-butene-1,4-diol were dried over molecular sieves for 2 to 3 weeks, distilled and stored over fresh molecular sieves.

Diphenylmethane-4,4'-diisocyanate (Bayer, Trade Name Desmodur 44 MS) was distilled under reduced pressure and stored in a sealed container at -20^{o}C. Immediately prior to use the material was warmed to room temperature in a dessicator over silica gel.

Polyethylene Glycol 400 (Sigma Chemicals Ltd) was heated at 100^{o}C in a rotary evaporator under reduced pressure for 6 to 8 hours before being stored in a dessicator over silica gel.

Polyethylene glycol 1000 and 1500 (BDH Ltd and Union Carbide Ltd respectively) were melted, concentrated HCL added and the mixture stirred at 50°C for 1 hour to destroy residual traces of catalyst left from its manufacture. The material was then placed in a rotary evaporator at 100°C for 6 to 8 hours under reduced pressure to remove any traces of water or excess HCL. The material was then poured into containers and allowed to solidify under vacuum before being stored in a dessicator over silica gel.

Acrylic acid (BDH Ltd), acryloyl chloride (BDH Ltd), isocyanatoethyl methacrylate (Dow Chemicals Ltd), N-vinyl pyrrolidone (Aldrich Chemical Co Ltd) and 2-hydroxyethyl methacrylate (Aldrich Chemical Co. Ltd) were all distilled and stored at +4°C prior to use.

Acrylamide (BDH Ltd) and benzoyl peroxide (Aldrich chemical Co. Ltd) were recrystallised from chloroform, dried in vacuo and stored at -20°C prior to use.

α-azo-iso-butyronitrile (BDH Ltd) was recrystallised from a 1:1 ethanol:chloroform solution and stored at 20°C.

Molecular sieves, 4A size, (Union Carbide) were heated to 250°C for 24 hours and stored in vacuo at room temperature prior to use.

Dibutyl tin dilaureate, hydroquinone, potassium and sodium chloride, potassium and sodium acetate, sodium carbonate, sodium hydrogen carbonate, self indicating silica gel (all from BDH Ltd), potassium thiosulphate (Fluka), benzoin ethyl ether and 4,4'-azo-bis-cyanopentanoic acid (both Aldrich Chemical Co. Ltd) were all used as supplied.

4.2 Systems based on 2-butene-1,4-diol.

4.2.1 Synthesis of Polymer PUPE1.

This synthesis was performed under nitrogen (see section 4.7.1 for equipment).

PEG1000 (3.20g, 0.0032 mol) in 20 ml of DMSO was added to MDI (4.60g, 0.0184 mol) in 20 ml of IBMK at 80°c over 10 minutes and reacted for a further 1 hour 50 minutes. A mixture of BD (0.576g, 0.00643 mol) and BDU (0.567g, 0.00643 mol) in 6.5 ml of DMSO was added over 10 minutes and reacted for 2 hours. A further 3.5 ml of DMSO containing BD (0.441g, 0.0049 mol) was then rapidly added and reaction continued for a further 40 minutes before the mixture was cooled to room temperature. The polymer was isolated by precipitation from 1 litre of water with rapid stirring and collected by filtration. It was then dried in vacuo at room temperature for 1 week and stored in the dark.

4.2.2 Radical Reactions.

These reactions were all carried out under an inert atmosphere. See section 4.7.2 for equipment details.

PUPE1 and AIBN.

AIBN (0.0168g, 0.0001mol) was added to a solution of PUPE1 (3.00g, ~0.001 mol) in 20 ml of DMF at 65°c and stirred for 1.75 hours before being cooled. The orange/red solution was added to 1.25 l of water with rapid stirring to precipitate the polymer. The white material was filtered off and dried in vacuo. The product was compared to the original polymer by GPC.

PUPE1 and Benzoyl Peroxide.

Benzoyl peroxide (0.0243g, 0.0001 mol) was added to a solution of PUPE1 (3.00g, ~0.001 mol) at 70°C and stirred for 3

hours before being allowed to cool to room temperature. The deep red/orange solution was added to 1.25 l of water with rapid stirring to precipitate the polymer, which was then dried in vacuo. The polymer was powder pink in colour. It was compared to the white starting material by GPC.

PUPE1 and Acrylic Acid and AIBN (1:2 molar ratio).

PUPE1 (3.00g, ~0.001 mol) was dissolved in 10 ml of DMF with acrylic acid (0.1642g, 0.00228 mol) amd warmed to 70°C. AIBN (0.0332g, 0.0002 mol) was added and the mixture stirred for 2.25 hours before being cooled to room temperature. The mixture was added to 1.25 l of water with stirring and the product collected by filtration and dried in vacuo before being studied using GPC.

PUPE1 and Acrylic Acid and AIBN (1:20 molar ratio)

PUPE1 (6.00g, ~0.002 mol) and acrylic acid (2.88g, 0.04 mol) were dissolved in 25 ml of DMF and heated to 70°C. AIBN (0.3456g, 0.0021 mol) was added and reaction continued for 3.5 hours. During this period the reaction became more viscous and turbid. The mixture was divided into two.

Half the mixture was added to 1.25 l of water with stirring and the polymer collected and dried in vacuo.

The other half was stirred rapidly as water was added to it until the polymer precipitated and flocculated. It was then collected by filtration washed with water and dried in vacuo.

The gel permeation chromatograms of the materials were then obtained.

4.3 Unsaturated Systems based on Acryloyl Chloride.

4.3.1 Preparation of Model Compound ACl-PEG-ACl.

Acryloyl chloride (4.07g, 0.045 mol) was carefully added dropwise to PEG400 (6.00g, 0.015 mol) over 10 minutes and stirred for 2 hours, all in a fume cupboard. Excess acryloyl chloride was then removed by rotary evaporation under reduced pressure at room temperature. The solubility of the resultant product was tested in water, THF and toluene.

4.3.2 Synthesis of Polymers.

These experiments were carried out under an inert atmosphere. See section 4.7.1 for details of the equipment.

Preparation of control polymer PUCN1.

A solution of PEG1000 (24g, 0.024 mol) and BD (2.882g, 0.032 mol) in 75 ml of DMSO was prepared and added to MDI (16.00g, 0.064 mol) in 55 ml of IBMK over 30 minutes at 80 ^{o}C and reacted for a further 1.5 hours. BD (1.443g, 0.016 mol) in 20 ml of DMSO was rapidly added with vigorous stirring and reacted for 2 hours to complete the reaction. After cooling, the polymer was precipitated from 2 l of water, collected by filtration and dried in vacuo.

Preparation of Polymer PUACl.

A quantity of PUCN1 (5.56g, ~0.001 mol) was dissolved in 20ml of dry THF and acryloyl chloride (0.222g, 0.0024 mol) in 5 ml of dry THF added. The resultant solution was stirred for 2 hours before being added to 1 l of water to precipitate the polymer. The polymer was collected on a buchner funnel, washed with 100 ml of acetone and dried in vacuo at room temperature for 36 hours. It was then stored at 4^{o}C.

It was noted that immediately upon addition of the acyl chloride solution, a deepening in colour to orange yellow from pale yellow occurred.

4.3.3 Radical Reaction of PUACl.

This reaction was performed under an inert atmosphere. See section 4.7.2.

PUACl (4.00g, ~0.0007 mol) was dissolved in 8 ml of DMF and acrylic acid (1.50g, 0.0209 mol) and AIBN (0.102g, 0.000621 mol) added to the solution. This reaction mixture was then heated to 65^{o}C and this temperature was maintained for 4 hours. The solution became turbid during this period. The final polymer was isolated by addition of water to the solution until no further material was precipitated and the solids present had flocculated, giving small particles. These were collected by filtration and dried in vacuo.

4.4 Non-ionic Unsaturated Systems based on IEM.

4.4.1 The Model Compound IEM-BD-IEM.

A solution of BD (1.80g, 0.02 mol), IEM (6.21g, 0.04 mol) and hydroquinone (0.044g, 0.0004 mol) in 20 ml of dry THF was prepared and 2 small drops of the catalyst dibutyl tin dilaureate (T-12) added. The flask was securely stoppered and a water bath used to keep the solution at room temperature. The reaction was observed to exotherm for half an hour.

Small samples of the reaction mixture were taken, diluted and studied by GPC at intervals of 1.5 hours, 1, 2 and 4 days. The product was recovered by evaporation of the solvent under vacuum at room temperature.

4.4.2 Preparation of Polyurethanes.

All these syntheses were performed under an inert atmosphere as described in section 4.7.1.

4.4.2.1 Preparation of Control Polymers.

Preparation of PUCN2.

PEG1000 (24.0g, 0.0024 mol) and BD (4.33g, 0.048 mol) were dissolved in 40 ml of DMSO and added to a solution of MDI (16.00g, 0.064 mol) in 55 ml of IBMK at 75^{o}C and reaction continued at this temperature for a further 1.5 hours. The resultant polyurethane was precipitated from 2 l of water with stirring and was allowed to stand for 1 hour before being collected by filtration and dried in vacuo. It was then stored in the dark at 4^{o}C. This polymer is a control for the reactive polymer PUIEM(1000).

Preparation of PUCN3.

PUCN3 was prepared by the same method as used for the synthesis of PUCN2, but PEG400 (9.60g, 0.024 mol) was used instead of PEG1000. PUCN3 is the control polymer for PUIEM(400).

Preparation of PUCN4.

PUCN4 was synthesised using the same method as described for PUCN2, but PEG1000 was replaced by PEG1500 (36.0g, 0.024 mol) and the material used as a control for PUIEM(1500).

4.4.2.2 Synthesis of Macromonomers.

Preparation of PUIEM(1000).

A solution of PEG1000 (24.0g, 0.024 mol) and BD (4.326g, 0.0480 mol) in 50 ml of DMSO was added to MDI (16.00g, 0.064 mol) in 30 ml of IBMK at 80^{o}C over 30 minutes. Reaction was continued for a further 90 minutes and cooled to room temperature.

Hydroquinone (0.011g, 0.0001 mol) was added. A solution of IEM (2.50g, 0.0161 mol) in 10 ml of DMSO was quickly added and stirred into the solution for 2-3 minutes. 4-5 small drops of dibutyl tin dilaureate catalyst were added and the solution was then allowed to stand for 36 hours in the dark at 15- 20^{o}C. The polymer was precipitated by addition to 3 l of water with stirring. It was allowed to stand in the water for 1 hour, collected by filtration and dried in vacuo for 24 to 36 hours before being stored in the dark at 4^{o}C.

Preparation of PUIEM(400).

This polymer was prepared by the same route as PUIEM(1000), but PEG400 (9.60g, 0.024 mol) was substituted for PEG1000. The precipitation step differed slightly in that the polymer initially formed a viscous sticky white material that became crumbly and hard when rubbed against the side of the beaker for a while. This allowed the material to be collected as a coarse powder, thus increasing its surface area to volume ratio and giving a faster rate of drying.

Preparation of PUIEM(1500).

PUIEM(1500) was prepared using the same method as described for PUIEM(1000) except for the use of PEG1500 (36.00g, 0.024 mol) instead of PEG1000. Care was needed during precipitation as this polymer was quite hydrophilic and use of insufficient water in the precipitation step led to the formation of an emulsion.

4.4.3 Radical Reactions of PUIEM(1000).

All radical reactions were performed under inert atmospheres and full details of the equipment used is given in sections 4.7.2 and 4.7.3.

4.4.3.1 Thermally Initiated Reactions.

Reaction of PUIEM(1000) and AIBN.

PUIEM(1000) (4.00g, ~0.000684 mol) was dissolved in 10 ml of THF with AIBN (0.0138g, 0.000084 mol) and heated in a securely stoppered flask for 6 hours at 60°C. The mixture was cooled and its solubility tested. It was noted that the solution viscosity had increased after 3 hours and an apparent gel had formed after 4 hours.

Reaction of PUIEM(1000), Acrylic acid and AIBN.

PUIEM(1000) (4.00g, ~0.000684 mol) was dissolved in 20 ml of THF with acrylic acid (2.29g, 0.032 mol) and AIBN (0.0584g, 0.00033 mol). This solution was then heated in a sealed flask for 6 hours at 60°C. After cooling, the solubility of the product was tested. The solution appeared to have gelled after 3 hours.

4.4.3.2 Photochemically Initiated Reactions.

Test Photolysis of PUIEM(1000) in DMF.

Four solutions, each of PUIEM(1000) (4.00g, 0.000684 mol) in 10 ml of DMF with benzoin ethyl ether (0.019g, 0.00008 mol) were poured into 8 cm diameter petri dishes and exposed to U.V. radiation from a medium pressure mercury vapour lamp (GEC, 250 W) at a range of 30 cm. Reaction times of 0.75, 1.5,3 and 6 hours were used for the 4 samples. The materials formed were studied for the presence of leachable components by swelling in THF followed by a GPC study of the leachate.

Reaction of PUIEM(1000) in THF at low temperature.

A solution of PUIEM(1000) (5g, ~0.00085 mol) and benzoin ethyl ether (0.0104g, 0.000043 mol) in 10 ml of THF was prepared. Two portions of this solution, each of 3g, were poured onto clean mercury in 5 cm diameter monax dishes which were then covered with optical quality silica windows and cooled to $0^{o}C$ in an ice/water bath. The two solutions were exposed to U.V. light for 2 and 4 hours respectively. The temperature of the solutions was periodically checked using a digital thermocouple.

Samples of the products were placed in THF as soon as the photolysis was ended and leached for 24 hours. The leachate was then examined for the presence of any leachable material that may have been extracted from the gels.

Preparation of Thin Poly(PUIEM(1000)) Samples.

PUIEM(1000) (2g, ~0.00035 mol) was dissolved in 4 ml of THF with benzoin ethyl ether (0.0043g, 0.000018 mol) and 2g of this solution poured onto clean mercury in a 5 cm diameter monax dish which was then covered with a silica window. The sample was reacted for 4 hours under a U.V. source. The sample was allowed to dry overnight at room pressure before being removed from the mercury surface and dried in vacuo. The sample thickness was measured using a micrometer at several points.

4.4.4 Preparation of crosslinked study Samples.

4.4.4.1 General Reaction Conditions.

These preparations were performed in an inert atmosphere. See section 4.7.3.

A glass mould was prepared from a flat glass plate and 4

strips of glass. These were arranged to give a rectangular mould of dimensions 190 mm by 50 mm by 3 mm. The strips of glass were secured to the base sheet using silicon grease. Care was taken to ensure no excess grease was present in the sample area of the mould. A fine layer of grease was polished onto the surface of the base plate with a clean tissue to act as mould release agent.

The mould was placed in a glove box and levelled with a spirit level prior to use. The reaction solution was poured into the mould, allowed to settle for 5-10 minutes and then exposed to U.V. light for 4 hours. The crosslinked sample, still in the mould was then removed from the glove box. It was carefully released from the mould and placed on a sheet of glass which had previously been coated with a fine layer of a PTFE mould release agent (Tygadure TFE spray from Fothergill & Harvey Ltd).

4.4.4.2 Drying Methods.

3 methods of drying the samples were tried.

(i) Samples were dried in vacuo at room temperature for 6 weeks.

(ii) Samples were dried in vacuo at 40^{o}C for 3 days and then swollen in water for 6 hours. They were then redried in vacuo at room temperature for 4 weeks.

(iii) Samples were dried overnight at 40^{o}C before being swollen in THF for 4 hours. The THF was then allowed to evaporate slowly in a dessicator for 2-3 days to prevent rapid and uneven sample drying which can result in severe sample damage. After a further day covered by a filter paper, the sample was dried at room temperature in vacuo for 2 months.

The samples used for further investigations were dried using

method (iii).

4.4.4.3 Monomer mixtures for specific Samples.

In all cases, the following quantities of reagents were dissolved in 24 ml of DMF.

Sample	Quty of PU	Quty of BEE	Quty of Comonomer
poly(PUIEM(400))	8.3g ~0.002 mol	0.0299g 0.000124 mol	NONE
poly(PUIEM(400)-co-NVP)	8.3g ~0.002 mol	0.201g 0.000837 mol	1.749g 0.0157 mol
poly(PUIEM(400)-co-HEMA)	8.3g ~0.002 mol	0.202g 0.000840 mol	2.091g 0.0161 mol
poly(PUIEM(400)-co-ACM)	8.3g 0.002 mol	0.202g 0.000840 mol	1.139g 0.0160 mol
poly(PUIEM(1000))	12g ~0.002 mol	0.0292g 0.000122 mol	NONE
poly)PIUEM(1000)-co-NVP)	12g ~0.002 mol	0.202g 0.000840 mol	1.748g 0.0157 mol
poly(PUIEM(1000)-co-HEMA)	12g ~0.002 mol	0.202g 0.000840 mol	2.087g 0.0160 mol
poly(PUIEM(1000)-co-ACM)	12g 0.002 mol	0.201g 0.000838 mol	1.138g 0.0160 mol
poly(PUIEM(1500))	15g ~0.002 mol	0.0294g 0.000122 mol	NONE
poly(PUIEM(1500)-co-NVP)	15g ~0.002 mol	0.202g 0.000840 mol	1.749g 0.0157 mol
poly(PUIEM(1500)-co-HEMA)	15g ~0.002 mol	0.202g 0.000840 mol	2.087g 0.0160 mol
poly(PUIEM(1500)-co-ACM)	15g 0.002 mol	0.202g 0.000840 mol	1.138g 0.0160 mol

Table 4.1 Monomer mixtures for PUIEM(X) based samples.

4.4.5 Casting of Control Films.

12g of control polymer (PUCN2, PUCN3 or PUCN4) was dissolved in 40 ml of THF and poured onto clean mercury in a 12 cm diameter monax dish and allowed to dry slowly in a dessicator for 2 weeks. The film was then removed from the mercury and dried in vacuo at room temperature for 2 months.

4.5 Ionic Polyurethanes.

4.5.1 Synthesis of TDOL.

4.5.1.1 From chloropropane diol.

Powdered potassium thiosulphate (57.10g, 0.361 mol) was dissolved in 70 ml of water and CPD (22.12g, 0.200 mol) added, followed by a further 70 ml of water used to rinse down any CPD remaining in the weighing boat into the reaction flask.

The solution was refluxed for 2 hours and cooled. Any traces of unreacted CPD were extracted with ether (2 X 20 ml). The water was then removed by rotary evaporation under vacuum at 100^{o}C. After cooling, the product was extracted from the inorganic salts with DMF (3 X 100 ml). The DMF extracts were centrifuged until clear and dried by rotary evaporation to yield a colourless to light yellow oil. This oil was dissolved in 30 ml of water to give a colourless solution. Ethanol (600 ml) was added to this solution to form an emulsion from which the product crystallised after 1-2 hours stirring. The yield was maximised by cooling the solution to 4^{o}C overnight. The product was collected by filtration and washed with cold ethanol before being dried in vacuo.

The material may be recrystallised from boiling ethanol, but this was generally not found to be necessary.

4.5.1.2 From Glycidol.

Potassium thiosulphate (28.55g, 0.180 mol) was dissolved in 30 ml of water and CPD (7.42g, 0.100 mol) added followed by a further 10 ml of water.

An immediate exotherm was noted and the solution became light yellow. The solution was refluxed gently for 3 hours,

cooled and the water removed by rotary evaporation.

The product was then separated from the inorganic materials by extraction with 50 ml of DMF.

The DMF extract was passed through a No.2 sinter glass funnel and the majority of the DMF removed by rotary evaporation. Industrial methylated spirits was added to precipitate the product, but only a viscous white oil which did not crystallise at 4°C was obtained.

4.5.2 Synthesis of the Ionomer Series PE-X-Th/BD.

4.5.2.1 General Method for all Samples.

These syntheses were performed under an inert atmosphere. See section 4.7.1 for details of the equipment.

A solution of PEG1000 (12.74g, 0.01274 mol) in 40 ml of DMSO was added to MDI (10.01g, 0.040 mol) in 20 ml of DMSO over 10 minutes at 100°C. After 1 hour, the mixture was cooled to 80°C and a solution of BD and/or TDOL (see section 4.5.2.3 for quantities) in 40 ml of DMSO was added over 10 minutes. Reaction was continued for 10 hours at this temperature.

The final polymer was then precipitated and dried in vacuo for 2 weeks before being stored in the dark at 4°C.

4.5.2.2 Precipitations.

Polymers PE-0-Th/BD and PE-25-Th/BD were precipitated by addition of the reaction solution to 5 l of water with rapid stirring and collected by filtration prior to drying.

Polymer PE-50-Th/BD was precipitated from 2 l of industrial methylated spirits which were decanted after 1 hour to leave a sticky white material still capable of flowing slowly. The

material was spread in a 15 cm diameter petri dish to be dried in vacuo.

Polymers PE-75-Th/BD and PE-100-Th/BD were precipitated from 3 l of IPA to yield a white sticky material that flowed readily. The IPA was decanted and the material dissolved in 45 ml of DMF. This solution was then added to 3 l of fresh IPA with stirring to yield a sticky white precipitate barely capable of flowing. The IPA was decanted and the product spread out in a 15 cm diameter petri dish for drying in vacuo.

4.5.2.3 Monomer Mixtures for specific Samples.

Quantities of solvents, PEG1000 and MDI are given in section 4.5.2.1 and apply to all samples.

Sample	Quantity of BD	Quantity of TDOL
PE-0-Th/BD	2.4658g, 0.0274 mol	NONE
PE-25-Th/BD	1.8440g, 0.0205 mol	1.5453g, 0.00683 mol
PE-50-Th/BD	1.2328g, 0.0137 mol	3.0083g, 0.0133 mol
PE-75-Th/BD	0.6014g, 0.00667 mol	4.6329g, 0.0205 mol
PE-100-Th/BD	NONE	6.0184g, 0.0266 mol

Table 4.2 Monomer mixtures for the PE-X-Th/BD polymers.

4.5.2.4 Synthesis of Polymer MDI/TDOL.

MDI (2.50g, 0.01mol) was dissolved in 5 ml of DMSO and heated to 85^{o}C. A solution of TDOL (2.263g, 0.01mol) in 20 ml of DMSO was added over 15 minutes and the solution stirred at 85^{o}C for a further 2 hours and allowed to cool overnight. The polymer was then precipitated from 2 l of ethanol and dried in vacuo for 1 week.

4.5.3 Casting of Films.

(i) Silanising of Glassware.

New unused 9 cm diameter petri dishes were totally immersed in a 2% solution of dimethyldichlorosilane in dichloromethane

(used as supplied by BDH Ltd) for 10 minutes, carefully removed and allowed to dry in the air. After drying, they were rinsed with distilled water followed by acetone. They were then finally dried with clean tissue paper and protected from contact with dust or grease prior to use.

(ii) Film Casting.

Silanised petri dishes were levelled with a spirit level in a vacuum oven and solutions of the polymers (4g in 40 ml of DMF) poured into the dishes. A strong vacuum was immediately applied for 5 minutes and all centres of degassing noted. The vacuum was gently removed and the solutions inspected without disturbing the dishes. Any specks of dust that were found to be acting as a centre for degassing were removed with a fine needle. The vacuum was then reapplied and the DMF lost without bubbling.

After 2.5 months, the samples were removed from the petri dishes and stored in vacuo in the dark.

4.6 Water Soluble Anionic Urethane Macromonomers.

4.6.1 Synthesis of Polyurethanes.

These syntheses were performed using the inert atmosphere equipment shown in section 4.7.1.

Preparation of control polymer PUTDOL

PEG1000 (12.00g, 0.012 mol) and TDOL (5.422g, 0.0240 mol) were dissolved in 10 ml of DMSO and heated to 80^{o}C. A solution of MDI (8.00g, 0.032 mol) was added over 5 minutes and the mixture maintained at this temperature for 2 hours. After cooling, the solution was slowly added to 2 l of dichloromethane with stirring. The polymer, which separated as a viscous oil, was allowed to settle and the DCM decanted. The oil was then dried

under a vacuum.

The rapid boiling of the remaining DCM foamed the polymer, which dried as a brittle foam in 24 hours. This was then stored in the dark at 4°C in a sealed container.

The material was observed to be hydroscopic and rapidly became sticky if left exposed to atmospheric moisture for any length of time.

Synthesis of polymer PUTDOL/IEM.

A solution of PEG1000 (24.00g, 0.024 mol) abd TDOL (10.84g, 0.0479 mol) in 30 ml of DMSO was prepared and heated to 80°C. To this solution was added MDI (16.00g, 0.064 mol) in a further 30 ml of DMSO over 15 minutes. After 2 hours, the solution was cooled to room temperature. IEM (2.50g, 0.0161 mol) and hydroquinone (0.01g, 0.000091 mol) in 7.5 ml of DMSO were stirred into the solution and 5 small drops of dibutyl tin dilaureate added. The mixture was stirred for a further hour and allowed to stand in the dark for 24-36 hours at room temperature.

The solution was then added to 3 l of DCM with stirring and the resultant oil allowed to settle. The excess DCM was decanted. The oil was then dried in vacuo, where residual quantities of DCM caused it to foam. After 24 hours. the brittle foam was transferred to a sealable container and stored in the dark at 4°C protected from moisture.

4.6.2 Synthesis of the Sodium salt of ACV.

1 molar aqueous $NaHCO_3$ solution was added dropwise to ACV (2.80g, 0.0100 mol). Care was taken to see that no strong exotherm was allowed to occur.

After approximately 15 ml of the solution had been added, the pH of the reaction solution was checked with narrow range pH paper. When the pH was in the region 6.5-7.0, addition was halted. The solution was filtered through a sinter funnel. The product was precipitated by addition of 200 ml of acetone, collected on a sinter funnel and washed with 50 ml of acetone. The white solid was dried in vacuo at room temperature for 24 hours before being stored at -20^{o}C in the dark.

4.6.3 Effect of TDOL on Radical Polymerisation.

This reaction was performed in an inert atmosphere, obtained as described in section 4.7.2.

3 solutions, each of methyl methacrylate (5.00g, 0.0499 mol) and AIBN (0.0088g, 0.0000536 mol) in 25 ml of DMF were prepared. One solution acted as a control experiment. The other two had TDOL added, 1.132g, 0.00500 mol and 0.1142g, 0.000505 mol respectively. The reaction flasks were sealed and warmed to 65^{o}C for 24 hours. The products from the reactions were precipitated from 1 l of water and dried in vacuo. The products were compared by GPC.

4.6.4 Effect of added salts on solutions of PUTDOL.

Solutions of PUTDOL (2.00g, ~0.0003 mol) in 8 ml of water were prepared and a small microspatula full of salt crystals added to each solution and the effects noted. The salts used were potassium acetate and chloride and sodium acetate, chloride and the sodium salt of ACV.

4.6.5 Radical Reaction of PUTDOL/IEM in Water.

The inert atmosphere technique used in this experiment is described in section 4.7.2.

A solution of PUTDOL/IEM (5.00g, ~0.0007 mol) and Na_2ACV (0.0247g, 0.0000762 mol) in 20 ml of water was prepared and heated at 60°C in a sealed flask for 24 hours. The resultant gel was firm and had to be cut from the reaction vessel. Its solubility in water and DMF was tested.

It was noted that the mixture appeared to have gelled after 1.5 hours. Bubbles were formed within that gel as the reaction proceeded. Most were formed in the earlier hours of reaction.

4.6.6 Photochemical Curing of PUTDOL/IEM in DMF.

This reaction was performed in a glove box under an inert atmosphere. See section 4.7.3.

PUTDOL/IEM (13.67g, ~0.002 mol) and benzoin ethyl ether (0.0295g, 0.000123 mol) were dissolved in 24 ml of DMF and poured into a glass mould 190 mm by 50 mm by 3 mm, which had been previously levelled with a spirit level, and exposed to U.V. radiation for 4 hours. After this time the solution was found to have formed a weak gel which was too fragile to remove from the mould without damage. It was therefore dried in the mould in vacuo for several weeks and formed a flexible and elastomeric material.

4.6.7 Preparation of Crosslinked Study Samples.

4.6.7.1 General Reaction Conditions.

These samples were prepared under an inert atmosphere. See section 4.7.3.

PUTDOL/IEM (13.66g, ~0.002 mol) was dissolved in a preprepared solution of Na_2ACV (0.0329g, 0.000102 mol) and the comonomer, where present (see section 4.6.7.2), in 45 ml of

water. The solution was poured onto clean mercury in a 15 cm diameter petri dish, allowed to settle and exposed to U.V. light for 4 hours. A few bubbles of entrapped gas were observed to form as the reaction proceeded.

The sample was dried in a dessicator over silica gel for 24 hours, released from the sides of the glass petri dish with a razor blade and dried over fesh silica gel for a further 24 hours. The samples were cut into thin strips while still soft before being dried until hard and brittle over silica gel followed by intensive drying in vacuo.

4.6.7.2 Monomer Quantities for specific samples.

Solvent,initiator and polymer quantities were as given in the general method for all the samples.

Sample	Quantity of Comonomer
poly(PUTDOL/IEM)	NONE
poly(PUTDOL/IEM-co-NVP	2.2298g, 0.0201 mol
poly(PUTDOL/IEM-co-ACM)	1.4215g, 0.0200 mol

Table 4.3 Monomer mixtures for PUTDOL/IEM based samples.

4.7 Procedures and Equipment for Inert Atmospheres.

In all cases, oxygen free nitrogen was used as the inert atmosphere.

4.7.1 Synthesis of Polyurethanes.

These syntheses were performed under nitrogen in order to exclude water vapour and prevent oxidation of the MDI residues within the polymer.

A 3-neck flask was fitted with a nitrogen inlet, a pressure equalising dropping funnel and a PTFE stirrer gland to allow mechanical stirring as shown in Figure 4.1.

Solutions were added via the dropping funnel. A constant

gentle flow of nitrogen was maintained to counteract the escape of nitrogen through the stirrer gland. The nitrogen was dried by being passed through concentrated sulphuric acid, sodium hydroxide and calcium chloride before entering the reaction vessel.

4.7.2 Thermally Initiated Radical Polymerisation.

Oxygen must be excluded from these reactions to prevent formation of peroxide groups in the growing polymer chain. After the monomers and initiator had been mixed, the reaction flask, normally a round bottomed flask was fitted with a white silicone rubber "Suba Seal". Ordinary red rubber suba seals were not used as they swell in solvents such as DMF and materials leach out of them, often colouring the reaction mixture red.

The reaction mixture was then purged for 10-15 minutes with fast flowing nitrogen entering through a steel canula, the end of which was immersed in the solution. Excess gas exited via hypodermic needles in the suba seal. When purging was complete, the exit needles were removed followed quickly by the canula to leave a gentle positive pressure of nitrogen in the flask.

4.7.3 Photochemically Initiated Radical Reactions.

As with thermal radical reactions, oxygen must be excluded to prevent peroxide formation.

These reactions were all performed in a glove box, fitted with an "air lock", inlets and outlets for purging gas and a gas tight electrical inlet.

Samples were either placed in a glass mould, which was placed on the base of the glove box and levelled prior to use, or were poured onto a mercury surface in a petri dish or monax dish.

The mercury surface is obviously self levelling (except for the meniscus at the edge). If required, a small monax dish was surrounded by a larger one containing an ice/water slurry. See Figure 4.2.

Sample solutions were passed into the box via the air lock and were allowed 10-15 minutes purging time under the nitrogen atmosphere before reaction was begun.

U.V. light was provided by a 250 Watt GEC medium pressure mercury vapour lamp mounted on a retort stand. It was allowed to reach maximum intensity before being rotated to shine vertically down onto the sample from a range of 30 cm. The power supply for the lamp was external to the glove box and power was fed to the lamp via the electrical inlet of the box.

Due to the large quantities of heat generated by the lamp, extensive cooling of the glove box was necessary. Two methods were simultaneously used.

(i) The flow of nitrogen into the glove box was passed through a cooling coil immersed in an acetone/Cardice bath at $-78^{o}C$ just prior to entering the box.

(ii) The edges of the upper surface of the glove box were built up with modelling clay and the whole upper surface covered by an ice/water slurry of 2-3 cm depth for the duration of the reaction. Excess water was removed with a water driven vacuum pump and ice lost through melting was frequently replaced.

This allowed temperatures to be maintained continuously at approximately $40^{o}C$ for up to 9 hours.

The nitrogen entered at the top of the box and exited via

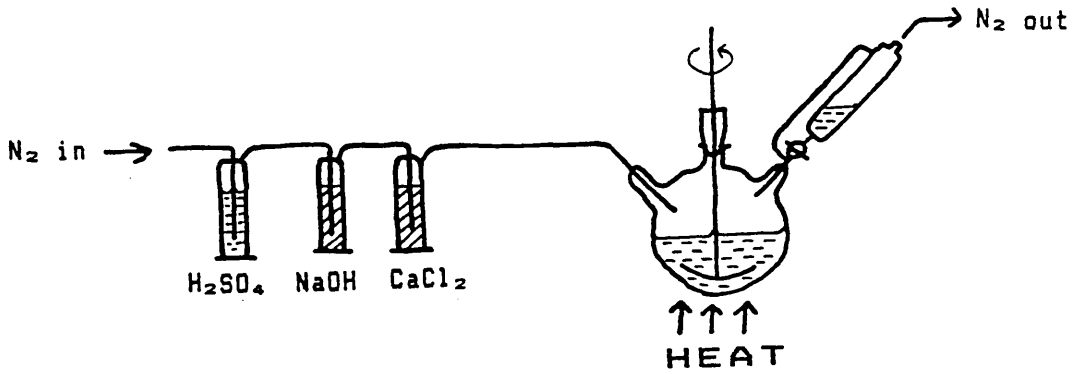


Figure 4.1
Inert Atmosphere Equipment
for Polyurethane Syntheses

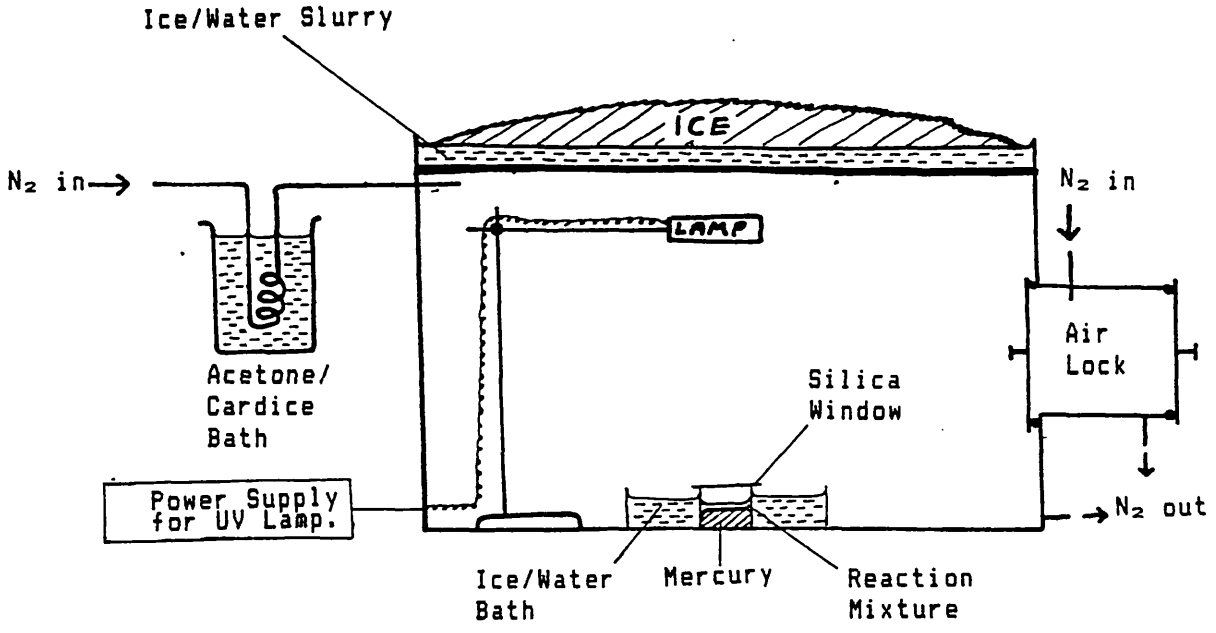


Figure 4.2
Inert Atmosphere Equipment for Photochemical
Initiation of Radical Polymerisation
(shown with reaction vessel for use of
low temperatures or volatile solvents)

the bottom outlet. This ensured complete purging of air by nitrogen which is slightly lighter than air. The glove box was initially purged for at least 1 hour with a rapid flow of nitrogen and a mild flow maintained throughout the reaction, giving a slight positive pressure at all times.

4.8 Methods of Polymer Characterisation.

4.8.1 Differential Scanning Calorimetry.

DSC was performed on a Dupont 9000 thermal analyser with a 910 DSC attachment using a heating rate of 10^{o}C/min. Sample weights varied between 5 and 20 mg and samples were placed in aluminium sample pans fitted with lids.

Samples were studied in the temperature ranges -100 to 30^{o}C and 30 to 170^{o}C It was necessary to use these two temperature ranges as the low temperature cooling attachment causes severe baseline noise above 50^{o}C due to its high heat capacity.

Samples were immediately quenched and rerun after the first run. Some samples which showed no low temperature features were also run in the range -10 to 170^{o}C

4.8.2 Tensile Testing.

Stress-strain curves were obtained using an Instron mechanical tester fitted with a 1-1000 N load cell. An extension rate of 5 cm/min was used. Samples were parallel sided strips of approximately 1 cm width and a test length of 5 cm or 10 cm was used. All samples were tested to breaking point.

4.8.3 Proton Nuclear Magnetic Resonance Spectroscopy.

NMR spectra were recorded using either a Perkin Elmer R32 90MHz scanning spectrometer. High definition spectra were obtained using a Bruker 250 MHz fourier transform spectrometer.

Samples were dissolved in DMSO D_6.

4.8.4 Equilibrium Solvent Uptakes.

Samples weighing approximately 0.5 g were cut from cast or crosslinked films of the test material and dried in vacuo until they were of constant weight. The dry samples were completely immersed in the solvent in sealable sample tubes. These were kept at a constant 31^{o}C in a thermostatted water bath. The samples were periodically removed and quickly but gently pressed on a clean filter paper to remove surface droplets of solvent and then weighed.

Two independent samples of each material for each solvent were run to measure the accuracy of measurements and to allow detection of contamination of solvent in either of the two samples during the experiment.

The solvents used were distilled water and absolute ethanol.

4.8.5 Gel Permeation Chromatography.

4.8.5.1 Equipment.

The apparatus used, with all connections, is shown in Fig 4.3. Specific items of equipment used were an Altex model 110A isocratic pump, a Rheodyne model 7125 injection valve with a 20 µl sample loop, a Rheodyne low volume 2 micron in-line filter and a 30 cm long analytical column and matching guard column packed with 5 micron mixed PLGel from Polymer Laboratories Ltd. The 2 detectors used were a Cecil model 2112 U.V. single wavelength spectrometer fitted with an 8 µl flow cell and a Beckmann model 156 refractometer fitted with a 10 µl flow cell. All connections between equipment were made using 0.01 mm

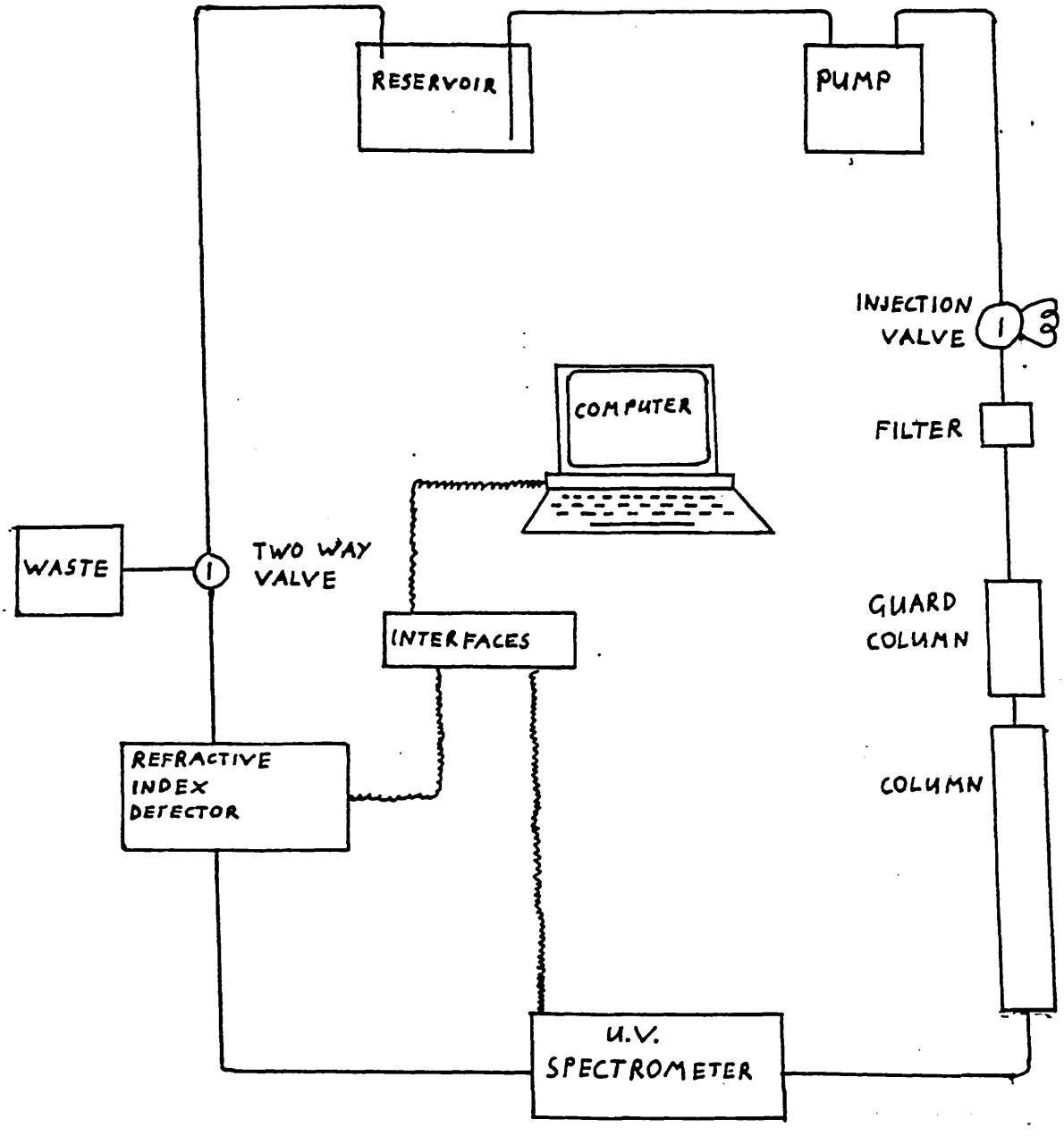


Figure 4.3
Gel Permeation Chromatography Equipment.

internal diameter tubing. Stainless steel tubing was used between the pumps and column where high pressures occur. Elsewhere, PTFE tubing was used.

Data collection was performed using a Trilab 2000 chromatography computer with voltage to frequency interfaces for both detectors (supplied by Trivector Systems Ltd). A data collection rate of 1 point per second per detector was used.

A flow rate of 1 ml/min was used with either THF or DMF as eluent. During a sample run, eluent was passed to a waste container for later redistillation. At other times, solvent was cycled back into the main solvent reservoir.

4.8.4.2 Sample Analysis.

Sample solutions of 0.1% to 0.3% w/v were prepared and, if necessary, filtered through a 0.45 micron filter prior to injection.

All chromatograms were printed with the same scale on the time axis to allow direct comparison of chromatograms taken within 1-2 months of each other.

Retention times alter slowly with time as the column packing deteriorates and noticeable shifts in retention time are detectable after approximately 3 months.

In order to distinguish between different types of material present, the U.V. recorder was set at a wavelength of 280 nm. The benzene rings of MDI residues absorb in this region, but many other components of reaction mixtures do not. This allows the molecular weight distribution of the polyurethane to be studied without interference from most, if not all, of the other materials present. Comparison of U.V. and R.I. traces allows

identification of peaks not due to the polyurethanes.

The system was calibrated with low dispersity (<1.05) polystyrene standards provided by Polymer Laboratories Ltd. Calculation of the calibration curve and of sample molecular weights was performed using the software provided with the computer system.

Molecular weights calculated in this manner are relative molecular weights, not true molecular weights, but they may be used for comparison of similar types of sample. Polymers differing widely in chemical nature will interact differently with the solvent-column system and care must therefore be exercised with comparisons of widely differing materials.

4.8.6 Infrared Spectroscopy.

Spectra were recorded on a Perkin Elmer 457 scanning spectrometer.

Polymer samples were dissolved in THF or DMF and a thin layer of the solution spread on the surface of a clean KBr disk and allowed to dry in vacuo. The spectrum was then recorded.

Crystalline or grindable samples were ground to a fine powder with spectroscopic grade KBr, with a sample:KBr ratio of 3:1, pressed to form a disk and the spectrum recorded.

5. Systems based on 2-Butene-1,4-diol.

5.1 Introduction.

It has been reported that polyurethanes containing alkene units may be synthesised by use of 2-butene-1,4-diol (BDU) as a chain extender [31]. The formation of graft copolymers by radical polymerisation with a variety of monomers such as N-vinyl pyrollidone and acrylamide has been investigated [72, 73, 74] and the use of γ-radiation to initiate radical reactions with these polyurethane macromonomers has also been studied [75]. In all of these studies, very high molar ratios of comonomer to unsaturated residues on the polyurethane were used, 74:1 being a typical example.

The following series of experiments set out to prepare fairly low molecular weight polyurethane mocromonomers containing unsaturated units derived from BDU. The applicability of this macromonomer to the formation of crosslinked networks, both with and without a co-monomer, was then studied using thermal initiators. γ-radiation induced reactions were not investigated as high energy radiation is known to be unsuitable for enzyme immobilisation.

5.2 Synthesis and Characterisation.

5.2.1 Formulation.

The polymer PUPE1 was prepared from four monomers, namely MDI, BD, BDU and PEG1000 in the ration 6:4:2:1 respectively. See chapt 4.2.1 for details of the method. The excess of hydroxyl groups over isocyanate groups gives a low molar mass of approximately 3000 g mol^{-1}. The material still has all of the features of normal polyurethanes, such as hard and soft segments.

On average, each molecule would be expected to have two independent unsaturated groups and should, therefore, act as a crosslinking agent when involved in radical polymerisations.

5.2.2 Infrared Spectroscopy.

The infrared spectrum of PUPE1 was typical of those seen for polyurethanes.

No specific peaks were seen for the BDU residues as the absorptions for these units are weak and hidden by the carbonyl stretch and aromatic C-C stretching bands of the more numerous urethane groups and MDI residues. The major absorptions were assigned as follows.

A strong band from 3400 to 3200 cm^{-1} is due to the N-H stretch of the urethane protons, the peak being broad due to hydrogen bonding and small peaks at 3280 amd 3220 cm^{-1} were also due to these N-H units.

A weak band at 3030 cm^{-1} is the C-H stretch of the aromatic rings and a strong absorption from 3000 to 2840 cm^{-1} with identifiable maxima at 2960, 2920, 2900 and 2870 cm^{-1} was caused by the numerous aliphatic C-H stretches.

The next absorption ranged from 1745 to 1675 cm^{-1} and was due to the urethane carbonyls. A maximum intensity at 1700 cm^{-1} suggests that hydrogen bonded carbonyls outnumber those not involved in hydrogen bonding. The former usually absorbs at 1700 cm^{-1} and the latter at 1750 cm^{-1}.

A strong sharp peak at 1595 cm^{-1} for the aromatic Carbon-Carbon stretch was present.

An N-H deformation similar to those seen for secondary

amides [79] was visible as a strong broad band between 1550 and 1500 cm^{-1} and a sharp aliphatic C-H deformation occurred at 1410 cm^{-1}.

A band 110 cm^{-1} wide and centred on 1250 cm^{-1} was attributed to a C-O single bond stretching frequency from the urethane group similar to those seen for esters.

A very broad, poorly defined absorbtion from 1150 to 1040 cm^{-1} with maxima at 1105 and 1070 cm^{-1} was most probably due to the C-O stretching frequency of the ether links in the polyether.

Aromatic C-H deformations were sharply visible at 900, 840 and 770 cm^{-1}.

Finally, a sharp peak at 1015 cm^{-1} and weak broad absorptions at 1450 and 930 cm^{-1} were the only unidentified peaks.

No sign of unreacted isocyanate was detected. This would have been visible by the presence of a very strong peak at 2270 cm^{-1}.

5.2.3 Gel Permeation Chromatography.

A near gaussian molecular weight distribution was observed, showing a tailing off towards low molecular weights. Similar tailing was seen for low dispersity standards and is a result of the equipment used.

From this curve, it is clear that the polymerisation has proceeded in a controlled manner with no spurious products and no residual traces of monomers. Although product isolation would be expected to remove the majority of unreacted water soluble monomers, it would also result in polyurea formation from any unreacted MDI, which would have been visible as a second peak in

the chromatogram.

Only standard molecular weight polystyrene samples were available to calibrate the GPC system and molecular weights calculated from such a calibration would only be "polystyrene relative" values. That is, they would be the molecular weights of a polystyrene with the same distribution curve and column retention time as those seen for the sample. Similarly, a calculated dispersity would be relative. In view of the dramatic differences in polarity between polyurethanes and polystyrenes, large differences between relative and true values might well arise due to the different degrees of polymer coiling in the solution. For this reason, relative molecular weights and dispersities were not calculated.

5.2.4 NMR Spectroscopy.

The study of the NMR spectra of model urethane and urea oligomers has been reported [76, 77], along with the investigation of polyether-urethanes and polyester-urethanes [78] and the reader is referred to the literature for a detailed analysis of the many possible resonances that may occur for these types of compounds.

The spectrum of PUPE1 is typical of those seen for segmented polyether-urethanes with the exception of an unresolved multiplet at δ5.8 due to the alkenic protons of the BDU residues and a further multiplet at δ4.75 due to the end methylene units in the BDU residues.

The resonances present in the spectrum were identified as follows.

Twin peaks at δ9.4 and δ9.3 were due to the urethane proton.

The probable cause of the uneven splitting of this resonance is the slightly different environments of those protons next to a polyether segment as opposed to those next to a short diol attached to another MDI unit.

The aromatic protons of MDI gave the characteristic pattern of 1,4 disubstituted rings, centred at δ7.2.

The central methylene group of the MDI units appears at δ4 to δ4.2.

A resonance at δ3.7 was assigned to the end methylene groups of the BD residues, neighbouring the urethane links.

The next easily identifiable peak is that due to the central methylenes of BD units at δ1.7.

The central region of the spectrum between δ4.5 and δ3.5 is frequently very crowded and may also be swamped by the presence of water, δ3.5, especially when hydrophillic units such as polyethylene glycol segments are present.

Splitting patterns are often incompletely resolved due to the slow rates of tumbling of macromolecules in solution and low concentrations of individual groups, though the use of the latest fourier transform spectrometers at 250 or 500MHz is now eliminating this problem.

The lack of any peaks for urea or allophanate protons is strong evidence that the polymerisation proceeded to completion leaving no residual isocyanates and forming no branches during reaction by allophanate formation.

5.3 Radical Reactions.

A series of reactions were performed, using PUPE1 as a macromonomer, to ascertain its suitability for gel formation by

radical polymerisation. Attempts to create gels by homopolymerisation or copolymerisation with acrylic acid (AA) were made. Full details of the methods are given in Chapt4.2.2.

5.3.1 Homopolymerisations.

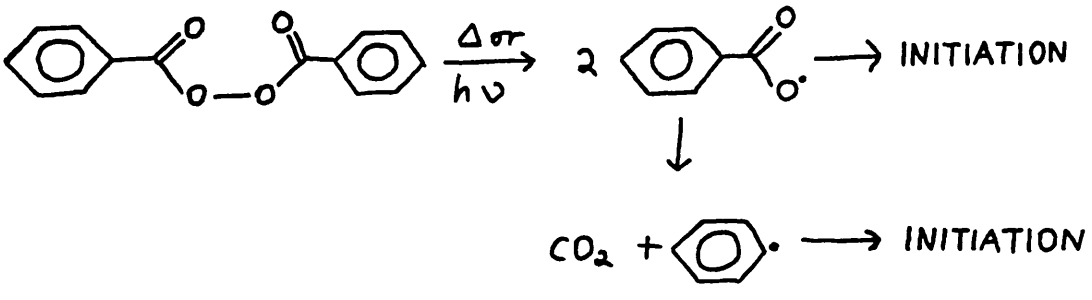
Attempts to form a crosslinked homopolymer from PUPE1 were made using the initiators AIBN and benzoyl peroxide and the reaction products compared to the starting materials by GPC.

In both cases, chromatograms of the polymer before and after the reaction could be superimposed and the column retention times were identical. No new peaks were detected. No gel particles were observed either in the bulk reaction mixture or on a filter paper through which it was passed.

The only sign of any reaction at all occurred when benzoyl peroxide was used. After isolation, the product polymer was found to be powder pink. The original material was white.

An investigation of this phenomenon was beyond the scope of this thesis but a possible reason may be as follows.

Benzoyl peroxide decomposes to form two benzoyloxy radicals (equation 5.1). These may then initiate radical polymerisation or undergo a further decomposition yielding phenyl radicals and carbon dioxide [80, 81].



Decomposition of benzoyl peroxide....Equation 5.1

It seems likely, that in the absence of any readily reactive sites for polymerisation, decarboxylation occurs and some of the phenyl radicals abstract protons from the urethane units to yield a relatively stable radical. A second phenyl radical may then couple to this to give an extensively delocalised system. See Figure 5.1.

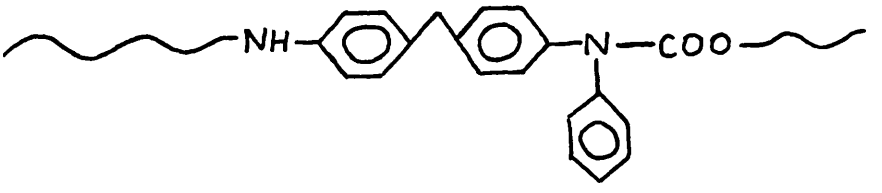


Figure 5.1 Possible Chromophore form benzyl radical attack on a urethane.

Alternatively, some form of redox reaction may occur, as has been reported for the monomer N-vinyl pyrollidone when treated with decomposing benzoyl peroxide [82]. However, oxidation of urethanes usually involves oxidation of activated groups attached to benzene rings. This would result in conversion of the central methylene of an MDI residue to a ketone. But this gives a yellow brown colouration, casting doubt on this latter possibility.

5.3.2 Copolymerisation with Acrylic Acid.

The possibility that the unsaturated units introduced into the polyurethane were incapable of homopolymerisation (c.f. maleic anhydride) was investigated using acrylic acid as a comonomer. Both acrylamide and methyl metacrylate are reported to copolymerise with BDU based macromonomers [72, 73, 74], so acrylic acid was chosen as a likely new comonomer.

Molar ratios of 1:1 and 1:10 for BDU residues to acrylic acid were used with a constant ratio of approximately 10:1 of carbon carbon double bonds to initiator. The molarity of the BDU

residues was calculated from the formulation of the polyurethane.

No visible signs of reaction were seen for the 1:1 mixture and comparison of the isolated product with the original macronomer by GPC gave no hint of any new products. The molecular weight distribution and column retention times were unchanged. No sign of free polyacrylic acid were seen.

With a 10:1 ratio of monomers, an obvious increase in viscosity coupled with a change in the appearance of the reaction solution from clear golden in colour to a turbid semi opaque white-orange mixture occurred.

Samples of product were isolated both by precipitation by addition of the reaction solution to water and by addition of water to the reaction solution. Subsequent analysis by GPC revealed no new materials in either sample. No sign of polyacrylic acid homopolymer was seen in the chromatogram and no materials of molecular weight greater than the original polyurethane were detected.

It was noted that addition of extra DMF to the turbid reaction mixture regenerated a clear orange solution.

The only conclusion that can be drawn from these results is that BDU based polyurethanes are completely unreactive towards acrylic acid under these conditions.

The apparent absence of traces of either acrylic acid or polyacrylic acid in the chromatograms despite visible evidence of a reaction may be explained as follows.

Unreacted acrylic acid is volatile and water soluble and would be largely removed during the precipitation and drying of

the product.

It is almost certain that polyacrylic acid is formed during these reactions. Its creation is the trigger for the viscosity changes and opacity of the reaction mixture, these being caused by the partial precipitation of one or both polymers present, possibly by polymer-polymer complexation. Hence, the addition of extra DMF gives a clear solution by fully redissolving all the polymeric material.

Comparison by GPC of samples of product isolated by two precipitation methods did not give any indication of polyacrylic acid.

In view of the low monomer to initiator ratio, a fairly low molecular weight polyacrylic acid would be expected. The low starting ratio of acrylic acid to polyurethane (20:1) would mean that even a low molecular weight polyacrylic acid could only be present in small quantities relative to the polyurethane and therefore would have been masked by the polyurethane peak in the chromatogram.

5.4 Conclusions.

In conclusion, the use of polyurethane macromonomers based on BDU is not a feasible method for enzyme immobilisation.

The conditions used, already harsh by standards for enzyme immobilisation, gave rise to neither crosslinking or even detectable levels of grafting.

The low reactivity of BDU residues is perhaps not particularly suprising, with no polarisation of the double bond by neighbouring groups. Resonance stabilisation of any radical formed is possible with the allylic protons present. Indeed,

abstraction of one of these protons has been suggested as one of the mechanisms of grafting by Egboh et al. These workers also reported some very low percentage yields of grafting in some systems initiated with AIBN.

It would seem that the increased levels of initiator and low monomer to macromonomer ratio simply resulted in consumption of the acrylic acid in homopolymer formation rather than in crosslinking or grafting.

6. Systems based on Acryloyl Chloride.

6.1 Introduction.

Gel formation from divinyl compounds such as ethylene glycol dimethacrylate has been known for many years and these systems can be regarded as simple models for an acrylate end capped polyurethane.

End capped polyethylene glycol has been prepared and used as a photocrosslinkable material for gel entrapment of enzymes [64] and gel formation with mono end capped polyethers has been observed[83]. In the latter case, gellation was believed to be a result of strong interactions between the polyether chains.

6.2 Model Compound ACl-PEG-ACl.

A reaction between PEG400 and acryloyl chloride was carried out (see chapt 4.3.1) to test the reactivity of the proposed system.

Attempts to isolate the product all led to gellation due to the high reactivity of the acrylate groups. Similar problems were encountered by Gramain and Frere [83]. That a completely insoluble gel was formed indicated both that the polyether had been end capped and that radical crosslinking occurred readily. No other reaction could be envisaged that would lead to gel formation under the conditions used.

These results were most promising, suggesting that an acrylate terminated polyurethane would be quite suitable for enzyme entrapment with regard to its reactivity.

6.3 Urethane Macromonomer.

A hydroxyl terminated polyurethane was treated with acryloyl chloride to yield polymer PUACl. See Chapt 4.3.2 for details.

Upon addition of the acid chloride, which took a few minutes, a deepening in the orange colour of the solution developed. Subsequent analysis of the polymer gave the following results.

A significant increase in column retention time was noted in the gel permeation chromatogram, suggesting a decrease in molecular weight had been effected.

Study of the NMR spectrum revealed no sign of alkenic protons. However, the aromatic region had become more complicated than usual. The symmetry of the 1,4 disubstituted ring pattern was disrupted by a second weak 1,4 substitution pattern. See Figure 6.1. This indicates that a low concentration of a new aromatic group is present and, in view of its 1,4 substitution, that it originated from the MDI residues. The rest of the spectrum was as one would usually see for a polyurethane.

Attempts to duplicate the deep orange colour by addition of concentrated hydrochloric acid to polyurethane solutions under similar conditions were all unsuccessful.

6.4 Radical Reactivity.

Reaction of PUACl with a 30 fold excess of acrylic acid were completely unsuccessful in forming either gelled or grafted material, though this came as no suprise since the NMR spectrum of the polymer had failed to reveal any unsaturated units in it.

6.5 Conclusions.

A probable sequence of events can be placed together from the above evidence.

The acid chloride, instead of reacting with the less

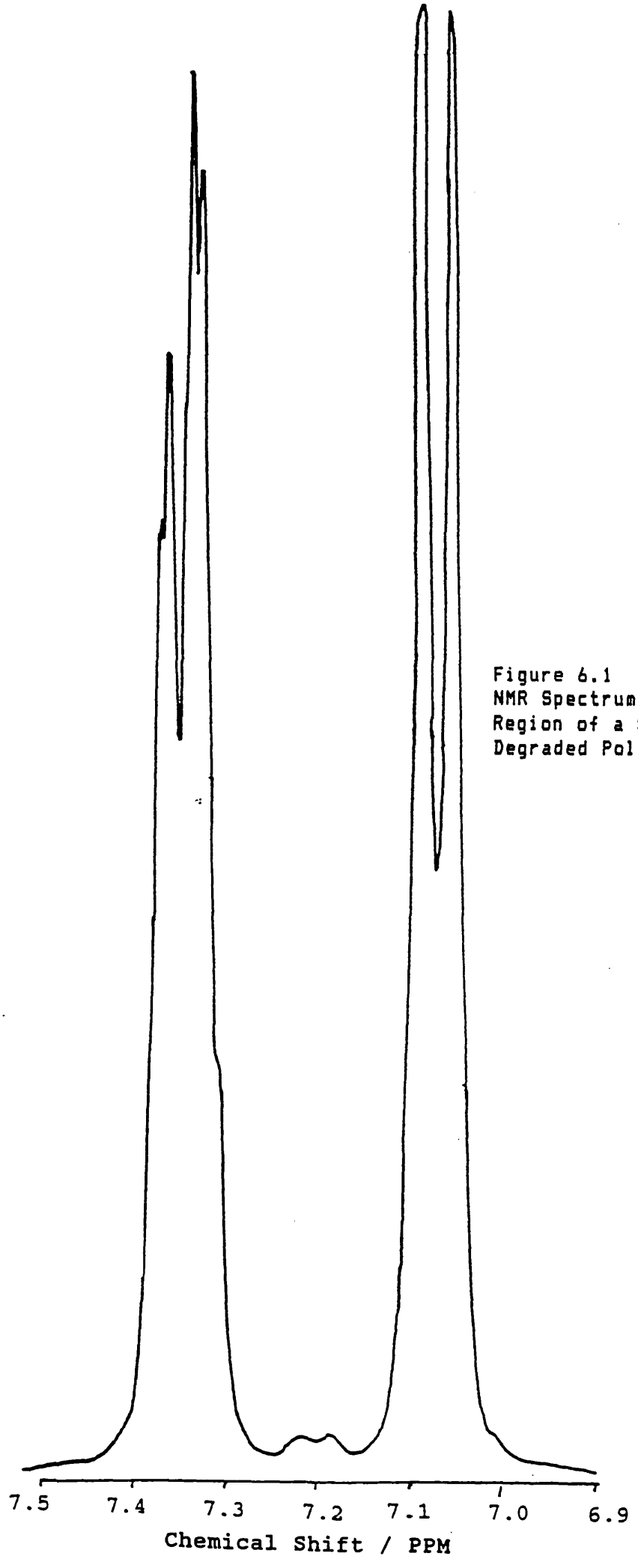
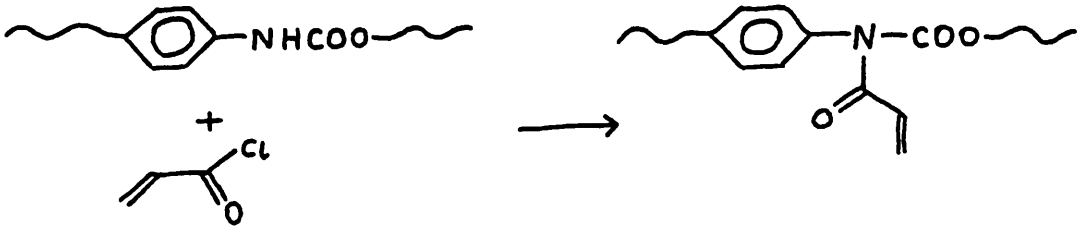


Figure 6.1
NMR Spectrum of Aromatic Region of a Slightly Degraded Polyurethane.

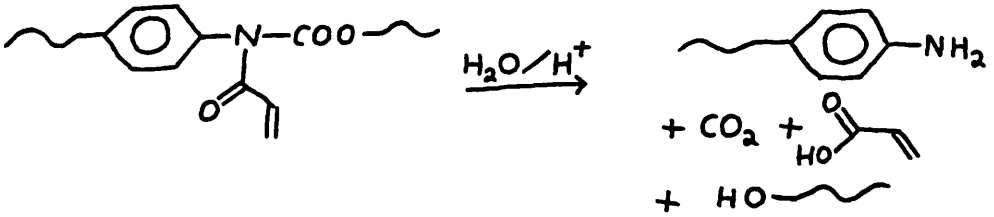
hindered terminal hydroxyl groups, is sufficiently reactive to attack the urethane links. It probably forms a species like those seen for reactions with acid anhydrides [84]. See equation 6.1.



Attack of acryloyl chloride on a urethane....Equation 6.1

Such species have been prepared with no aromatic groups attached to the nitrogen and may be more stable than the one formed in the PUACl system. Certainly, non aromatic urethane linkages are more stable than those attached to aromatic linkages[6]. In addition, HCl was not present in the experiment reported in the literature [84].

Having been rapidly formed, this unit may then decompose, aided by the HCl, present in very high localised concentrations, and by the traces of water always associated with polyethylene glycol containing polyurethanes. The products are most likely acrylic acid,carbon dioxide and a terminal amine and hydroxyl group on the two chain ends. See equation 6.2.



Hydrolysis of a derivatised urethane....Equation 6.2

The net result is chain scission giving a decrease in molecular weight, loss of the unsaturated group as acrylic acid and a new 1,4 substituted ring.

The ratio of polymer to acid chloride was approximately 1:2, so it would be expected that a random reduction in molecular weight involving most of the chains present would take place. This would result in the smooth distribution with longer retention time seen in the chromatogram.

The low concentration of terminal aromatic amines with 1,4 substituted rings fits the NMR data and the lack of carbon-carbon double bonds is easily explained by removal of the free carboxylic acid during isolation of the product polymer.

In conclusion, acryloyl chloride is too reactive and lacks the selectivity required for the preparation of a polyurethane diacrylate monomer from a hyrdoxyl terminated prepolymer.

7 Macromonomers based on Isocyanatoethyl Methacrylate.

7.1 Introduction.

The introduction of radically reactive functional groups onto hydroxyl terminated polymers to give curable macromonomers is of considerable industrial and academic interest[85].

In the past this has been achieved by preparing a molecule with both isocyanate and radically reactive groups from, for example, a hydroxyalkyl (meth)acrylate and a diisocyanate such as isophorone diisocyanate or toluene diisocyanate. The lower reactivity of the second isocyanate favours formation of molecules with one free isocyanate group. This is then reacted with a hydroxyl terminated polymer.

A vast body of literature exists on such methods and the properties of the products, both before and after curing. Studies of the synthesis and curing, with or without comonomers, have been reported both by Wilkes[85, 91] and Cooper[92, 93] and NMR spectroscopy used to investigate the curing rates of these macromonomers[87, 88].

An alternative route to these monomers is the synthesis of isocyanate terminated polyurethanes which are then reacted with hydroxyalkyl (meth)acrylates or copolymers derived from such methacrylates to yield, respectively, macromonomers[86, 87, 88] or grafted copolymers[89, 90].

Recently, a new monomer, isocyanatoethyl methacrylate (IEM), has become available. This material, first reported in 1955[94], received little attention until it became available as an experimental monomer from Dow Chemicals (monomer XAS-10743.00).

This material (Shown in Fig 7.1) has no active protons,

giving it a major advantage over isocyanate terminated urethanes, which are prone to gellation caused by allophanate formation. IEM can be stored in the same manner as any other methacrylate monomer.

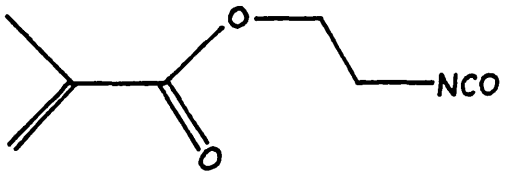


Figure 7.1 Structure of isocyanatoethyl methacrylate.

Its second important feature is that it may be used directly with hydroxyl terminated polymers, thus eliminating one step of the more traditional methods. The only synthetic step necessary is the coupling of IEM to the polymer.

Reviews of the possible uses of IEM have been published[95, 96] and its reactivity relative to other common isocyanates[95] and with a wide range of blocking compounds[97] reported.

Cooper et al[93, 100, 101] have prepared oligourethanes from IEM and some typical soft block materials (polyesters and polyethers). These workers have investigated the properties of crosslinked materials prepared from their oligomers, both with and without other comonomers. Comparisons between IEM based macromonomers and similar materials prepared from hydroxyethyl methacrylate and toluene diisocyanate were made.

To date, there have been no reports of the use of IEM with segmented polyurethanes.

7.2 Macromonomer Synthesis and Characterisation.

7.2.1 Model Compound IEM-BD-IEM.

In order to model the reaction of IEM with a polyurethane based on polyethylene glycol and butane diol, and to reveal potential problems in the process, IEM was reacted with butane diol to form IEM-BD-IEM (see chapt 4.4.1 for method).

The first observation of interest was an exotherm during the first half hour of reaction. Examination of the reaction products by gel permeation chromatography revealed reaction to be effectively complete after 1.5 hours. The solution was found to be stable for 4 days at room temperature in the presence of an inhibitor. Attempts to isolate the product at 10-25^{o}C by evaporation of solvent all led to a gel, which was subsequently found to be insoluble.

From these observations, it was decided that the system was potentially viable. However, the presence of an inhibitor and careful temperature control was deemed necessary. The low concentration of hydroxyl groups present in the prepolymer solution was counterbalanced by addition of dibutyl tin dilaureate (T-12) as a catalyst and 36 hours reaction time was allowed, the model compound having been proved stable for longer periods.

7.2.2 Polyurethane Macromonomers.

7.2.2.1 Synthesis.

Three macromonomers, PUIEM(1500), PUIEM(1000) and PUIEM(400) were synthesised, using PEG1500, PEG1000 and PEG400 respectively as soft blocks (see chapter 4.4.2.2). In all cases, the molar ratio 8:6:3:2 for MDI:BD:PEG:IEM was used in order to study the

effect of changing polyol molecular weight without changing the number of units in the polyurethane.

Control polymers lacking the reactive double bonds were also prepared (see chapter 4.4.2.1) to provide materials with which effects not due to radical crosslinking could be identified. The control materials for PUIEM(1500), PUIEM(1000) and PUIEM(400) were PUCN4, PUCN2 and PUCN3 rspectively.

7.2.2.2 Infrared Spectroscopy.

The infrared spectra of PUIEM(400) and PUCN3 are shown in figures 7.2 and 7.3. Spectra for PUIEM(1000) and PUIEM(1500) were almost identical except that absorbtions arising from the methacrylate units were weaker due to their lower concentration per unit mass of polymer.

The absorbtions usually expected for a segmented polyurethane of this type are all present. Assignments for these bands have already been given (see chapter 5.2.2).

Comparison of the spectra of PUIEM(400) and PUCN3 reveals two new bands that are probably due to the presence of methacrylate units. A band at 1630 cm^{-1} is due to the C=C stretch of a conjugated double bond. This absorbtion is frequently used in kinetic studies on radical reactions of methacrylate based macromonomers[93]. A very weak band at 985 cm^{-1} is just visible and may be due to the C-H deformation on the conjugated double bond. Both new bands are marked in figure 7.2.

These new bands are weak compared to the other bands present because of the low relative concentration of methacrylate units. For this reason, the C=O stretch of the ester in the IEM units is

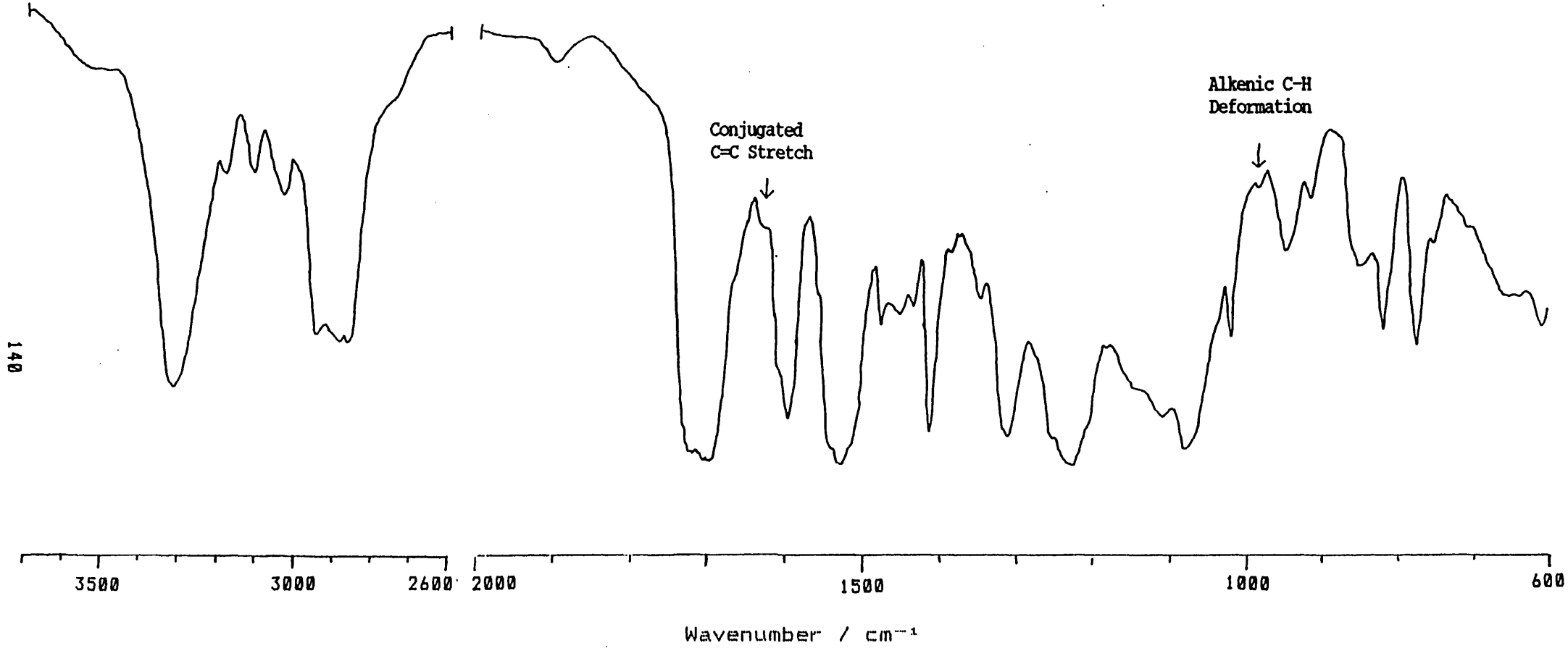


Figure 7.2
Infrared Spectrum of PUIEM(400).

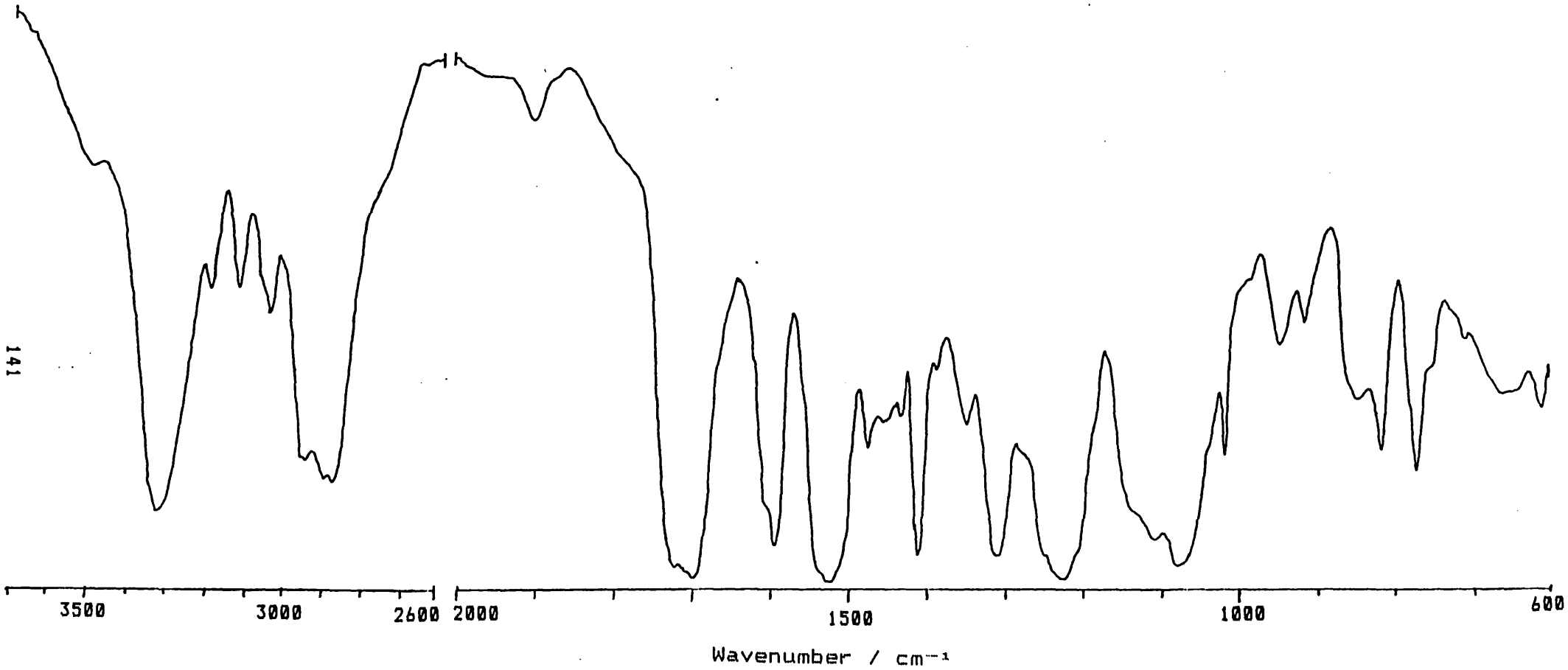


Figure 7.3
Infrared Spectrum of PUCN3.

invisible below the C=O stretch for the urethane units.

7.2.2.3 Proton NMR Spectroscopy.

The NMR spectrum of PUIEM(400) is shown in figure 7.4. It should be noted that some of the multiplets are incompletely resolved and the peaks somewhat broadened by the low tumbling rates of macromolecules in solution. The resolution could, in general, have been improved by using more dilute solutions, but the lower concentration would have rendered the resonances from the IEM units almost invisible.

The major peaks present for segmented polyurethanes similar to the macromonomers have been discussed already (chapter 5.2.4).

The important new features in this spectrum are the 2 peaks at 6.05ppm and 5.65ppm. These are due to the two alkenic protons of the methacrylate groups and have an integral ratio of 1:1 as expected.

The ratio of MDI:IEM units (based on the integrals of the aromatic and alkenic protons respectively) was approximately 3:1. The theoretical value is 4:1. However, the integrals of the alkenic region are small compared to those for the aromatic region and their exact magnitude can only be determined with limited accuracy. A ratio of 4:1 could be obtained within the errors of measuring the integrals. The "apparent" extra IEM is thus due to these errors.It seems reasonable, therefore, to conclude that most if not all of the IEM used has reacted with the polymer. This is further supported by the ratio of urethane to MDI protons.

Only an extremely weak urea peak was visible suggesting

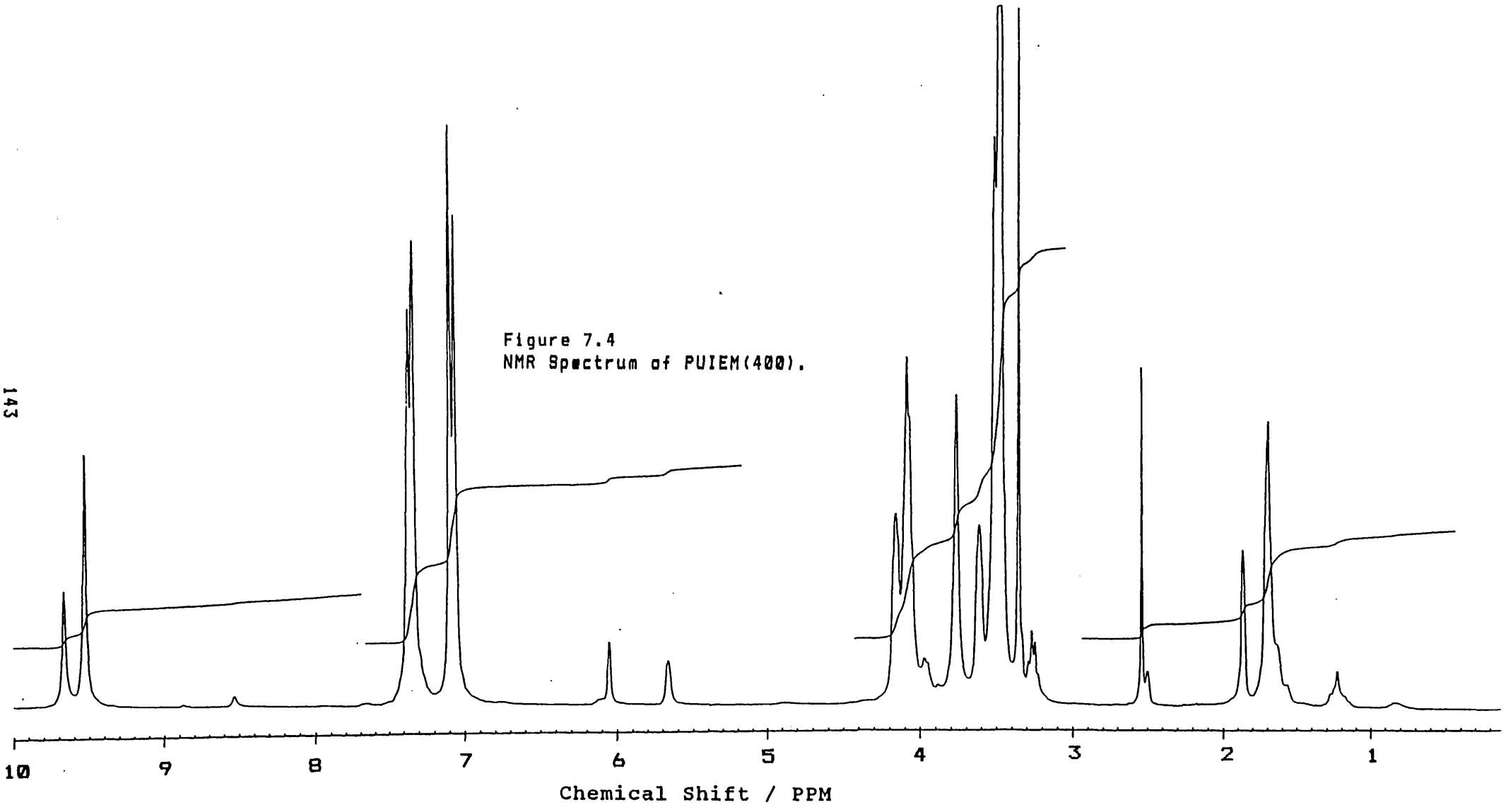


Figure 7.4
NMR Spectrum of PUIEM(400).

almost no hydrolysis had occurred and that traces of water, often found in reagents and solvents, were successfully eliminated.

Two strong peaks were present at 9.5 and 9.7ppm with an integral raio of 1.8:1. This is very close to the 2:1 ratio of BD:PEG and this splitting of the urethane resonance is most probably caused by the slightly different environments of a urethane proton next to a long polyether segment and one next to a diol residue attached to an MDI unit only a few atoms further down the chain. The deviation from the expected value of 2:1 may be fully accounted for by the presence of the urethane protons from the IEM units underlying the peak at 9.5ppm. No separate peak is visible for these protons.

The total MDI:Urethane+Urea ratio is 3.67:1 and the theoretical value is 3.55:1. This close agreement supports the conclusion that both the IEM used in the reaction has added to the chains and that there have been almost no side reactions. No sign of allophanate or biuret peaks were seen.

7.2.2.4 Gel Permeation Chromatography.

Chromatograms of all 3 macromonomers and their respective controls were obtained and found to be reliably repeatable.

No signs of unreacted monomers were seen. Smooth, near gaussian, molecular weight distributions were seen and no differences in curve shape or column retention time were observed between macromonomers and their respective controls. No signs of unusually high molecular weight materials were seen.

This evidence shows that the polymers have formed homogeneously and that, for the macromonomers, there has been no

premature radical polymerisation. In support of the latter conclusion, it should be noted that no insoluble residue was observed and no gel particles detected.

Similarly, GPC chromatograms have also shown that the macromonomers can be stored at 4^{o}C in the dark for 2-3 months without any noticeable radical reaction taking place.

Molecular weights based on calibration of the column with polystyrene standards were found to contain large errors due to the sensitivity of the computer method of calculation to the precise start and end points of a peak and are,therefore, not given here. These values are, in any case, not particularly meaningful for the reason given in chapter 5.2.3.

From the stoichiometry of reagents used, it is possible to calculate the theoretical molecular weight that would be achieved for 100% conversion. While useful as a guide for adding quantities of different polymers to reactions, these values are not true values for the number average molecular weight as conversion is rarely fully 100%. The values were PUIEM(1500) = 7350 g/mol, PUIEM(1000) = 5850 g/mol and PUIEM(400) = 4050 g/mol.

It would be expected that the column retention times would fall in the order PUIEM(400) > PUIEM(1000) > PUIEM(1500). In fact, the order was PUIEM(400) < PUIEM(1000) ≈ PUIEM(1500). All 3 retention times were fairly similar, but the difference between PUIEM(400) and PUIEM(1000) cannot be accounted for by experimental error alone. All 3 materials are of low molecular weight (for polymers) and lie at one end of the range of the column (full range 0-3 million g/mol). It may therefore be that the materials separated not only by size but also by the changes

in nature of the polymer chains.

PUIEM(1500) has polyether chains nearly 4 times the length of those in PUIEM(400) not only 1.5 times the length of those in PUIEM(1000). The number of MDI and BD units is equal for all 3 polymers. The higher ratio of polar urethane groups to less polar ether groups may increase the tendency for the molecules to remain in the main solvent flow (THF $\varepsilon r=7.58$[102, 103]) rather than to diffuse into all the available pores in the column material (polystyrene gel) which is less polar. A similar but less marked effect may explain the similar retention times seen for PUIEM(1000) and PUIEM(1500). That the solubility of the materials is dependent on the polyether segment length is shown in section 7.2.2.5. Use of a narrower molecular weight range column, E.G. 0-10,000 g/mol, would be expected to resolve these materials in the expected order.

7.2.2.5 Solubility.

The solubilities of the 3 macromonomers (see table 7.1) in assorted solvents is typical for these types of segmented polyurethanes. The solubility of these materials is dependent on the degree of phase separation and on the ability of the solvent to dissolve the resulting hard domains. The soft polyether segments are compatible with all the solvents tested.

The polar protic liquids water, ethanol and methanol were non solvents for the urethanes. These liquids are incompatible with the closely packed benzene rings of the MDI residues and are therefore unable to dissolve the hard domains. The polymers therefore swell, but do not dissolve.

Toluene is also unable to dissolve the hard domains due to the hydrogen bonding network formed between the urethane units in the domains.

1,4 dioxan	Relative Dielectric Constant	PUIEM(1500)	PUIEM(1000)	PUIEM(400)
Water	78.54	Insoluble	Insoluble	Insoluble
DMSO	46.6	Soluble	Soluble	Soluble
DMA	37.78	Soluble	Soluble	Soluble
DMF	36.71	Soluble	Soluble	Soluble
Methanol	32.6	Insoluble	Insoluble	Insoluble
Ethanol	24.3	Insoluble	Insoluble	Insoluble
THF	7.58	Soluble	Soluble	Soluble
Diethyl Ether	4.34	Insoluble	Insoluble	Insoluble
Toluene	2.38	Insoluble	Insoluble	Insoluble
1,4 Dioxan	2.21	Soluble	Soluble	Soluble

Table 7.1 Solubility of the PUIEM(X) macromonomers.

The highly polar aprotic solvents DMA, DMF, and DMSO readily dissolve the polymers, being compatible with all the residues in the chain. THF, while of relatively low polarity, is still capable of dissolving all 3 polymers. However, PUIEM(400) takes some time to dissolve. This suggests that THF requires the presence of the polyether chains to disrupt the surface of the hard domains in order to aid the dissolution process.

1,4 dioxan dissolves PUIEM(1500) and PUIEM(1000) despite its low polarity. However PUIEM(400) merely swells in this solvent. This is probably an indication of the need both for a high polyether content which this solvent can dissolve and a

requirement for the hard domains to be partly disordered by the polyether. Both THF[11] and dioxan[13] can be used in the synthesis of 100% hard block model compounds, so it seems likely that the actual polymer molecules would remain in solution in dioxan if the energy required to disrupt the well ordered hard domains was not so great.

It is interesting to note that dioxan has a lower dielectric constant than diethyl ether and toluene, both of which are non-solvents for all the polymers. This is due to its symmetry which leaves both oxygen atoms exposed and able to readily form hydrogen bonds and bridges as shown in figure 7.5.

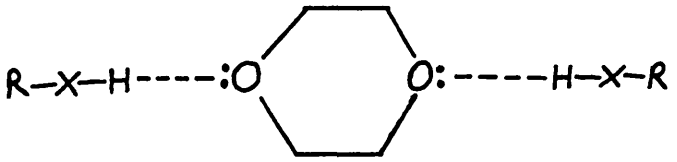


Figure 7.5 Hydrogen bond bridge formation with 1,4 dioxan.

Diethyl ether on the other hand has two bulky ethyl groups that are able to move freely and partly shield the oxygen atom by steric hindrance. For this reason, dioxan can disrupt the network of hydrogen bonds and dissolve the hard domains whereas ether cannot.

7.3 Preliminary Investigations into Curing.

7.3.1 Thermally Initiated Curing.

Two solutions of PUIEM(1000) in THF were polymerised using AIBN as the initiator. Acrylic acid was added to one of the solutions as a comonomer and the total molar ratio of radically

reactive groups to initiator was kept constant for both experiments. See section 4.4.3.1.

In both experiments, fairly firm gels, insoluble in THF, DMF and DMSO, were obtained at the end of the 6 hour reaction period. An approximate estimate of the time required for gellation was made using the halting of magnetic stirring as an indicator, both experiments being performed using the same equipment and control settings. Gellation occurred after 2 hours for the copolymer and after 4 hours for the homopolymer. The shorter gel time for the copolymer is a reflection of the higher overall reaction rate due to the greater total monomer and initiator concentrations.

The crosslinked copolymer was free from the distinctive smell of acrylic acid. A sample of the material was swollen for 2 days in THF and the supernatant studied for signs of leachable materials using GPC.

The chromatogram of the supernatant yielded the following information. A peak due to unreacted polyurethane macromonomer was identified and a further peak, of lower apparent molecular weight with only a weak absorbence at 280 nm, was believed to be due to polyacrylic acid homopolymer. A third minor peak was identified as a trace of unreacted acrylic acid.

The trace of acrylic acid indicates that conversion of monomer to polymer was less than 100% and this is confirmed by the presence of some unreacted macromonomer. It would also be expected that a small proportion of the macromonomer would be end capped at only one end and these monofunctional macromonomer molecules would have a smaller chance of being incorporated into

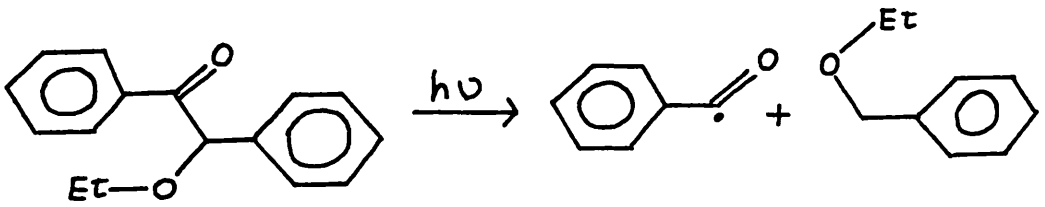
the network at lower conversions.

The leachable materials made up only a tiny fraction of the gel and the reactivity of the macromonomer as a crosslinking agent was clearly established.

7.3.2 Photochemically Initiated Curing.

7.3.2.1 Reactions in DMF.

Solutions of PUIEM(1000) in DMF, with benzoin ethyl ether as initiator, were exposed to UV radiation for 0.75, 1.5, 3 and 6 hours, as described in section 4.4.3.2. The decomposition route of the initiator[104] is shown in equation 7.1.



Decomposition of benzoin ethyl ether.....Equation 7.1

Visual observation of the samples suggested gels had formed after approximately 70 minutes. The gel observed at this stage would tear when disturbed. After 3 hours, the gels were self supporting.

Chromatograms of leachates from the samples were obtained and compared with the chromatogram of the unreacted macromonomer. Identical molecular weight distributions were obtained for all the samples and no sign of any soluble higher molecular weight material was seen.

The absence of soluble species of higher molecular weight than the monomer in mixtures that are clearly reacting may be explained as follows.

Firstly, the polymerisation of the macromonomer rapidly

leads to species of both high molecular weight and high functionality, as suggested by Oraby and Walsh[85, 91]. The chances of these star shaped entities linking with each other rises rapidly as their functionality rises. Since the concentration of such species grows quickly as the reaction proceeds, large "micro-gel" species form, that are removed during filtration of solutions to be used for GPC studies. Thus, no sign of high molecular weight species are seen in the chromatograms.

Secondly, some physical gellation of the starlike species may occur by interaction of chains that are linked together at one end. Such phenomena have been observed in studies on the behaviour of monofunctional polyethylene glycolbased macromonomers by Gramain and Frere[83]. Gel particles formed in this manner were found to be indistinguishable from chemically crosslinked gels. Such particles would be removed by filtration of the solutions to be analysed by GPC and would therefore not be seen in the chromatograms.

It is possible that use of short reaction times or dilute solutions to obtain low degrees of polymerisation and reduce polymer-polymer interactions would give rise to species of intermediate molecular weight that would be visible in chromatgrams.

7.3.2.2 Reactions in THF.

The use of THF as a solvent to allow more rapid drying of crosslinked samples and the cooling of reaction mixtures to give conditions more acceptable for use with enzymes were investigated together. The use of a volatile reaction solvent presents

problems of premature evaporation of solvent and this may be reduced by use of lower temperatures. The reduction of evaporation of the solvent and the prevention of condensation of atmospheric moisture on the cold reaction mixture were both achieved by covering the reaction vessel with an optical quality silica window as described in section 4.4.3.2.

Macromonomer and initiator concentrations were similar to those used with DMF and gelled products were obtained both at room temperature and at $0^{o}C$. Once cooled, samples remained stable at $0^{o}C$ and the cooling method was also found suitable for maintaining stable room temperatures, the high heat capacity of the mercury upon which the solution floated acting as a heat sink.

As for reactions in DMF, chromatograms of leachates from gels formed after 2 and 4 hours reaction time showed no high molecular weight materials.

The low evaporation rates allowed thinner reaction solutions to be used and samples of dry thicknesses of 0.16-0,18 mm were obtained readily.

7.4 Preparation and Testing of Cured Samples.

7.4.1 Curing of samples.

Crosslinked samples of all 3 macromonomers were prepared, the resultant materials being designated polyPUIEM(X) where X=400, 1000 or 1500. In addition 3 copolymers were prepared with each macromonomer, using 2-hydroxyethyl methacrylate, N-vinyl pyrrolidone or acrylamide as the comonomer. These materials were designated polyPUIEM(X)-co-Y where x=400, 1000 or 1500 and Y=HEMA, NVP or ACM. When a comonomer was present, a macromonomer

to comonomer ratio of 1:8 was used. As the addition of a monofunctional comonomer reduces the crosslink density, the total monomer to initiator ratio was kept constant, although this results in an increase in initiator concentration. This should result in a higher degree of conversion, which means that more of the macromonomer will have formed crosslinks and the dilution effects of the comonomer will be offset.

Once the solution has gelled, the presence of small comonomer molecules, that are still mobile in the swollen gel, allows chain growth to continue in a manner analogous to the formation of interpenetrating networks. In such a situation, the growing chains will encounter unreacted macromonomer units and will continue to increase the degree of crosslinking. This will be much less likely to happen in the absence of a small comonomer as the large macromonomer molecules will have poor mobility.

It is recognised that the homopolymers will have a different degree of crosslinking to the copolymers and this will affect any comparisons of properties that are made. Differences between the copolymers, however, should be due to the effects of inclusion of different comonomers, though any large differences in reactivity ratios could also give rise to changes in the properties of the final materials.

7.4.1.2 Sample Drying.

Immediately after crosslinking, the majority of the DMF from the initial reaction solution was still entrapped in the gel and had to be removed before meaningful testing of the samples could be performed.

Three approaches were investigated, namely evaporation, immersion in water and immersion in THF. In all cases, the bulk of the DMF was removed by evaporation in vacuo overnight.

Evaporation, even for several weeks, in vacuo at room temperature was unsatisfactory. Although the majority of the solvent was quickly removed, the samples remained plasticised. The use of elevated temperatures to accelerate the process was not possible as degradation of the polyurethane was also accelerated.

Immersion in water, in order to exchange DMF with water in the soft phase of the sample and allow the DMF to diffuse out of the hard phase, was more successful than evaporation. However, the water, being incompatible with the MDI residues of the hard phase, caused uneven contraction of the samples and left ridges in the surface of the material. Such samples were thus not suitable for testing.

Immersion in THF was the most successful approach. The samples became heavily swollen and the process of removal of DMF by diffusion out of the expanded network allowed to proceed for a few hours. The THF, being compatible with all sections of the polyurethane chain, readily takes the place of DMF in solvating the groups present. After careful evaporation of the THF, as detailed in section 4.4.4.2, the samples were thoroughly dried in vacuo. This was much more effective for removal of THF than DMF because of the lower boiling point and higher vapour pressure of THF.

All the test samples were dried using the DMF/THF exchange method.

7.4.2 Tensile Testing.

The test conditions are detailed in section 4.8.2. Because of the size of minimum sample required, only one test per material was performed. There was, therefore, no averaging of results to ensure that the values of ultimate tensile strength or elongation at break were not affected by flaws from sample preparation or effects at the point of clamping. Values for the elastic modulus at 0% extension (obtained from the tangent to the stress-strain curve at zero extension), are given in table 7.2, 7.3 and 7.4 respectively. The stress strain curves of PUCN4 and polyPUIEM(1500)-co-HEMA are shown in figures 7.6 amd 7.7 and are typical of the curve shapes seen for cast and crosslinked samples respectively.

Comparison of the moduli of the samples revealed the following.

The control polymer films, cast from THF, all have a higher modulus than any of the corresponding crosslinked samples. This supports the observation, in the literature[92], that the introduction of crosslinks restricts molecular movement and, hence, as solvent is lost, restricts the degree of phase separation/domain formation that can take place. This was further confirmed by the DSC study of these samples in which the cast films were found to have the best phase separation. See section 7.4.3.

Both polyPUIEM(400) and its uncrosslinked control, PUCN3, show a very high modulus compared to the other samples. These materials have a high hard block content and probably have a

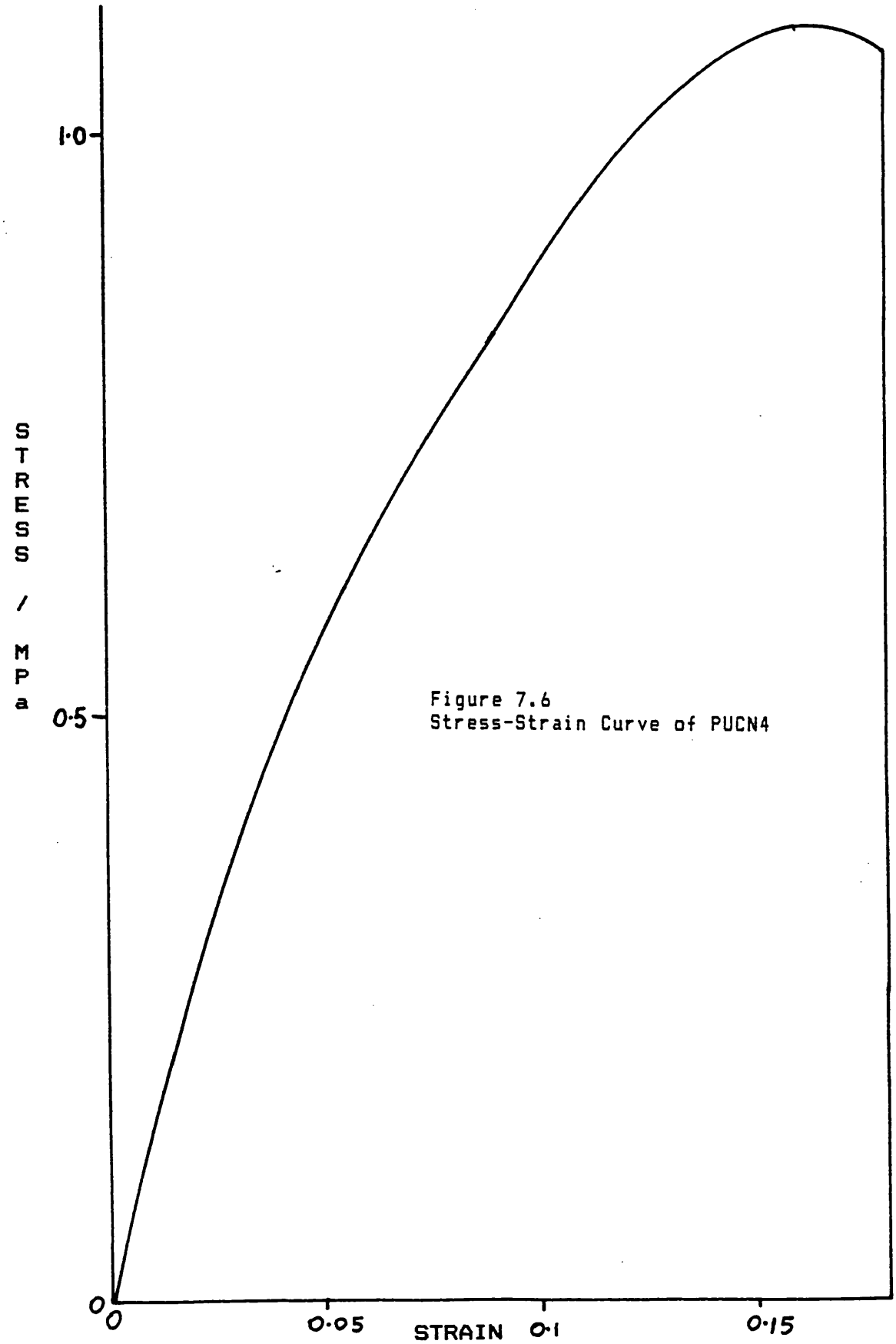


Figure 7.6
Stress-Strain Curve of PUCN4

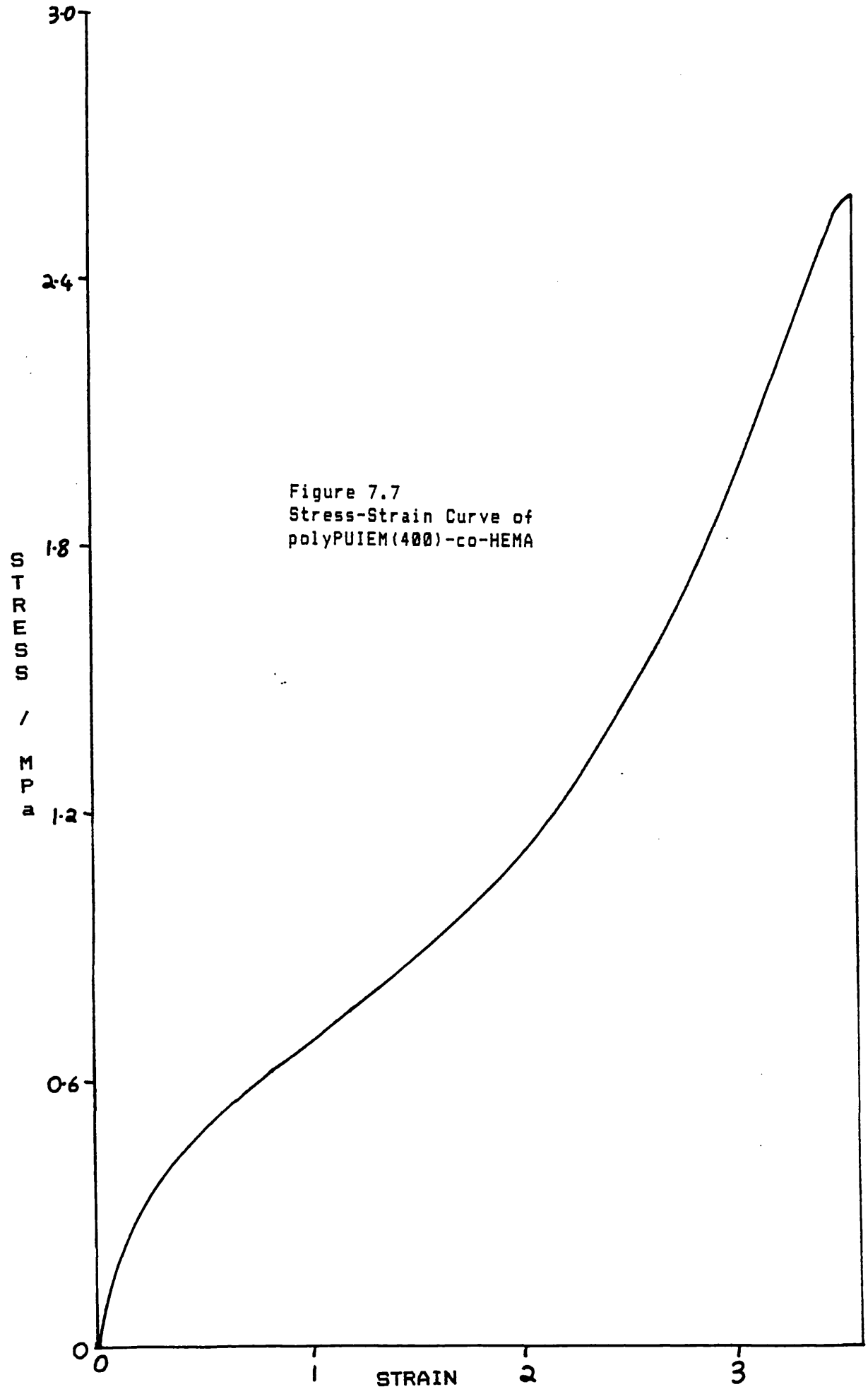


Figure 7.7
Stress-Strain Curve of
polyPUIEM(400)-co-HEMA

fully continuous hard phase rather than hard domains. Being continuous, it greatly reduces the elasticity of the sample. Hence, the high modulus.

Macromonomer	MODULUS / MPa				
	Control	Homo	HEMA	NVP	ACM
PUIEM(400)	158	74.06	10.0	14.19	11.47
PUIEM(1000)	10.50	6.012	9.56	7.41	4.80
PUIEM(1500)	19.98	2.941	3.158	4.81	1.874

Table 7.2 Youngs Moduli for cured polyPUIEM(X) samples.

As mentioned in section 7.4.1.1, the homopolymers will have a different crosslink density to the copolymers and, therefore, comparisons with the copolymers must take this into account. However, simple direct comparisons between the different copolymers can be made.

The moduli of both the PUIEM(1000) and the PUIEM(1500) copolymers fall in the order ACM < NVP < HEMA. The moduli for the PUIEM(400) series lie in the order HEMA < NVP < ACM. The reversal of the order is due to the different morphology of the latter series of samples.

In the PUIEM(1000) and PUIEM(1500) based materials, there will be the usual continuous soft phase with hard domains within it. However, the observed order of moduli does not match the order for the degree of phase mixing that is seen in the DSC study (section 7.4.3). Nor does it match the order of glass transition for pure polymers of the comonomers. Instead, it matches the order of size+mobility of the side group introduced with the comonomer, ACM being the smallest and HEMA the largest. See figure 7.8.

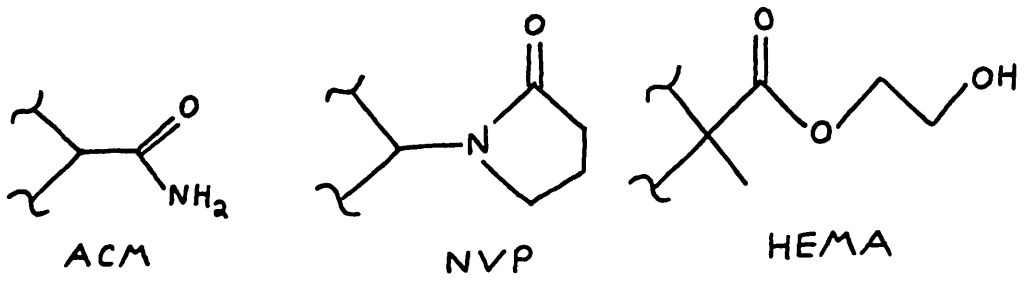


Figure 7.8 Comonomer side groups.

For these materials, the soft phase is a continuous medium with the hard domains dispersed in it. The modulus is affected by the crosslink density, the degree of phase mixing and the extent of interactions between the hard and soft phase. The hard domains will be most regular and reinforced by ACM units, less ordered for the bulky but regular ring of the NVP unit and least ordered for the randomly oriented side chain of HEMA units. As a result, the HEMA containing domains interact most with the surrounding soft phase and the ACM containing domains the least. This is confirmed by the order of the soft phase glass transition widths for these materials (see section 7.4.3), which reflect the size of the interfacial region between the hard and soft phases and which can, therefore, be regarded as a measure of the interaction between the two phases. So, when strain is applied to a sample, the greater the degree of interaction between the hard and soft phases, the greater the reinforcement of the continuous soft phase and the higher the modulus.

For the PUIEM(400) materials, where a continuous hard phase is present, the modulus is a direct measure of the elasticity of the hard phase. Disorder in the hard phase increases its elasticity and reduces the modulus. Hence the reversal of the order seen for the other two series of samples.

The properties of the samples at the point of failure,

ultimate tensile strength and elongation at break, are dependent on both the crosslink density and the strength of any other interactions such as hydrogen bonding.

Macromonomer	Ultimate Tensile Strength / MPa				
	Control	Homo	NVP	HEMA	ACM
PUIEM(400)	9.153	24.04	3.135	3.374	5.541
PUIEM(1000)	1.739	2.281	2.963	4.429	6.954
PUIEM(1500)	1.073	1.059	1.830	2.581	3.953

Table 7.3 Ultimate tensile strength of cured PUIEM(X) samples.

Macromonomer	Elongation per unit length at break				
	Control	Homo	NVP	HEMA	ACM
PUIEM(400)	0.94	2.27	2.20	2.425	1.925
PUIEM(1000)	0.97	2.98	3.41	3.78	3.75
PUIEM(1500)	0.18	2.40	3.03	3.58	4.48

Table 7.4 Elongation at break of cured PUIEM(X) samples.

Sample	Maximum Stress / MPa	Corresponding Strain
PUCN3	9.356	0.915
PUCN2	2.479	0.87
PUCN4	1.093	0.16

Table 7.5 Maximum stress of control films of PUIEM(X) series.

The films of the control polymers PUCN2-4 all have lower extensions at break than any of the analogous crosslinked samples. This reflects the absence of any chemical, as opposed to physical, crosslinks. Because the samples flow just before failure, the ultimate tensile strength is less than the maximum tensile strength. The latter is achieved just before the hard domains, that are held together by reversible hydrogen bonding and regular packing, start to fail. This is perhaps a truer

indication of the strength of the sample than the stress, as the sample tears in half. The maximum stress of the cast films is higher than that of the analogous homopolymer for PUCN2 and PUCN4. This reflects the strength of the purer hard phases formed in the uncrosslinked samples. PUCN3 is not as strong as polyPUIEM(400) as the high hard block content gives both samples a continuous, highly ordered, hard phase. The addition of chemical crosslinks on top of this improves the ultimate strength of polyPUIEM(400).

It is worth noting that none of the crosslinked samples show the flow of the cast films as the former are dominated by irreversible chemical crosslinks and the latter by reversible intermolecular interactions. In all cases, the ultimate strength and maximum strength of the cured samples are the same.

The ultimate strength of the copolymers in all 3 series of materials fall in the order NVP < HEMA < ACM. This may be explained on the basis of the extra hydrogen bonding introduced by the comonomers. which strengthens the samples.

NVP has no labile protons and, therefore, can only replace existing inter-urethane hydrogen bonds. HEMA introduces an extra hydroxyl group which boosts hydrogen bonding, but the bulky disordered nature of the side chain bearing this group somewhat offsets the benefits by disrupting the existing inter-urethane hydrogen bonding to a degree. ACM is highly polar and readily forms hydrogen bonds. In addition, it is the least bulky of the comonomers and, therefore, allows the most inter-urethane hydrogen bonding. As a result, it gives the strongest samples.

All the crosslinked materials achieve a longer ultimate extension than the cast films, as greater chain movement is possible without disrupting the chemical crosslinks than is possible for the cast films, held together by their reversible physical crosslinks.

For the PUIEM(1000) and PUIEM(1500) copolymer samples, there seems to be some correlation between ultimate strength and elongation, the former series giving the order NVP < HEMA ≈ ACM and the latter series giving the order NVP < HEMA < ACM. The order of ultimate strength was NVP < HEMA < ACM.

The effect of increasing polyether segment length and hence weight percent of soft block on the ultimate tensile strength and modulus of the samples is clear. Increasing soft block content gives a lower modulus as there is more soft, easily deformable, material present. The longer polyether chain length increases the distance between crosslinks and allows greater uncoiling of the chain before the crosslinks are strained. Thus, a lower modulus is seen. The dilution of the hard phase material with increasing soft block content isolates the hard domains and reduces the extent of interchain hydrogen bonding and thus reduces the ultimate strength.

7.4.3 Differential Scanning Calorimetry.

Details of the soft phase glass transitions are given in table 7.6 and a typical DSC trace is shown in figure 7.9.

As expected, the glass transition temperatures of the PUIEM(1500) based samples are the lowest and those of the PUIEM(400) based samples the highest. For pure polyethers, the order is the reverse. I.E. PEG400 < PEG1000 < PEG 1500. Often a

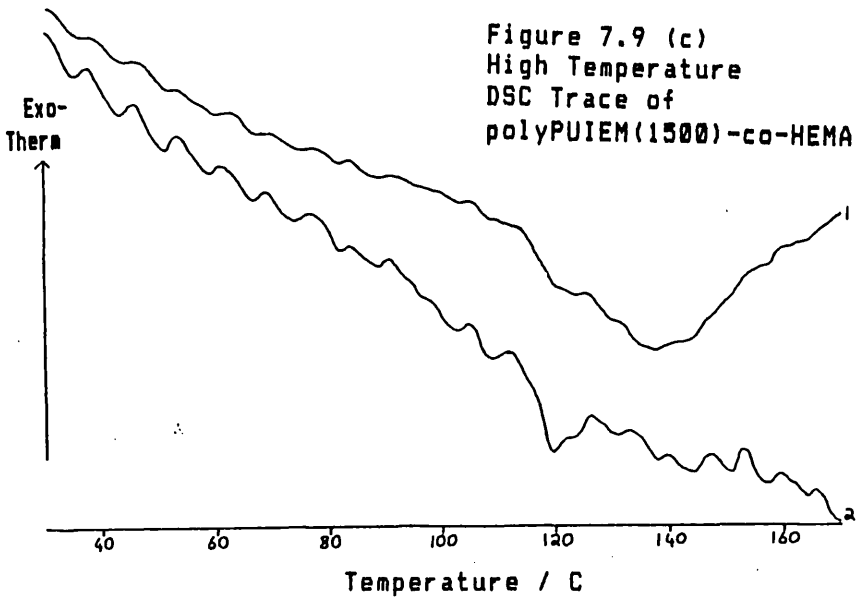


Figure 7.9 (c)
High Temperature
DSC Trace of
polyPUIEM(1500)-co-HEMA

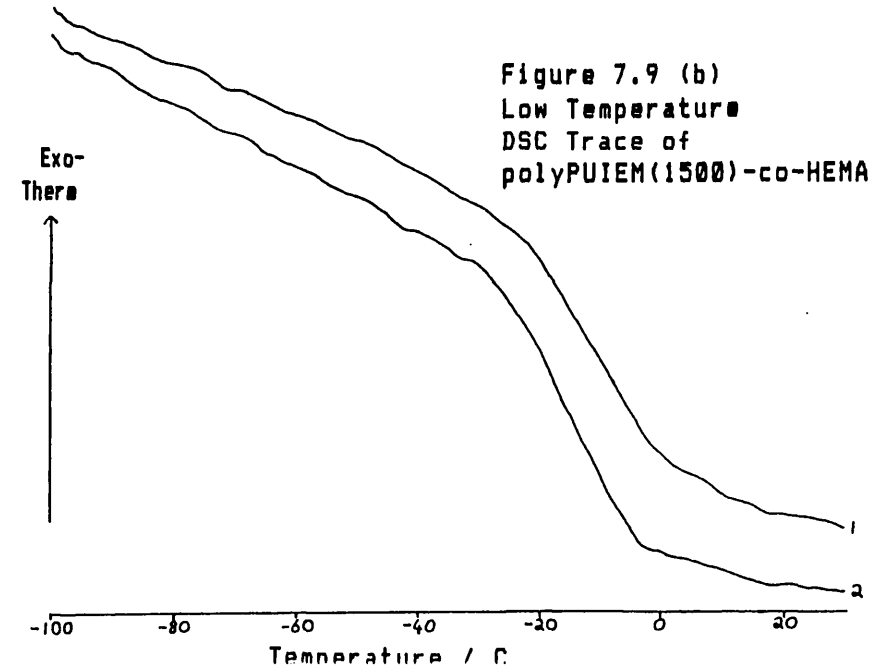


Figure 7.9 (b)
Low Temperature
DSC Trace of
polyPUIEM(1500)-co-HEMA

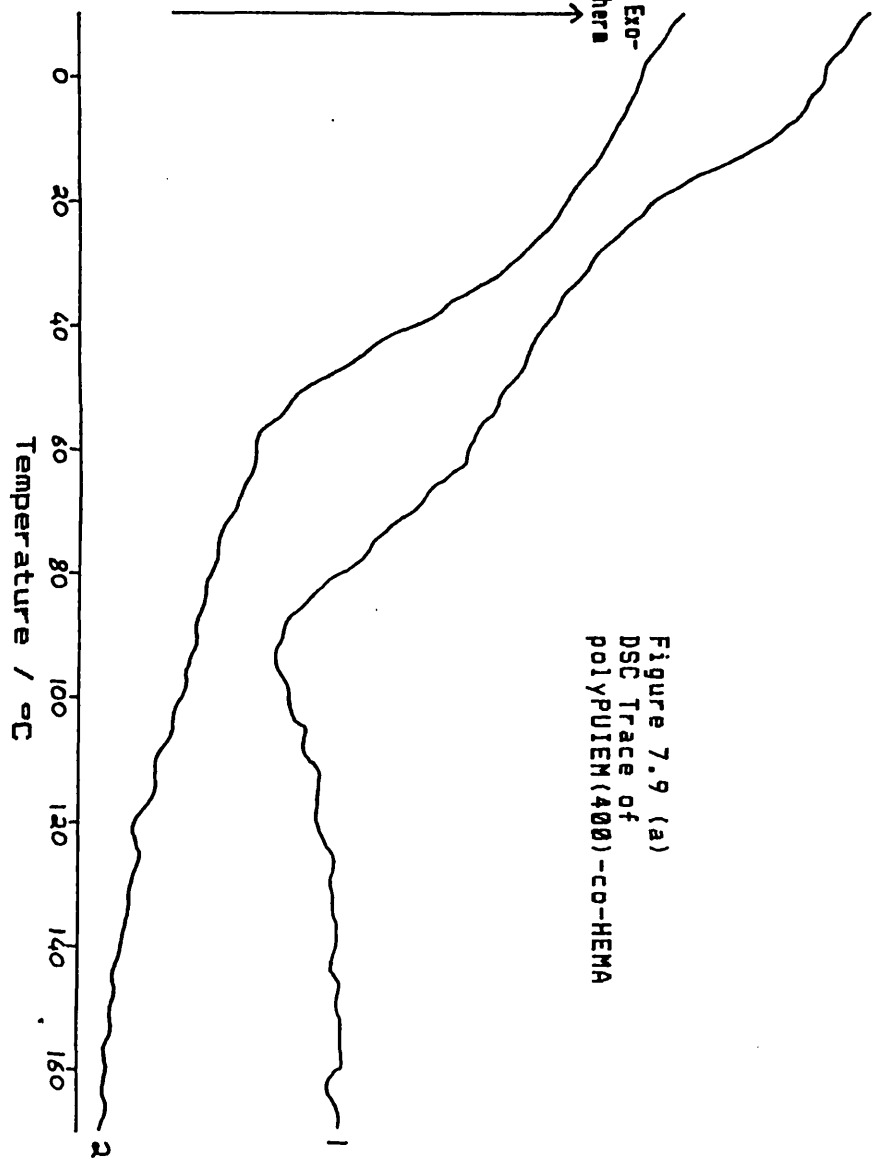


Figure 7.9 (a)
DSC Trace of
polyPUIEM(400)-co-HEMA

Tg for PEG1500 cannot be observed as it tends to crystallise[39]. This reversal of the order of the soft phase Tg is well known[92, 100] and is due to the effect of attaching groups to the end of the polyether molecule. These groups disrupt the soft phase to an extent. As a result, the longer the polyether chain, the purer the soft phase that can be formed and the lower the Tg.

It is noticeable that the soft phase Tg for the cast control films is always lower than that of the corresponding crosslinked homopolymers. This is due to the restriction on molecular mobility introduced by crosslinking the sample. This restriction reduces the degree of phase separation possible, (and hence the purity of the phases), by preventing long distance migration and orientation of polymer chains during phase separation.

All the samples, be they cast films, homopolymers or copolymers, show an increased soft phase Tg upon being rerun. The change is largest for the materials based on PEG400 soft segments and smallest for those with PEG1500 soft segments.

When heated to temperatures near the melting transition of the hard domains (or phase), the molecular motion of the polymer chains cause hard segments to be pulled free of the hard domain and "dissolve" in the soft phase. Upon quenching, these hard segments are frozen into the soft phase, increasing its Tg. It is this increase that is seen on the second run. The effect is most significant for samples with smaller polyether segments as the shorter length of these segments means they are less able to cope with motions by uncoiling, and more hard segments are, therefore, pulled into the soft phase. The sudden reduction in temperature

and molecular motion on quenching prevents the newly dissolved hard segments from reseparating from the soft phase on the timescale of these experiments.

Sample	Run No	Starting temp / °C	Centre °C	Ending temp / °C
PEG400	1	-89	-85	-81
PEG1000	1	-24	-21	-18
PEG1500	1	Melting endotherm only		
PUCN3	1	3	10	17.5
	2	28	33	38
polyPUIEM(400)	1	8	17	26
	2	36	46	56
" "-co-NVP	1	12	27	40
	2	32	45	58
" "-co-HEMA	1	11	18	25
	2	32	43	55
" "-co-ACM	1	14	27	41
	2	30	41	52
PUCN2	1	-22	-14	-6
	2	-12	-6	0
polyPUIEM(1000)	1	-12	-4	+3
	2	-9	-1	+7
" "-co-NVP	1	-16	-8	0
	2	-11	-1	+7
" "-co-HEMA	1	-8	+2	+12
	2	-5	+5	+14
" "-co-ACM	1	-14	-6	+1
	2	-10	-1	+2
PUCN4	1	-31	-24	-16
	2	-26	-19	-2
polyPUIEM(1500)	1	-30	-21	-12
	2	-31	-21	-14
" "-co-NVP	1	-34	-23	-14
	2	-34	-23	-13
" "-co-HEMA	1	-26	-11	+3
	2	-27	-15	-4
" "-co-ACM	1	-25	-16	-8
	2	-23	-15	-6

Table 7.6 Soft phase glass transition of PUIEM(X) Samples.

The PUIEM(1000) and PUIEM(1500) based copolymers show a consistent pattern for the soft phase Tg, which lies in the order NVP < ACM < HEMA in both first and second runs. This means the

purity of the soft phase of the copolymers lies in the order HEMA < ACM < NVP.

The degree of phase mixing is determined by a combination of the size of the side group introduced by the copolymer and its ability to form hydrogen bonds with the polyether. See Figure 7.8. HEMA has a bulky side group, terminated with a hydroxyl, capable of hydrogen bonding with the polyether. It therefore gives the greatest degree of phase mixing. ACM has a small amide side group that readily forms hydrogen bonds to the polyether. It is therefore second in degree of phase mixing. Finally, NVP has a fairly bulky group that has no active protons with which to form any hydrogen bonds to the polyether. Indeed, the use of NVP as a comonomer is reported by Cooper et al to improve the degree of phase separation[92, 93] and the NVP copolymers reported here all have a greater phase purity (lower soft phase Tg) than the analogous homopolymers, confirming the observations in the literature.

The relationship between Youngs modulus and the size of the interfacial region between the phases, as measured by the width of the glass transition, for the PUIEM(1000) and PUIEM(1500) based materials has already been discussed in section 7.4.2. The transition width was found to be related to the size and disorder of the group attached to the comonomer and the disruption caused by it in the hard phase and the interfacial region.

The PUIEM(400) based materials do not give the same pattern as the other polymers. For these samples, the high hard block content is the dominating feature and there was no visible relationship between comonomer properties and either phase purity

or size of interfacial zone.

The initial high soft phase Tg, ≈20°C, and subsequent shift to ≈40°C indicate extensive hard block content and interactions in the soft phase, and a large increase in phase mixing on heating. It is probable that these materials have two continuous phases, one hard and one soft with extensive inter-mixing and that, after heating, they are largely amorphous. The degree of phase mixing and the magnitude of changes that occur completely obscure any minor effects due to the comonomer groups.

The other features visible in the DSC traces do not fit any consistent pattern. Almost all of the samples display high temperature exotherms, which are most probably connected with the rearrangements during changes in phase separation. These exotherms are not normally present in the second runs of the samples, though exotherms are seen in the reruns of PUCN3 and PUCN4. These cast samples may undergo more rearrangements because of the lack of any strong restraints on mobility. Such restraints are present in the cured samples with their chemical crosslinks.

The PUIEM(400) based copolymers also display an endotherm at moderate temperatures (see table 7.7) that resembles a glass transition more than a melting or solvent loss endotherm in shape. This endotherm is not present in the reruns.

Copolymer	Start / °C	Centre or lowest point / °C	End °C
NVP	70	96	114
HEMA	62	95	117
ACM	62	96	106

Table 7.7 High temperature endotherm of PUIEM(400) samples.

It might be due to the glass transition of the disordered hard phase. The rearrangement of the sample to an amorphous single phase material means that only the Tg previously discussed is seen and this second hard phase Tg no longer exists.

The disorder of the hard phase material is probably due to the presence of the crosslink chains, formed from the comonomer, disrupting the hard segment packing and hydrogen bonding network. This phenomenon is only visible in the PIUEM(400) based materials because their high hard block content magnifies the effect. No distinction between the effects of the different comonomers was apparent.

7.4.4 Equilibrium Solvent Uptakes.

Another method of examining the effect of inclusion of a comonomer on sample properties is the measurement of equilibrium solvent uptake. The nature of the crosslink chains, formed from the comonomer, should affect the overall compatibility of the network with different solvents.

The percentage equilibrium uptake is defined as:-

$$\frac{\text{Increase in sample weight}}{\text{Dry sample weight}} \times 100\%$$

All results are the average of values from duplicate experiments.

7.4.4.1 Water Uptakes.

The water uptake behaviour of the PUIEM(1000) and PUIEM(1500) based samples is quite conventional and the uptakes of the PUIEM(1000) materials with time are shown in figure 7.10 to illustrate the approach to equilibrium of these two sets of samples. The equilibrium uptakes are given in table 7.8.

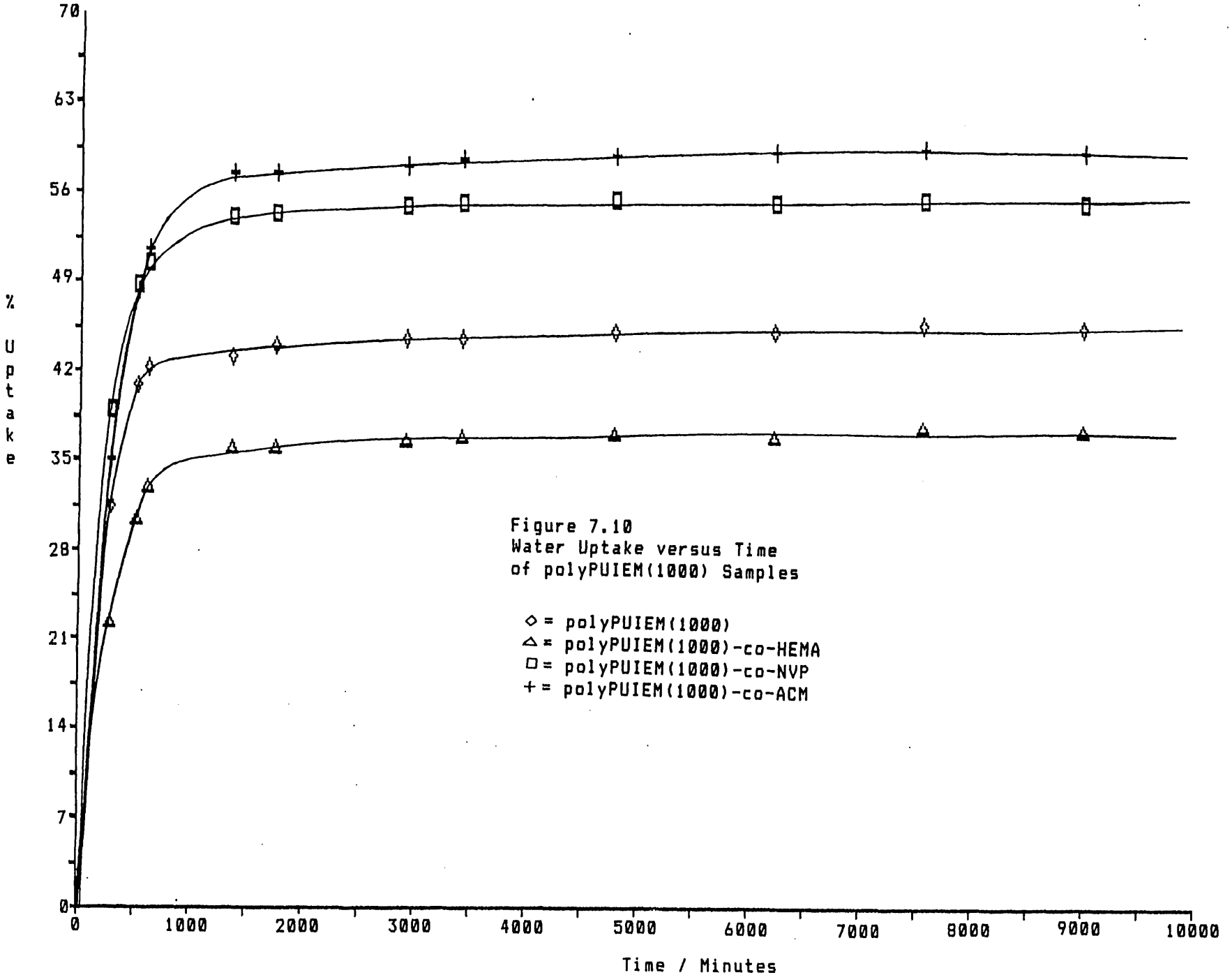


Figure 7.10
Water Uptake versus Time
of polyPUIEM(1000) Samples

The order of uptake was found to be HEMA < Homo < NVP < ACM both for these and the PUIEM(400) based samples. The order of the copolymer samples is a reflection of the increasing hydrophilicity of the 3 comonomers. A faint pattern of increasing water uptake of the NVP copolymers with increasing polyether content, relative to the other copolymers, was visible. It was mentioned in section 7.4.3 that NVP gives the greatest phase separation of the comonomers, and it may be that the increasing purity of the hydrophilic soft phase gives an increase in water uptake as there are fewer hydrophobic hard segments dispersed in it. The effect is more significant for the samples with longer polyether segments as they are capable of achieving greater phase purity.

The homopolymer sample has a lower crosslink density and, therefore, can swell more, which is why it has a higher uptake than the HEMA copolymer, despite the presence of the hydrophilic HEMA crosslink chains in the latter.

The cast films of PUCN2 and PUCN3 both have uptakes higher than those of polyPUIEM(1000) and polyPUIEM(400) respectively, reflecting the absence of any chemical crosslinks in the cast films. This allows greater swelling and higher water uptake before equilibrium is achieved between diffusion of water into the sample, to solvate the hydrophilic, chains and the resistance of the chains to the uncoiling required as the network swells. Suprisingly, PUCN4 has a significantly lower equilibrium uptake than polyPUIEM(1500) and the reason for this is not known.

Sample	Percentage Uptake	
	Equilibrium	Maximum
PUCN3	3.26	4.67
polyPUIEM(400)	-2.70	3.65
" "-co-HEMA	-2.94	7.23
" "-co-NVP	0.63	7.51
" "-co-ACM	8.70	14.60
PUCN2	63.2	-----
polyPUIEM(1000)	46.8	-----
" "-co-HEMA	38.3	-----
" "-co-NVP	56.7	-----
" "-co-ACM	60.6	-----
PUCN4	82.0	-----
polyPUIEM(1500)	98.5	-----
" "-co-HEMA	86.2	-----
" "-co-NVP	107.0	-----
" "-co-ACM	108.8	-----

Table 7.8 Equilibrium water uptakes of PUIEM(X) samples.

In all cases, comparison of the corresponding samples for the 3 series of materials shows that the uptake is dramatically affected by the polyether content. The lower the polyether content, the lower the uptake. This is due to two factors. Firstly, and probably most importantly, the polyether segments are far more hydrophilic than the hard segments of the polyurethane and form an essentially water soluble phase in the material. It is the polyether phase that is responsible for the vast majority of the swelling and uptake of the samples. Dissolution of this phase is prevented by the hard domains, which

are hydrophobic and act as crosslinks. Secondly, the reduction of the polyether content in these materials is accomplished by reducing the polyether chain length. The length of the hydrophilic chain that can uncoil as the sample swells limits the possible degree of swelling and, thus, the shorter chains will give smaller uptakes.

The uptakes of the PUIEM(400) based materials were much more complex than those of the other samples and the uptake/time graphs are shown in figure 7.11.

As mentioned, the order of uptake for the crosslinked samples matches that seen for the other analogous samples. However, all the PUIEM(400) based samples reach a maximum uptake before falling back to an equilibrium value, with 2 samples showing a new loss in weight. The samples were observed to be brittle upon completion of the experiment.

The reasons for this behaviour are probably twofold. Firstly, residual traces of THF may diffuse out of the hard phase and will not be replaced by water. These losses will have a much larger impact on the PUIEM(400) series of materials, than on any of the other materials, because of their low uptake values. The loss of residual THF is responsible for the "negative" uptakes of 2 of the samples. The loss of the residual solvent may cause the increase in brittleness of the samples by removing the plasticisation of the hard phase that may have been caused by the presence of these residual traces of solvent.

A second possible contributing factor is that the incompatibility of the hard phase with water may cause it to contract. Since the hard phase is continuous in these samples,

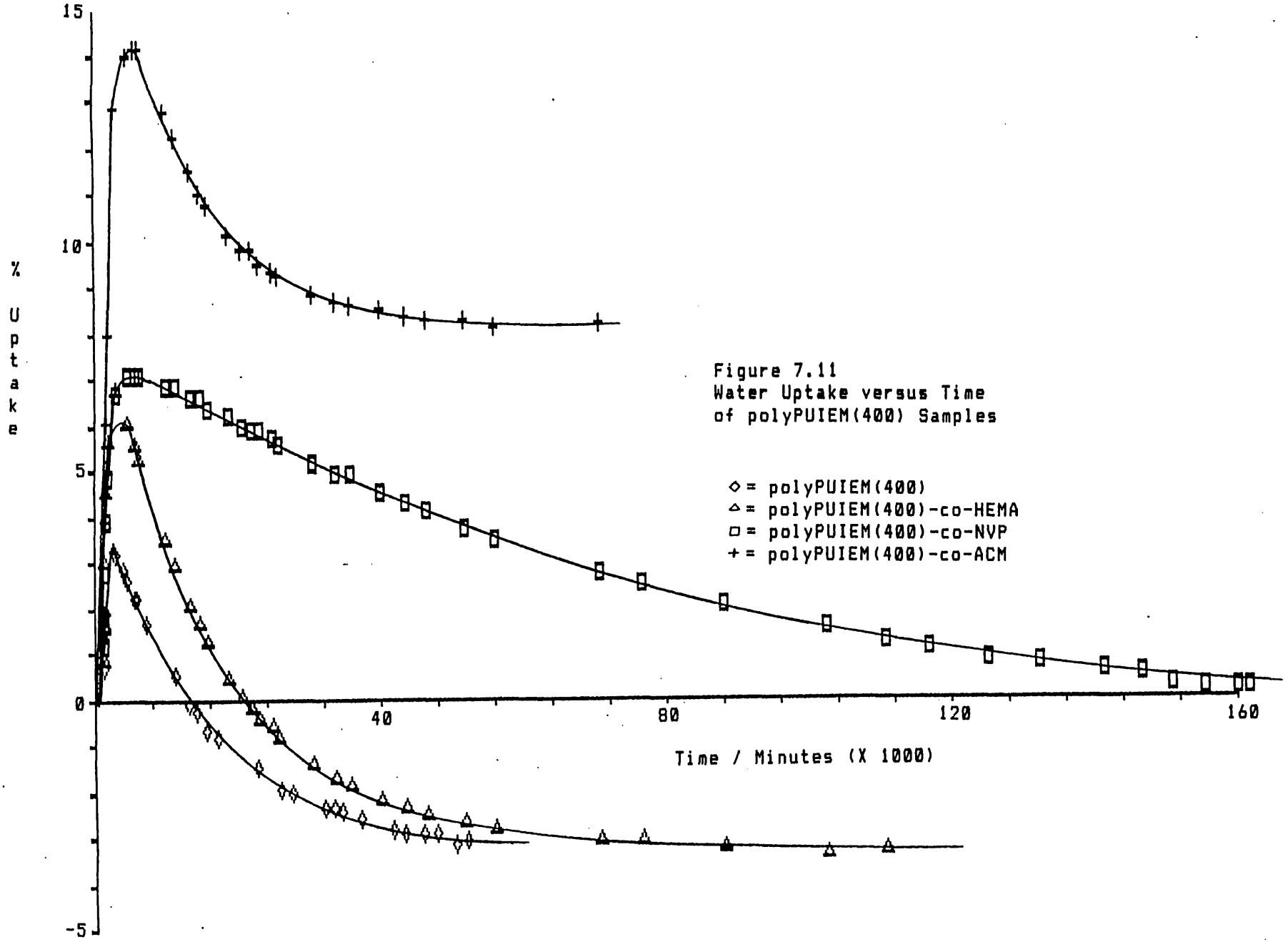


Figure 7.11
Water Uptake versus Time
of polyPUIEM(400) Samples

this contraction would constrict the swollen soft phase, forcing water back out of the sample. Such a contraction would have little effect on the uptakes of the other series of samples as they lack a continuous hard phase.

Both factors are believed to be present, because the latter factor cannot account for the net weight losses of 2 of the samples. The former cannot account for the large difference between maximum and equilibrium uptakes. If this difference was solely due to loss of residual traces of THF, a similar difference would be seen for the ethanol uptakes. However, the differences seen for the ethanol uptakes are much smaller.

7.4.4.2 Ethanol Uptakes.

The results of the ethanol uptakes are given in table 7.9. The ethanol uptake/time graphs for the PUIEM(1000) series of materials are representative of those for the PUEIM(1500) materials and are shown in figure 7.12. The uptake curves of the PUIEM(400) series, with their slight maximum, are shown in figure 7.13.

As for the water uptakes, a general trend of increasing uptake with increasing polyether content is seen, and for similar reasons. The magnitude of the uptake is, however, reduced due to the lower compatibility of the polyether phase with ethanol. The difference between ethanol and water uptake is most marked for the PUIEM(1500) based samples as they have the highest polyether content.

The PUIEM(400) series of materials all display maxima before settling down to an equilibrium value. None reach a net negative

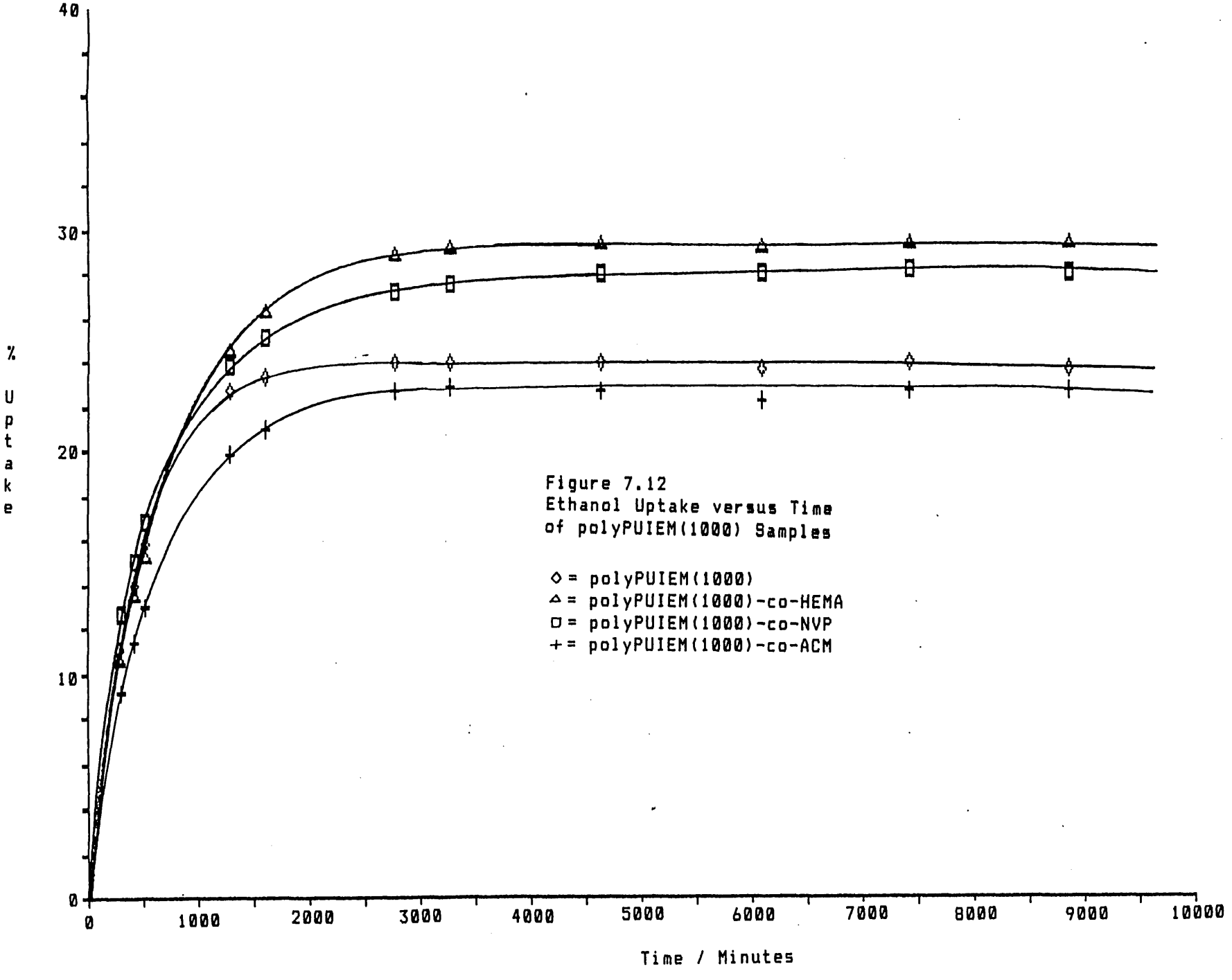


Figure 7.12
Ethanol Uptake versus Time
of polyPUIEM(1000) Samples

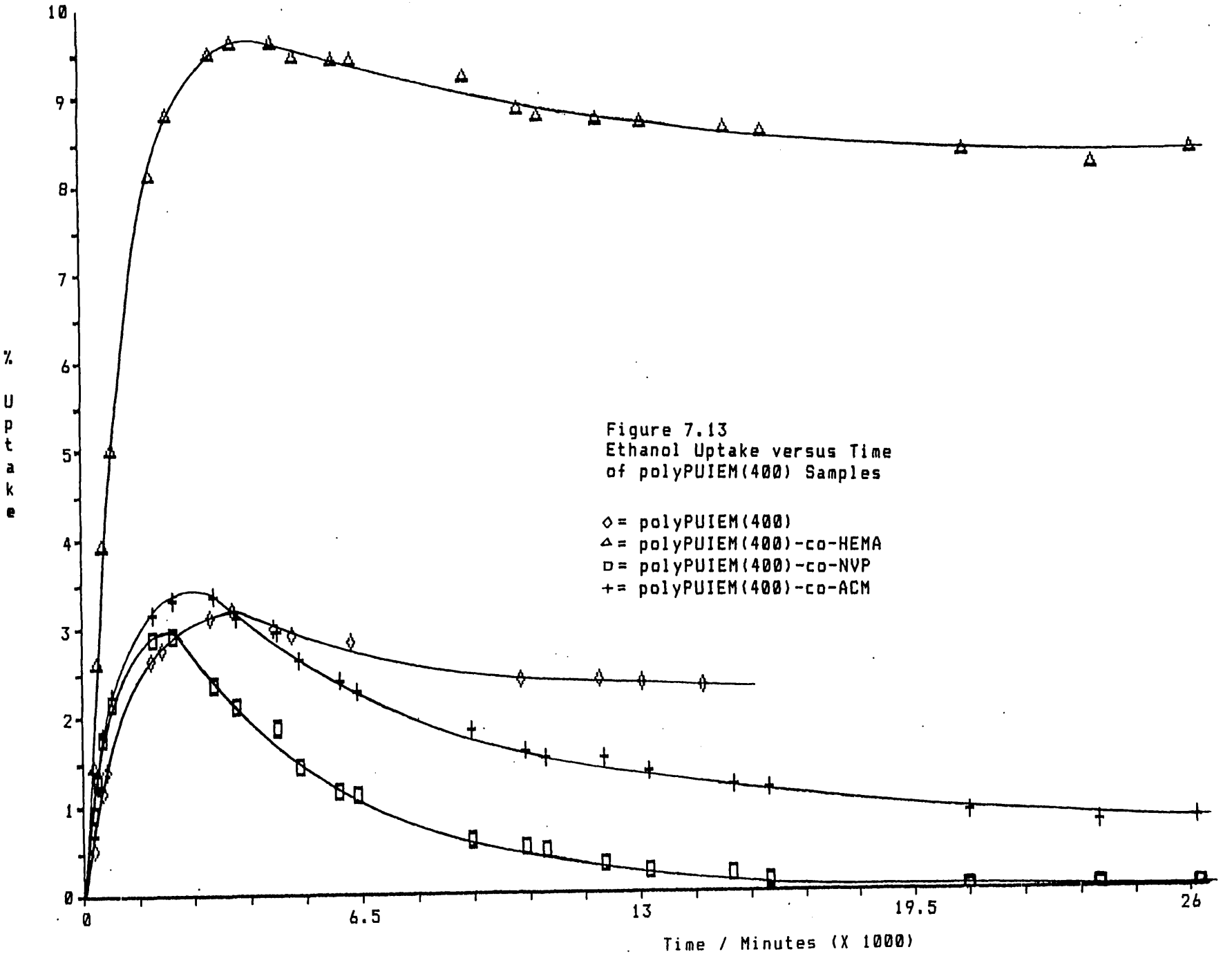


Figure 7.13
Ethanol Uptake versus Time
of polyPUIEM(400) Samples

value. The size of the difference between maximum and equilibrium uptakes are smaller than those seen for water uptake and it would not be unreasonable to account for the fall purely from the loss of residual traces of THF.

Sample	Percentage Uptake	
	Equilibrium	Maximum
PUCN3	4.66	7.42
polyPUIEM(400)	2.60	3.44
" "-co-HEMA	8.50	9.83
" "-co-NVP	0.11	3.12
" "-co-ACM	1.01	3.59
PUCN2	22.3	-----
polyPUIEM(1000)	24.7	-----
" "-co-HEMA	29.6	-----
" "-co-NVP	28.8	-----
" "-co-ACM	23.2	-----
PUCN4	(30.2) See Note	-----
polyPUIEM(1500)	51.5	-----
" "-co-HEMA	46.1	-----
" "-co-NVP	65.4	-----
" "-co-ACM	31.4	-----

Note:- Samples of PUCN4 degraded and the result is unreliable.

Table 7.9 Equilibrium ethanol uptakes of PUIEM(X) samples.

Unlike the water uptakes, only one clear effect is seen for comonomer type, namely the depression of ethanol uptake by the polyacrylamide crosslink chains in the ACM copolymer. This is to be expected as polyacrylamide is highly incompatible with ethanol. Indeed, ethanol is often used to precipitate pure

polyacrylamides from solution.

Another visible, but less marked, trend is that the ethanol compatibility of the NVP copolymers seems to increase more markedly with increasing polyether content reative to the other copolymers. The reason for this may be that NVP gives greater phase separation between hard and soft phases (see section 7.4.3). The soft phase compatibility with ethanol will be increased as its purity improves because it will contain fewer ethanol incompatible hard segments. The effect increases with polyether content because the longer polyether segments are capable of achieving greater purity. Hence, NVP has a greater effect on the higher polyether content materials. A similar, but weaker, trend was seen for the water uptake measurements (see section 7.4.4.1). This phenomenon is a reflection of the changing polyether segment length rather than gross polyether content and is more visible in the ethanol uptakes than the water uptakes because the lower overall ethanol compatibility is more affected by phase purity than the water compatibility.

7.5 Conclusions.

Isocyanatoethyl methacrylate has been shown to be a convenient end capping reagent, suitable for use with polyurethanes in the synthesis of radically reactive macromonomers. The resultant macromonomers have been shown to be readily crosslinkable under the mild conditions necessary for applications involving enzymes.

Preparation of crosslinked samples, using photochemical initiation, was successful and a series of samples with varying polyether content and different comonomers were prepared.

Variation of polyether content was shown to be a method for the coarse control of sample morphology and properties.

The use of comonomers in the curing stage was found to provide a method of fine control of the general properties of the samples and was proven to be a useful route for the modification of the solvent selectivity of the material. The variation of the quantity of comonomer used was not investigated, but would provide another mechanism for fine tuning the final properties of the materials.

Although not specifically investigated, variation of crosslink density was indicated to be a further tool for adjustment of the properties of the final samples.

The overall system is highly adaptable and suitable for use in immobilisation procedures with any enzyme tolerant of DMF or THF. Brief test tube experiments suggested that DMF/water solvent mixtures may be used and could increase the range of enzymes compatible with an immobilisation system based on these macromonomers.

8 New Polyurethane Ionomers.

8.1 Introduction.

The literature on polyurethane ionomers was reviewed in chapter 2. As previously discussed, one of the methods of forming an ionomer is to include an ionic monomer in the chain forming reaction.

One class of organic salts of possible use in ionomer synthesis are the alkyl thiosulphates, formerly known as Bunte salts. Their properties, reactions and synthesis was reviewed by Milligan and Swan[105].

The preparation of a diol, for use in polyurethane synthesis, which contains a thiosulphate group was therefore investigated.

8.2 Synthesis and Characterisation of Potassium-S-1,2-dihydroxy propyl thiosulphate.

8.2.1 Synthesis.

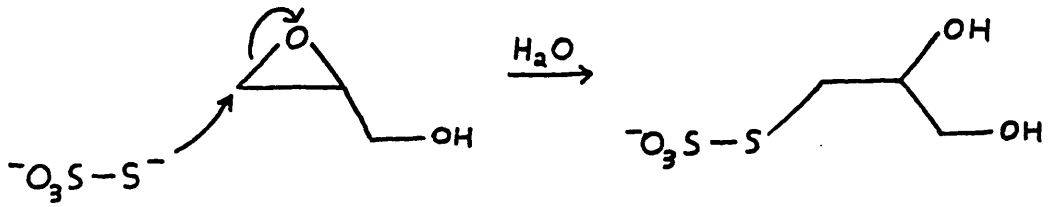
Two potential routes for the synthesis of potassium-S-1,2-dihydroxy propyl thiosulphate (TDOL) were devised, both based on the review of alkyl thiosulphate chemistry[105].

Both methods were based on the S_N2 attack of the nucleophilic thiosulphate anion on a substrate. The mechanism of such an attack is well known[51] and occurs via attack of the charged sulphur atom on the substrate. Reaction occurs wholly with the sulphur atom as its orbitals are more diffuse than those of the oxygen atoms, giving better orbital overlap and having a lower degree of solvation. The latter means that much less solvation energy is lost in the transition state and the activation energy is therefore lower.

The first substrate investigated was 3-chloro-1,2-propane diol, nucleophilic displacement of chloride by thiosulphate yielding the desired product. The byproduct of the reaction is potassium chloride.

The method is described in section 4.5.1.1 and the reaction encouraged by use of a 1.8:1 excess of potassium thiosulphate relative to substrate. Final yields of 80-90% purified product were obtained.

A second possible route to TDOL was attack on the epoxide ring of glycidol by thiosulphate anions. See equation 8.1. The method is given in section 4.5.1.2.



Attack of potassium thiosulphate on glycidiol....Equation 8.1

From the observations during the procedure, namely the strong initial exotherm and the isolation of a white oil, it seems probable that TDOL was successfully formed. However, the reaction byproduct is potassium hydroxide, which is more soluble than potassium chloride in DMF and hence was only poorly separated from the product. Crystallisation and isolation of pure TDOL from this route was not therefore achieved. It is likely that acidification to neutral pH with dilute hydrochloric acid prior to extraction with DMF will render this route viable.

8.2.2 Characterisation.

The characterisation of TDOL was performed in close cooperation with Mr T.Y.T.Chui[30].

8.2.2.1 Infrared Spectroscopy.

A previous work on infrared spectroscopy of thiosulphates [106] allowed assignment of the following characteristic bands.

Two S-O stretching vibrations were identified at 1210 cm^{-1} and 1030cm^{-1}, the absorptions being strong-broad and strong-sharp bands respectively. S-O deformations were seen as a strong broad band centred on 650 cm^{-1} and a strong sharp absorption at 535 cm^{-1}. A weak but sharp peak at 420 cm^{-1} was identified as being due to the S-S stretching vibration.

8.2.2.2 NMR Spectroscopy.

The NMR spectrum of TDOL revealed the material to be of high purity, the major peaks all being identified as due to TDOL. The assignments were as follows. See also figure 8.1

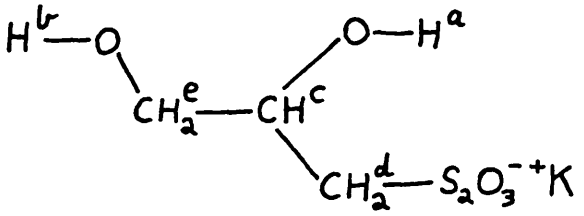


Figure 8.1 Protons of TDOL identified by NMR spectroscopy.

The secondary hydroxyl proton, H_a, gave a doublet centred at 4.6 ppm and the primary hydroxyl proton, H_b, a triplet at 4.35 ppm. The methine proton, H_c, was seen as a multiplet centred on 3.65 ppm. In theory, this proton should give a signal split into 18 peaks by coupling with protons H_a, H_d and H_e, but in practice, the full pattern was not resolved.

The two methylene protons neighbouring the thiosulphate, H_d,

were observed as a doublet at 3.32 ppm and the methylene protons next to the primary hydroxyl group, H_e, seen as a distinct double doublet centred on 2.90 ppm.

8.2.2.3 Elemental Analysis.

Elemental analysis (performed by Imperial College microanalytical laboratory) gave values of 15.8% carbon, 3.02% hydrogen and 27.6% sulphur. The calculated values were in good agreement, predicting 15.9% carbon, 3.10% hydrogen and 28.3% sulphur. The differences between calculated and found results were all within the normal error range of the analytical service.

8.2.2.4 Solubility.

TDOL was insoluble in most common organic solvents. It was moderately soluble in hot DMSO and soluble in DMF. It could be recrystallised from boiling ethanol but appeared insoluble in cold ethanol. It was highly water soluble.

TDOL also showed a sparing solubility in molten polyethylene glycol. This material is compatible with the organic part of TDOL and can also complex the potassium counter ion[107], thus dissolving small to moderate quantities of TDOL.

8.2.2.5 Conclusions.

In conclusion, a procedure for synthesis and purification of TDOL has been successfully developed and the purity of the final material confirmed by spectroscopic and elemental analysis. Its observed properties were exactly what would be expected of a small highly polar organic salt molecule.

8.3 Synthesis and Characterisation of Polyurethane Ionomers.

8.3.1 Synthesis.

A series of ionomers were synthesised using a 1:1 ratio of isocyanate to alcohol and a total monomer ratio of 1:2.15:3.15 for polyether:small diol:MDI. Full experimental details are given in chapter 4.5.2. The 5 polymers were designated PE-X-Th/BD where X was the molar percent of ionic diol in the mixture of small diols. The other small diol used was 1,4-butane diol. Quantities of 0, 25, 50, 75 and 100% ionic diol were used. One further polymer, designated MDI/TDOL was prepared from a 1:1 molar ratio of MDI and TDOL.

The ionomer syntheses differed from standard syntheses in two respects.

Firstly, only DMSO was used as a solvent due to the insolubility of TDOL in IBMK. The presence of IBMK led to unreliable preparations caused by premature precipitation of polymer and gellation.

Secondly, high ionic content polymers (50% TDOL and above) were water soluble and hence volatile organic solvents were used as the precipitating medium. Reprecipitation was found to be necessary in order to reduce the quantities of DMSO retained in the precipitated polymer.

8.3.2 Characterisation.

8.3.2.1 Infrared Spectroscopy.

The infrared spectra of this series of polymers are, for the most part, similar to those seen for non ionic polyurethanes, a detailed description of which has already been given in section 5.2.2. The spectrum of PE-0-Th/BD is typical of a non ionomer.

Comparison of the spectra of the ionomers and non ionomer (figures 8.2 to 8.6) revealed the following differences.

A weak shoulder at 530 cm^{-1} appears on a band at 510 cm^{-1} for PE-100-Th/BD and PE-75-Th/BD. The shoulder is almost certainly due to an S-O deformation of the ionic group. This deformation appears at 535 cm^{-1} in the ionic diol. The main band at 510 cm^{-1} is a feature of all polyurethanes and is unconnected with the ionic group.

All the ionic polymers show a weak band at 665 cm^{-1}, not present in the non ionomer, which has been assigned as an S-O deformation. A similar absorption is seen at 650 cm^{-1} for pure TDOL. The band is most clearly visible for PE-75-Th/Bd and PE-100-Th/BD.

A strong sharp absorption at 1025 cm^{-1}, increasing in magnitude with ionic content, was due to an S-O stretching frequency and obscured a weak band present at this frequency in the non ionomer. An S-O stretch was seen at 1030 cm^{-1} in the spectrum of the ionic diol.

The carbonyl region of the spectrum was also subject to some changes.

The ratio of the hydrogen bonded to free carbonyl peaks (1665 cm^{-1} and 1730 cm^{-1} respectively) changes with ionic content. PE-100-Th/BD and PE-75-Th/BD both show near equal intensities for free and hydrogen bound carbonyl absorptions. The lower ionic polymers show a clear excess of free carbonyls, with a trend towards larger excess for smaller ionic content.

The appearance of new bands in the spectrum of the ionomers

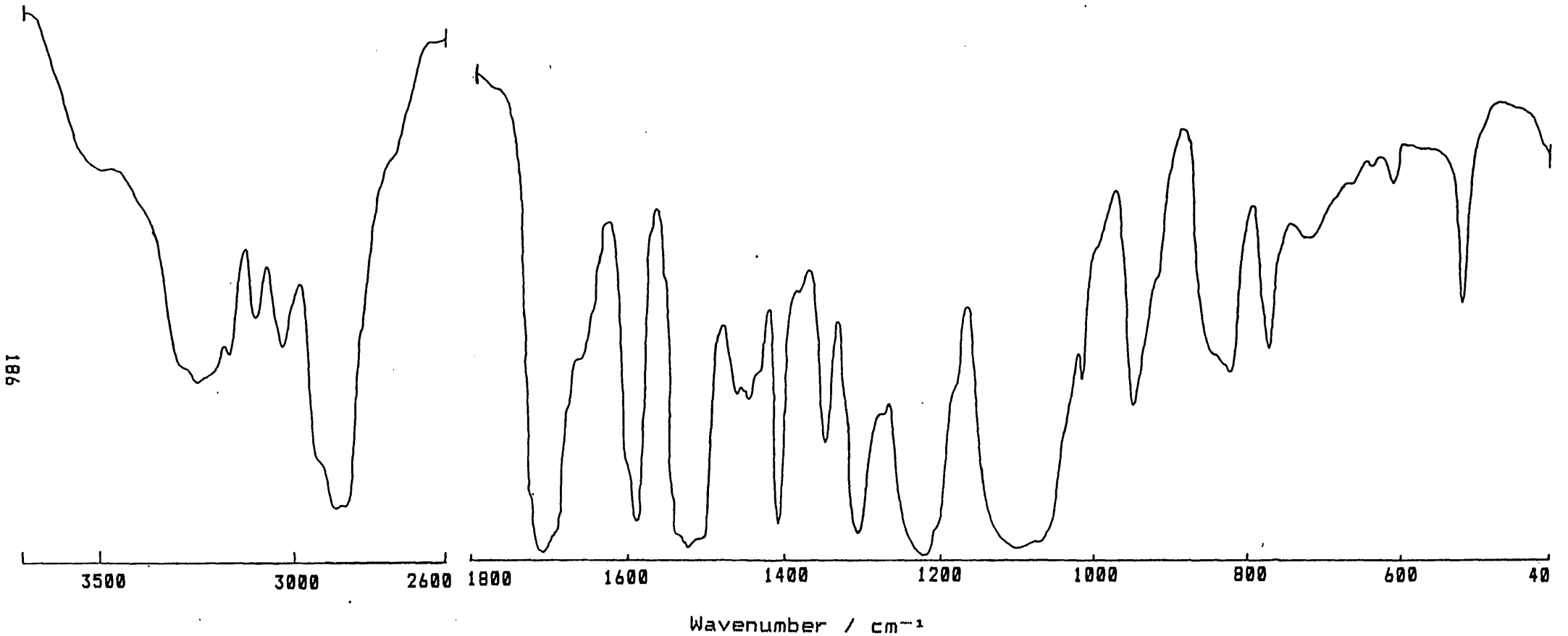


Figure 8.2
Infrared Spectrum of PE-0-Th/BD

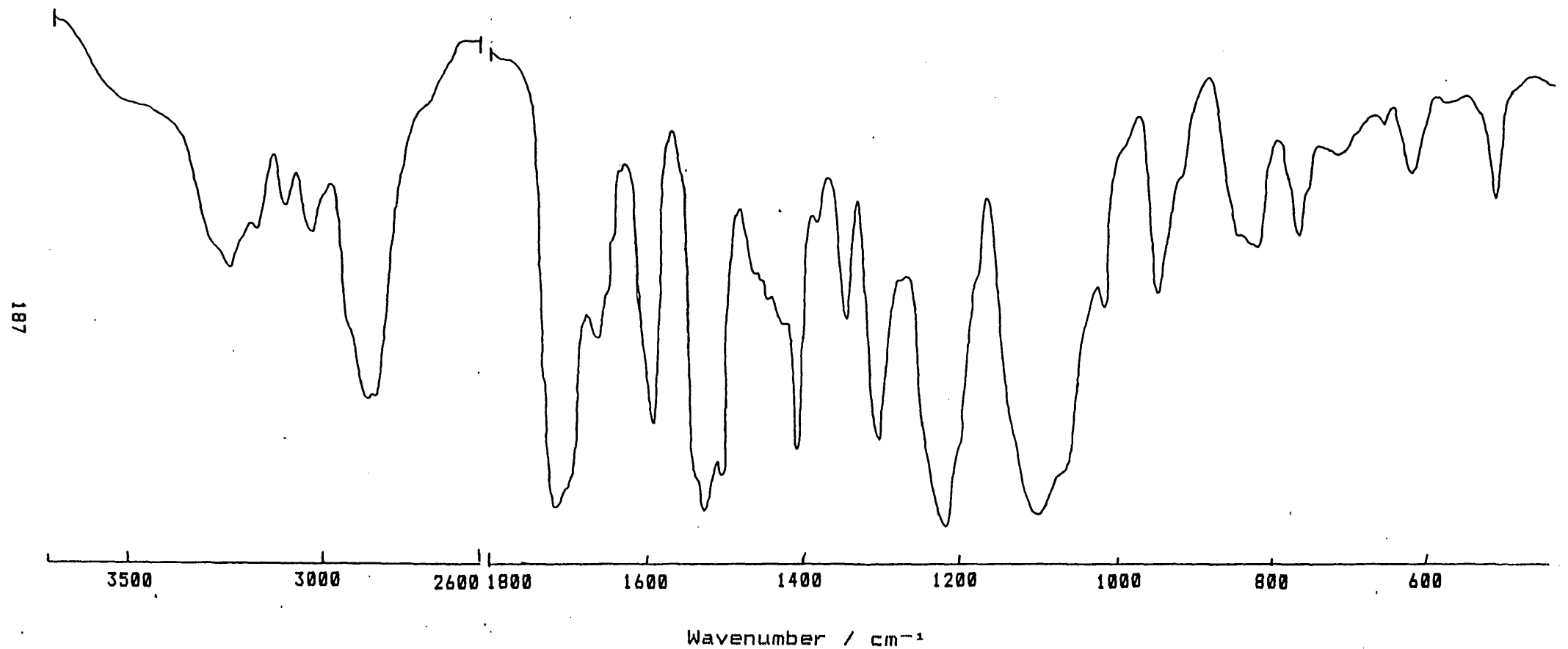


Figure 8.3
Infrared Spectrum of PE-25-Th/BD

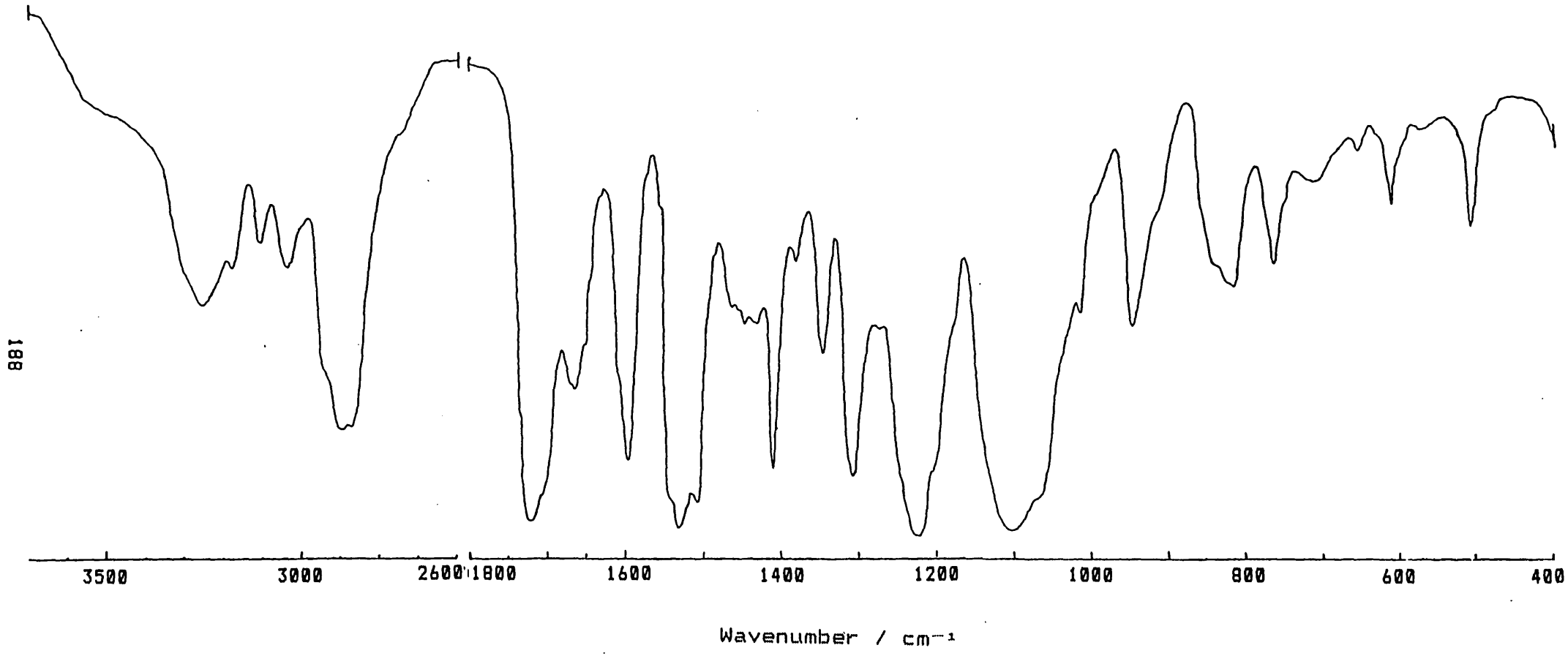


Figure 8.4
Infrared Spectrum of PE-50-Th/BD

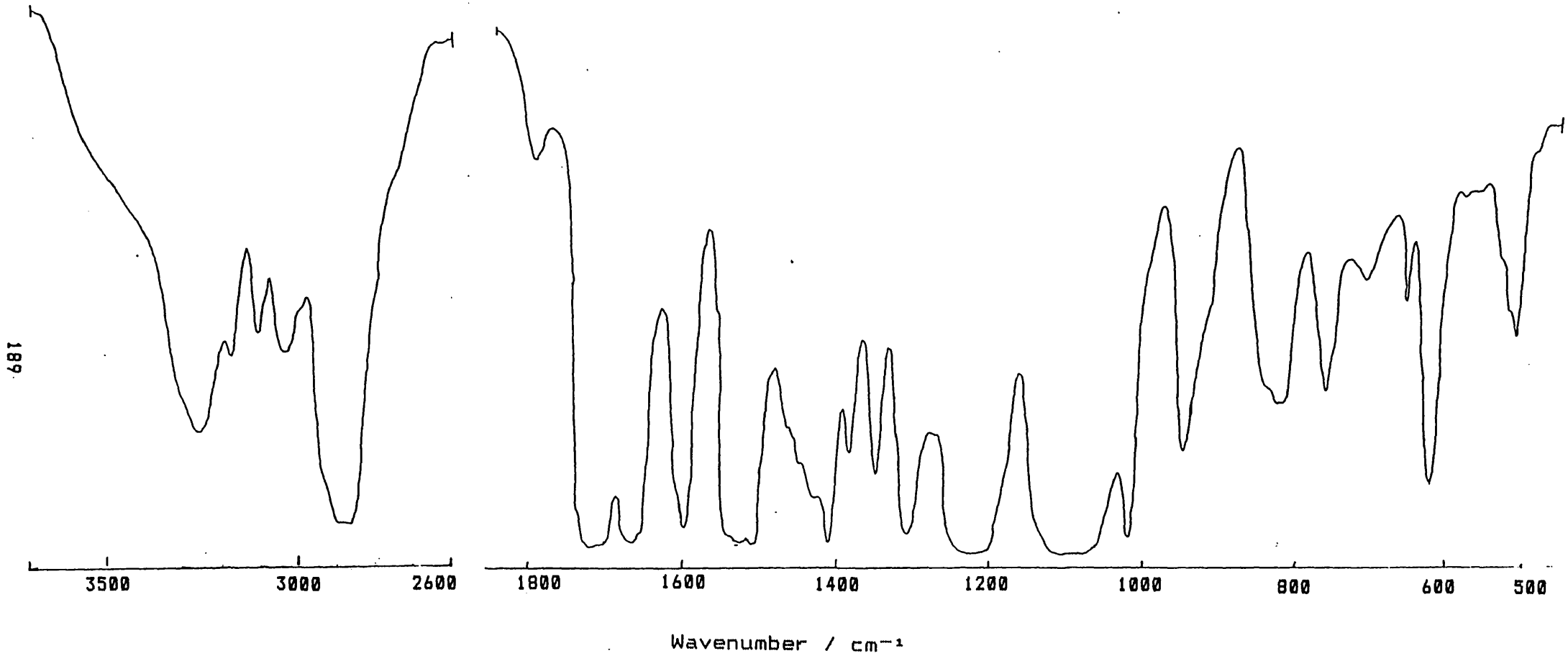


Figure 8.5
Infrared Spectrum of PE-75-Th/BD

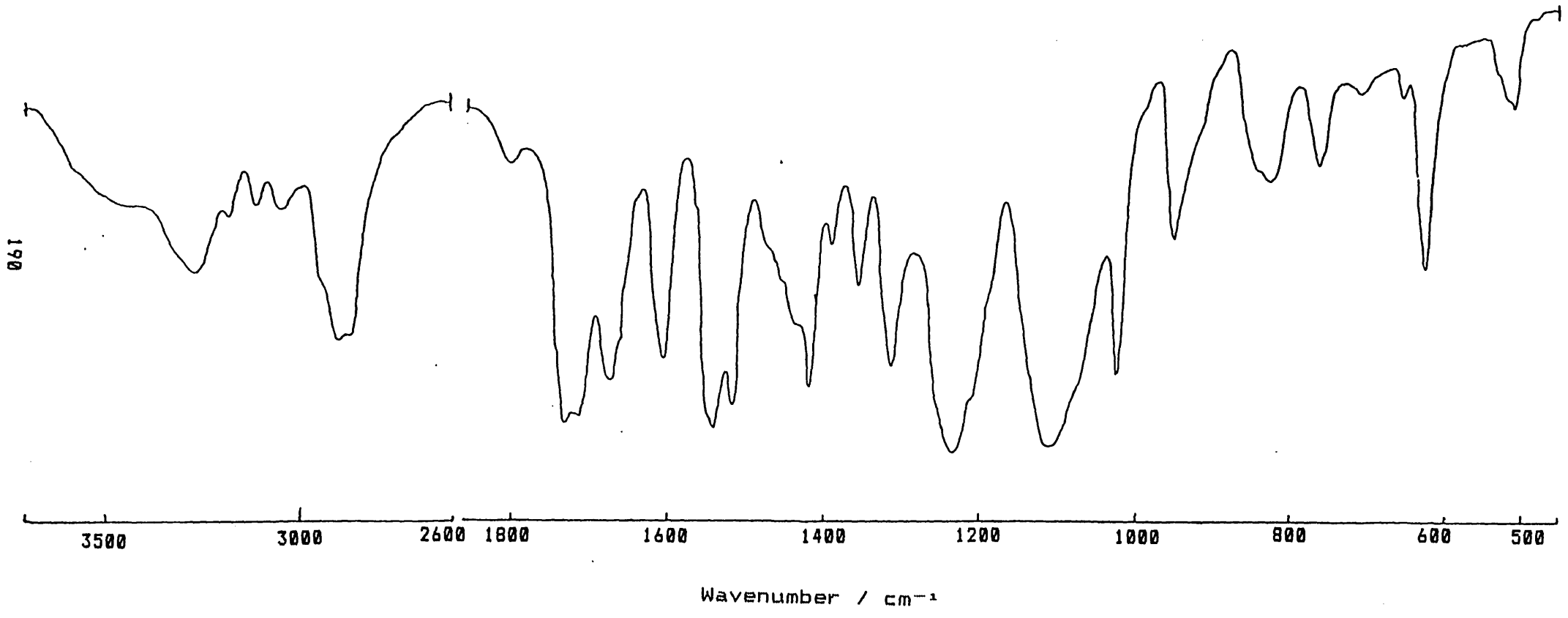


Figure 8.6
Infrared Spectrum of PE-100-Th/BD

is to be expected, though not all the bands seen for TDOL were visible in the polymers. An S-O stretch at 1210 cm^{-1} in TDOL was masked by the urethane C-O single bond stretch in the polymers. The S-S stretch at 420 cm^{-1} was not visible, possibly being too dilute and hence too weak to be seen so close to the cutoff of the KBr plates used to mount the samples.

The change in the ratio of free to hydrogen bound carbonyl groups probably reflects a considerable increase in domain separation in the material.

For PE-0-Th/BD, phase mixing is extensive, and a high degree of hydrogen bonding between N-H groups and the ether groups of the PEG segments is present along with some bonding to the more polar but much less numerous carbonyl groups. Hence, only a weak bonded carbonyl peak is seen. As the ionic content increases, the increasing polarity of the hard segments results in improving phase separation and hydrogen bonding with the carbonyls increases as the local excess of ether groups is reduced. The effect reaches its maximum for PE-100-Th/BD. However, there are still a large number of free carbonyls as many N-H protons bind to the highly polar ionic groups that are now present in the hard segments.

It should be noted that, in all samples, the N-H protons, are all involved in hydrogen bonding and no N-H stretching frequency for free N-H groups is seen.

One further spectral change was observed. The S-O deformation frequency, at 650 cm^{-1} in TDOL, was shifted to 665 cm^{-1} in the ionomers. This indicated a minor increase in the energy required for this deformation. However, for a similar

ionomer based on polypropylene glycol[30], the frequency was reduced to 640 cm^{-1}. The likely explanation for this is the involvement of the potassium counter ion and polyether segments in a degree of complexation. Such complexation is known for pure polyethylene glycols[107] and cyclic polyethers such as 18-crown-6.

The formation of such a complex would increase the distance between the thiosulphate and the counter ion. This in turn would increase the equilibrium O-S-O bond angle as repulsion between the oxygen atoms would become more dominant as the electrostatic attraction between the oxygen atoms and the potassium atom is reduced. Hence, the energy required for the deformation of the thiosulphate would increase slightly.

The atactic nature of polypropylene glycol, the steric effects of its methyl groups and its low polarity would prevent complex formation in a PPG based polymer and might force a slightly tighter ion pair, marginally reducing the deformation energy.

These observations are in line with the results reported for PEG based ionomers by Cooper et al[39], who reported an amorphous non ionomer and dramatic increases in both phase separation and the size of the interfacial region between the phases. The latter effect, observed using thermal mechanical analysis, may have been aided by complexation of the potassium counter ion by the PEG segments, though this was not suggested in the publication[39].

8.3.2.2 NMR Spectroscopy.

The general NMR spectra of polyether-urethanes has been discussed in chapter 5.2.4. The effects of inclusion of the ionic

diol on the spectra are discussed here. The spectra are shown in figures 8.7 to 8.12.

8.3.2.2.1 The Urethane Region, 7.5 to 10 ppm.

A progressive change is seen in the urethane signal with increasing ionic content. All the spectra show a single peak at 9.65 ppm, but a single peak at 9.50 ppm disappears as the BD content falls. A new minor peak appears at approximately 9.56 ppm and the total urethane signal increases in complexity with ionic content up to polymer PE-75-Th/BD, which has 1 major and 2 minor peaks at 9.65 ppm, 9.57 ppm and 9.50ppm.

The polymers PE-100-Th/BD and MDI/TDOL both show a major peak and a minor peak at 9.65 and 9.60 ppm, both peaks having poorly resolved side peaks. All the polyether containing ionomers show a new unidentified peak at 7.95 ppm. Several very weak unidentified resonances were present in the region 7.5 to 8.5 ppm for MDI/TDOL.

The urea signal varied only in intensity from sample to sample and was always at 8.5 ppm.

The steady loss of the peak at 9.5 ppm, the major peak in the non-ionomer, reflects the replacement of the butanediol based hard segments by the TDOL based ionic hard segments. A new minor peak at 9.6 ppm appears with increasing ionic content. The shorter aliphatic chain length and bulky ionic side group of the TDOL residue probably gives rise to this spectral change by changing the possible chain conformations and altering the local environment of the urethane protons. This is supported by the relatively small changes in the spectra of PE-100-Th/BD and MDI/TDOL, which further indicates that it is short range

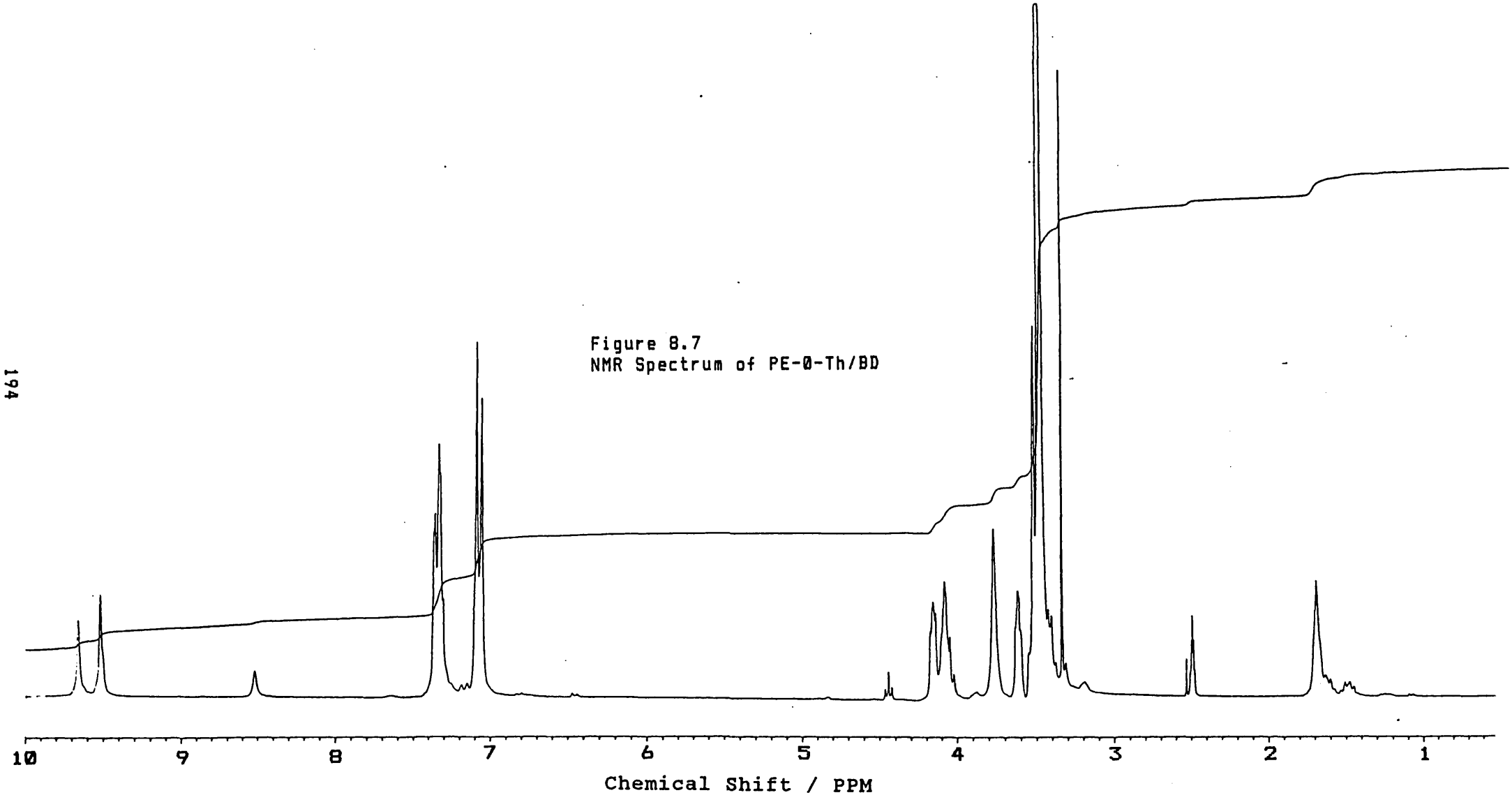


Figure 8.7
NMR Spectrum of PE-Ø-Th/BD

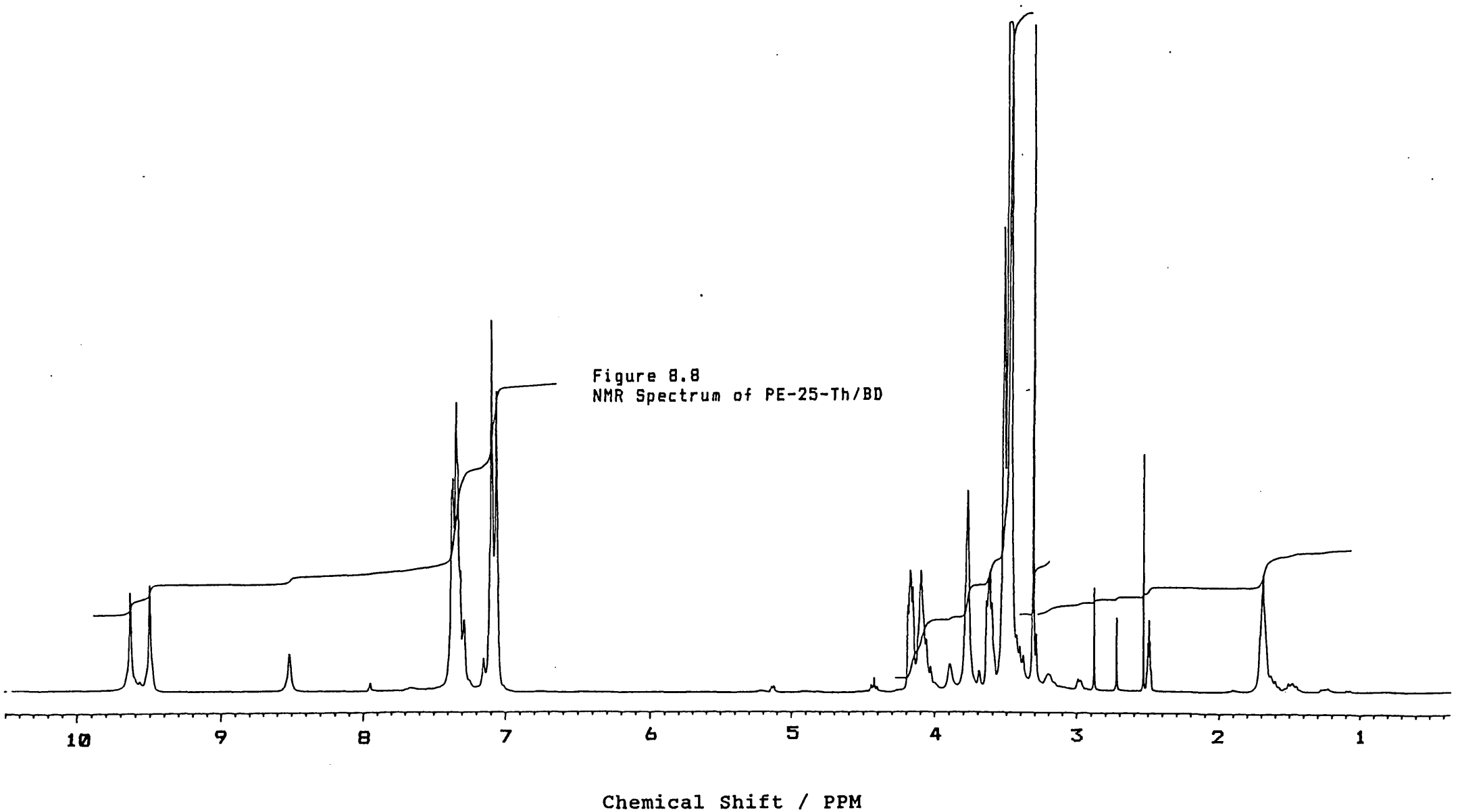
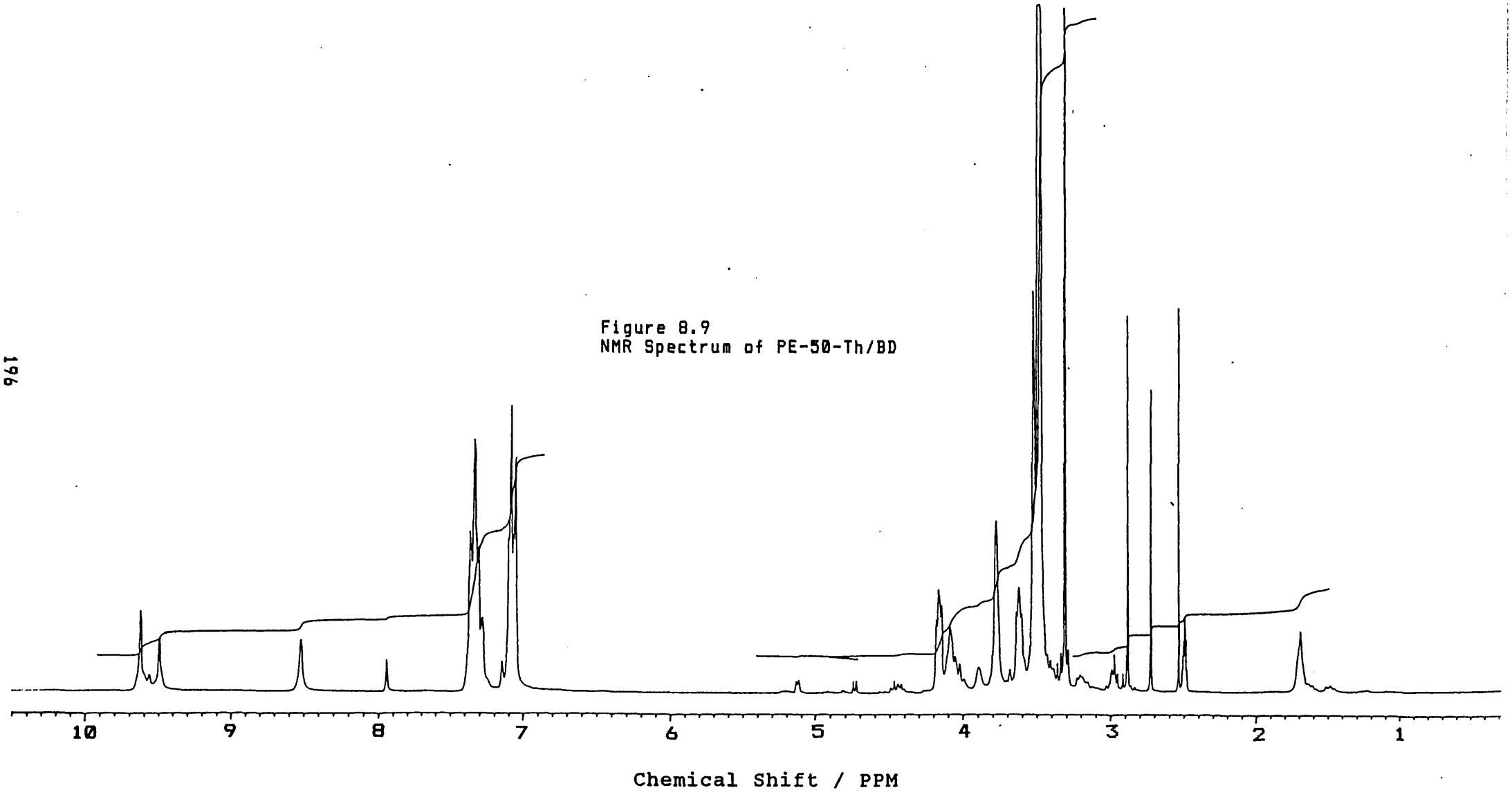


Figure 8.8
NMR Spectrum of PE-25-Th/BD

Figure 8.9
NMR Spectrum of PE-50-Th/BD



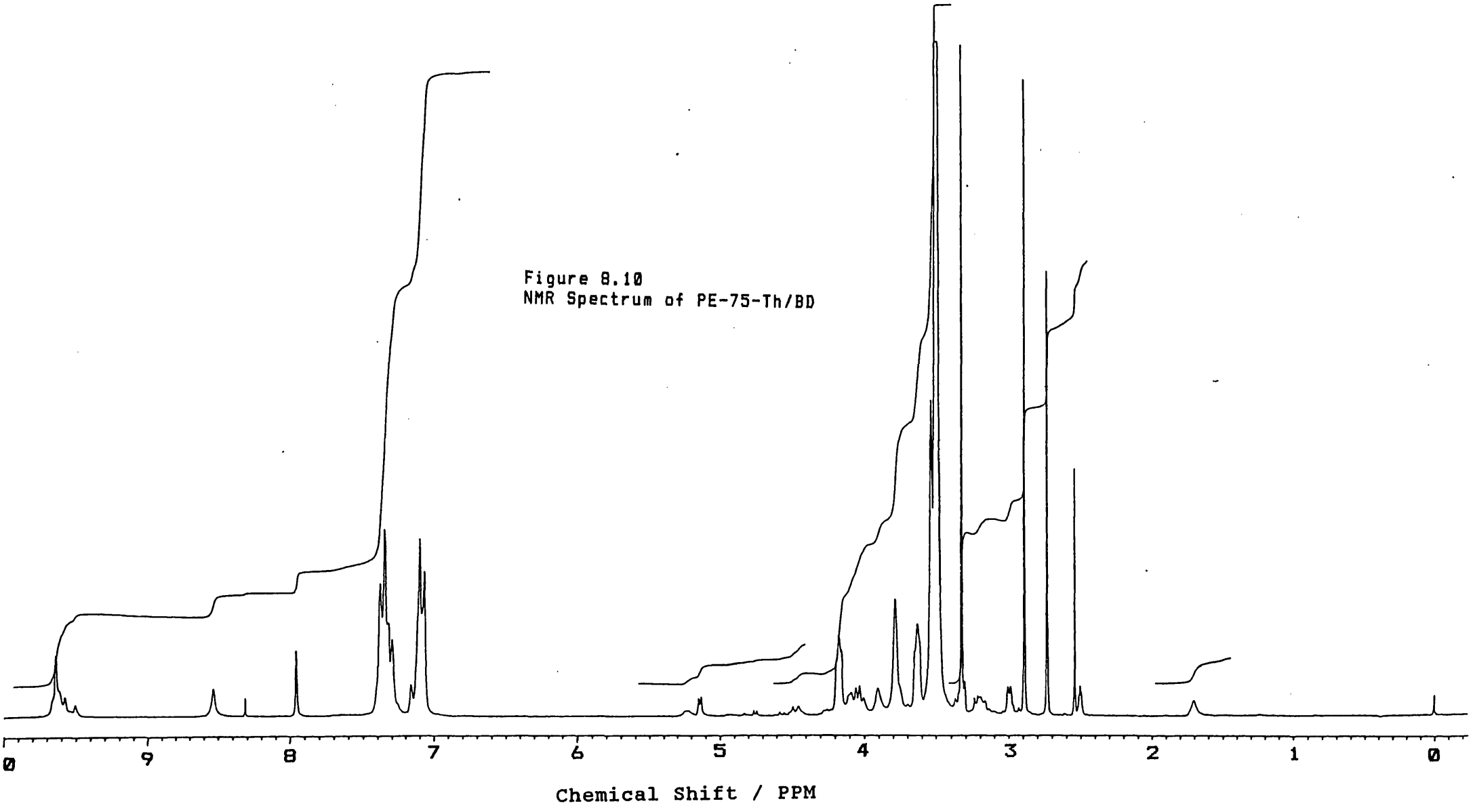


Figure 8.10
NMR Spectrum of PE-75-Th/BD

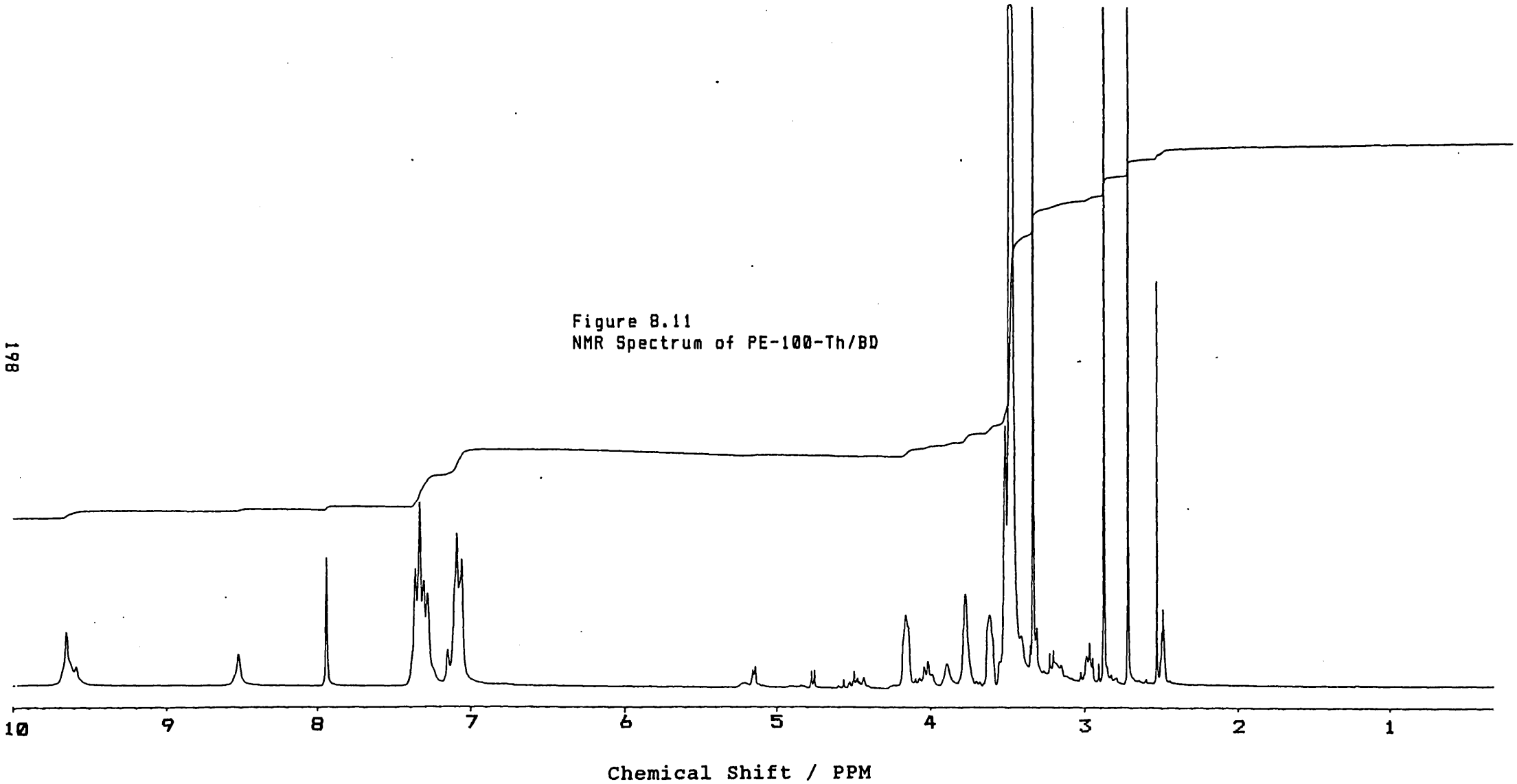


Figure 8.11
NMR Spectrum of PE-100-Th/BD

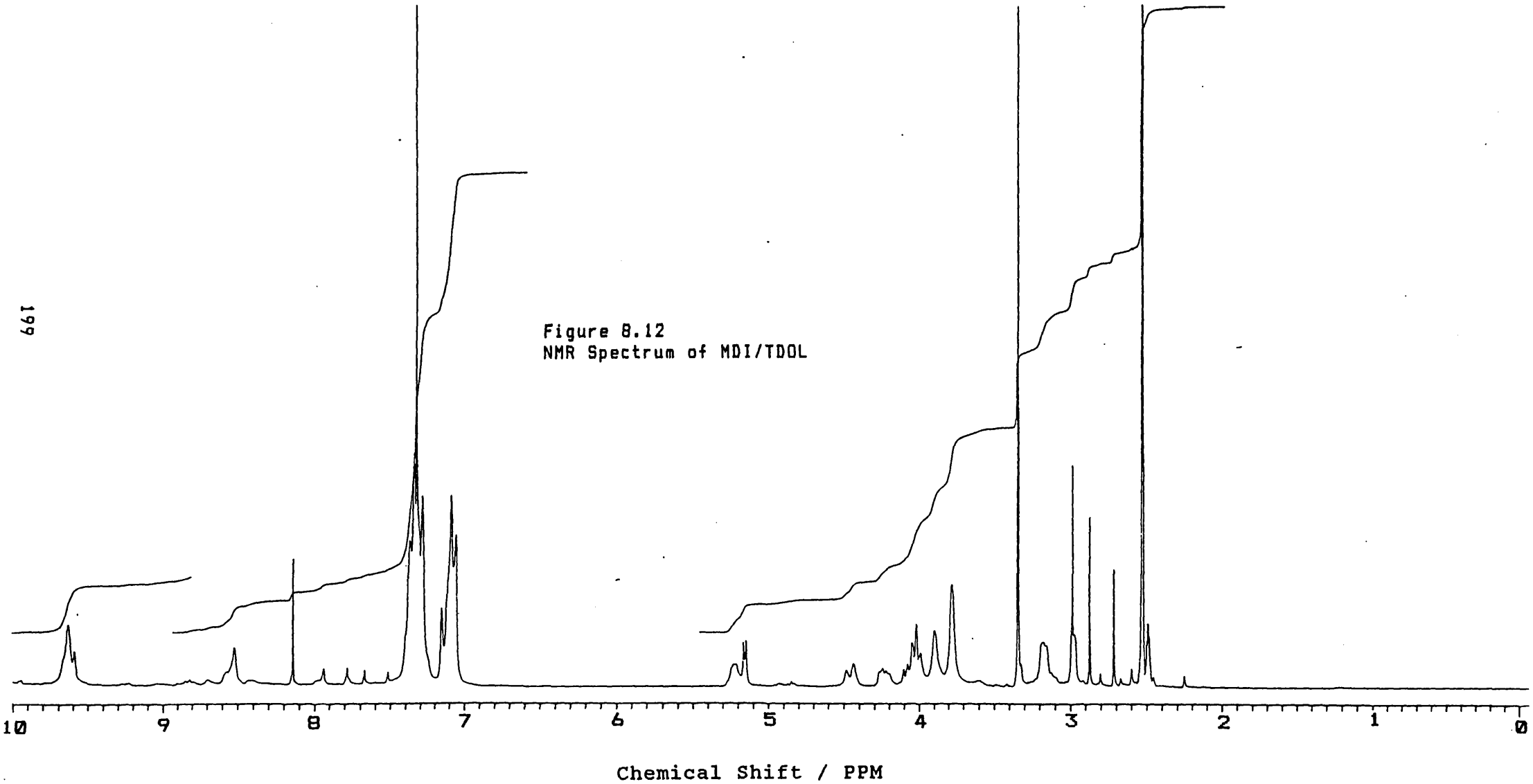


Figure 8.12
NMR Spectrum of MDI/TDOL

interactions that are dominant. The loss of the lengthy polyether segments has an impact on only a minority of urethane protons.

The magnitude of the urea:urethane ratio increased somewhat with increasing ionic content, suggesting some traces of water were being introduced with the ionic diol solution during polymer synthesis. This water may have been present in the diol, but was probably absorbed by the DMSO used to dissolve the TDOL. Longer dissolution times and heating were required for higher quantities of ionic diol.

8.3.2.2.2 The Aromatic Region, 7.0 to 7.5 ppm.

A standard 1,4 substituted ring pattern with peaks at 7.01, 7.1, 7.33 and 7.38 ppm is present for all the polymers. However, the presence of increasing quantities of ionic diol residues gives rise to a new pattern as well. This grows steadily in strength as ionic content rises and introduces new peaks at 7.15, 7.30 and 7.40 ppm. The latter two peaks tend to overlap with the original pattern, distorting its symmetry. It is noticeable that the peaks at 7.30 and 7.40 ppm gain in strength much more rapidly than the peak at 7.15 ppm.

The likely cause of this additional set of peaks is the very close proximity of the ionic group to one side of the benzene ring (figure 8.13).

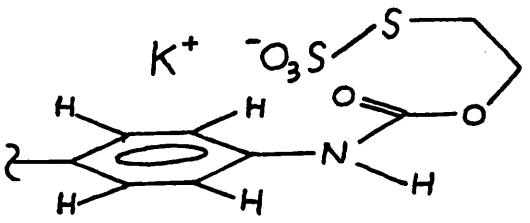


Figure 8.13 Proximity of ionic group to benzene ring of MDI.

The possibility of this effect being enhanced by complexation of the potassium counter ion by the polyether segments may be largely discounted as the effect is strongly present in the spectrum of MDI/TDOL, which has no polyether segments. The effect may be marginally enhanced by interaction of the potassium counter ion with the electron density of the benzene ring, though this is unlikely as solvation of the cation by the much more polar DMSO molecules would probably be more favourable.

The presence of the ionic groups close to one side of the benzene ring would have a much greater effect on the two ring protons closest to the ionic group. This matches the observations, with two new strong peaks shifted from original values of 7.1 and 7.07 ppm to new values of 7.30 and 7.40 ppm. The two protons are still equivalent and the resonance is split into two peaks by coupling with the other ring protons. Shifts of this type are known for a variety of materials. Lanthanide shift reagents are specifically used to separate aromatic resonances.

The new peak at 7.15 ppm may be accompanied by a second peak at 7.10 ppm hidden underneath the existing peak at 7.1 ppm, which is slightly enhanced in some of the ionomer spectra. This would correspond to a smaller shift, probably due to the MDI unit attached to the end of the ionic diol that is less able to come close to the ionic group.

Comparison of the integrals for each peak was not possible at the resolution used, but comparison of the gross integrals for the two sets of peaks (7.0-7.2 ppm and 7.2-7.4 ppm) showed an increasing ratio from 1:1 for the non ionomer rising to

approximately 2:1 for MDI/TDOL in favour of the 7.2-7.4 ppm region. This further supports a shift of the resonances of the protons on one side of the ring to lower applied field. Hence, there is an overall increase in the ratio between the two regions.

It is worth noting that even for MDI/TDOL, the major pattern is the original 1,4 pattern, suggesting that only a minority of conformations allow the ionic group to approach the ring and give rise to the shift.

8.3.2.2.3 The Aliphatic Region, 1 to 6 ppm.

The spectra of the PE-X-Th/BD series of polymers show only a few changes as TDOL replaces BD.

The peak at 1.7 ppm, due to the central methylene protons of butanediol, is steadily reduced in intensity and is completely absent for PE-100-Th/BD. The triplet at 3.62 ppm, due to the methylene groups of the polyether and the end methylenes of butanediol, is consistently reduced in intensity as the latter methylene groups are removed.

The gains in the spectrum are a doublet at 2.98 ppm due to the methylene protons of the primary hydroxyl residue of TDOL. This peak is seen at 2.90 ppm in free TDOL. A new peak at 3.90 ppm is possibly due to the methine proton of TDOL. A value of 3.65 ppm was obtained for this resonance in free TDOL. An unresolved hump, 5.24-5.24 ppm, and a doublet at 5.12 ppm appeared to be associated with one another, growing in intensity at the same rate. These resonances might be due to traces of unreacted secondary alcohols, though why the signal should be

shifted by 0.6 ppm, as would be the case if this assignment were correct, is not clear. In free TDOL, this resonance occurred at 4.6 ppm.

Two very sharp singlets at 2.88 ppm and 2.72 ppm were probably due to soluble impurities in the polymer. In general, peaks due to the polymer were markedly broadened by the slow tumbling motions of the macromolecules in solution.

The spectrum of MDI/TDOL shows both extra features and absences when compared to the other spectra. Firstly, the polyether peaks are absent and the intense peak caused by water molecules associated with the polyether segments is absent, leaving the range 3.4 to 3.7 ppm free of peaks. An unresolved peak at 4.15 ppm was lost, revealing a previously obscured small multiplet at 4.25 ppm that could not be identified. Further unidentified peaks were present at 4.46 ppm and 3.77 ppm. A broad peak at 3.15-3.2 ppm was assigned to the methylene protons of the thiosulphate bearing group.

Inclusion of TDOL in the polymer chain appears to result in some shifts of resonant frequencies for protons in TDOL. Also, it is likely that the lower reactivity of the secondary hydroxyl group in TDOL results in TDOL residues at the chain ends where any shift effects would be minimised. The spectrum would thus be more complicated than might be expected. For these reasons, complete assignment of all bands was not possible.

8.3.2.3 Elemental Analysis.

Comparison of calculated and experimental results for elemental analysis (see table 8.1) gave good agreement for all the elements analysed.

It was noted, however, that in all of the polyether containing ionomers, the sulphur content was lower than expected. These polymers were prepared by a two step process and small traces of water in the reaction mixture may have consumed small quantities of isocyanate. Since the sulphur containing ionic diol is included in the polymer during the second step, this loss of isocyanate may have resulted in a genuine small reduction in the quantity of ionic diol (and hence sulphur) in the polymer. The low sulphur levels, coupled with the high errors at these levels mean that no estimate of loss can be made. The absence of a large urea signal in the NMR spectrum suggests that the losses are small.

The error in sulphur content for MDI.TDOL, which is prepared by a one step reaction, gives an indication of the normal errors (±1%) at higher sulphur levels. This is supported by the good agreement found for the other elements.

Polymer	% C		% H		% N		% S	
	Calc	Fnd	Calc	Fnd	Calc	Fnd	Calc	Fnd
PE-0-Th/BD	60.87	60.34	7.28	7.50	4.45	4.53	----	---
PE-25-Th/BD	58.36	58.71	6.94	7.40	4.29	4.64	1.68	1.06
PE-50-Th/BD	56.06	55.82	6.63	7.12	4.14	5.00	3.23	2.57
PE-75-Th/BD	53.89	52.75	6.33	6.64	4.01	5.04	4.69	3.78
PE-100-Th/BD	51.86	51.95	6.06	6.60	3.88	4.98	6.05	4.31
MDI/TDOL	45.36	44.14	3.60	4.31	5.88	5.68	13.45	14.60
TDOL	15.93	15.80	3.10	3.02	----	----	28.32	27.56

Table 8.1 Elemental analysis of PE-X-Th/BD Samples.

8.4 Some Properties in Solution.

The ionomers were found to exhibit highly complex behaviour in solution and only a brief investigation was possible, the results of which are discussed in this section.

8.4.1 Solubility.

There were few unusual results for the solubilities of the series of ionomers in a selection of solvents. See Table 8.2

Polymer	DMSO	DMF	THF	H_2O	EtOH	IPA	IBMK	CH_2Cl_2
PE-0-Th/BD	YES	YES	YES	NO	NO	NO	NO	NO
PE-25-Th/BD	YES	YES	YES	NO	NO	NO	NO	NO
PE-50-Th/BD	YES	YES	YES	YES	NO	NO	NO	NO
PE-75-Th/BD	YES	YES	NO	YES	NO	NO	NO	NO
PE-100-Th/BD	YES	YES	NO	YES	NO	NO	NO	NO
MDI/TDOL	YES	YES	NO	NO	NO	NO	NO	NO

Table 8.2 Solubility of PE-X-Th/BD Samples.

All the materials were soluble in the highly polar organic solvents DMSO and DMF, these solvents being compatible with the non polar MDI residues, mildly polar polyether segments and the highly polar ionic groups that constitute the polymer molecules.

THF, which is a solvent for many segmented polyurethanes, did not dissolve the higher ionic content polymers. It is insufficiently polar to dissolve the large number of ionic groups in these materials.

Ethanol, dichloromethane, isopropyl alcohol and IBMK are all unable to dissolve any of the materials, including the non ionomer. All are incompatible with one or more of the groups found both in ordinary polyurethanes and the ionomers.

The most significant observation is the solubility of the higher ionic content segmented materials PE-50-Th/BD, PE-75-Th/BD and PE-100-Th/BD in water.

PE-50-Th/BD was only sparingly soluble and tended to form an emulsion if too much material was present and the solution disturbed.

PE-75-Th/BD and PE-100-Th/BD were both readily soluble in water, giving clear solutions.

These observations reflect the increasingly dominant effect of the ionic groups on the solubility of the polymers. The low solubility and facile formation of an emulsion for PE-50-Th/BD illustrates the opposing forces of the hydrophobic MDI residues and hydrophilic ionic and polyether residues. The emulsion droplets are likely to be held together by hydrophobic interactions between MDI residues of the molecules. Precipitation of the material in the emulsion is prevented by the hydrophilic groups.

The higher ionomers simply give increasing viscosity as the polymer content rises and the solid PE-100-Th/BD appears to be slightly hydroscopic.

Rather suprisingly, MDI/TDOL was insoluble in water. This is probably due to two factors.

Firstly, the absence of a polyether segment means that the mass % of a sample that is due to MDI residues is high.

Secondly, there will be no phase separated structure in the solid. It will therefore have a low degree of disruption of the aligning of the benzene rings in the MDI residues and hence, water will be unable to separate the molecules in the dissolution

process. Any similar regions present in PE-100-Th/BD will be in the form of microscopic domains and will have a very high surface area to volume ratio, whereas MDI/TDOL is a single phase material. They can therefore be broken apart by motion of the dissolved sections of the molecules. Such motion cannot easily occur for MDI/TDOL.

8.4.2 Solvent Retention.

Films of the ionomers cast from DMF, or samples containing DMSO, were found to retain traces of these solvents in sufficient quantities to severely affect their properties for much longer periods of time than seen for non ionomers. In general, the higher the ionic content of the polymer, the more tenacious its retention of these solvents.

The ionic groups in these molecules are solvated by the polar organic solvent molecules. Loss of these molecules is unfavourable as a high solvation energy must be overcome. This energy barrier is greatly enhanced by the incompatibility of the ionic groups with the benzene rings of the MDI residues that are their nearest neighbours in the polymer chain. The DMF or DMSO molecules are compatible with both ionic and aromatic groups and act in a manner analogous to a phase mixing agent.

Thus, the higher the ionic content, the higher the energy barrier to loss of the solvent molecules, and the longer the drying time required.

This can be contrasted to the behaviour of samples from aqueous solutions. These solutions and a comparable solution in DMF were made up from polymer PUTDOL, an ionomer similar to

PE-100-Th/BD but of lower molecular weight (see chapter 9).

Once again, samples from DMF solutions required extensive drying times in vacuo. However, samples from water were dry and brittle after a few days in a dessicator over silica gel at room pressure.

Two causes probably contribute to this. Firstly, the boiling point and vapour pressure of water are higher than those of DMF and it therefore evaporates more quickly. Secondly, water, unlike DMF, is not compatible with the MDI residues of the molecules. Thus, although it readily solvates the ionic groups, no interfacing between the ionic and aromatic groups takes place. There is thus a much lower smaller barrier to the loss of water and drying times are reduced.

8.4.3 Gel Permeation Chromatography.

The complexity of the behaviour of the ionomers in solution became clear during studies on the materials using GPC. The chromatograms of the ion containing polymers were found to be concentration dependent.

Two effects, one major and one minor, were seen.

The major effect is illustrated in the chromatograms (figures 8.14 to 8.19) of the materials at concentrations of 0.3%, 0.08% and 0.03% w/v. As the sample concentration is reduced, the peak retention time is significantly reduced. For PE-25-Th/BD and PE-50-Th/BD, the number of peaks present is also altered.

The non ionomer PE-0-Th/BD acts as a control sample and, as is usually the case for GPC, shows no concentration dependence.

The solution behaviour of the ionic materials is highly

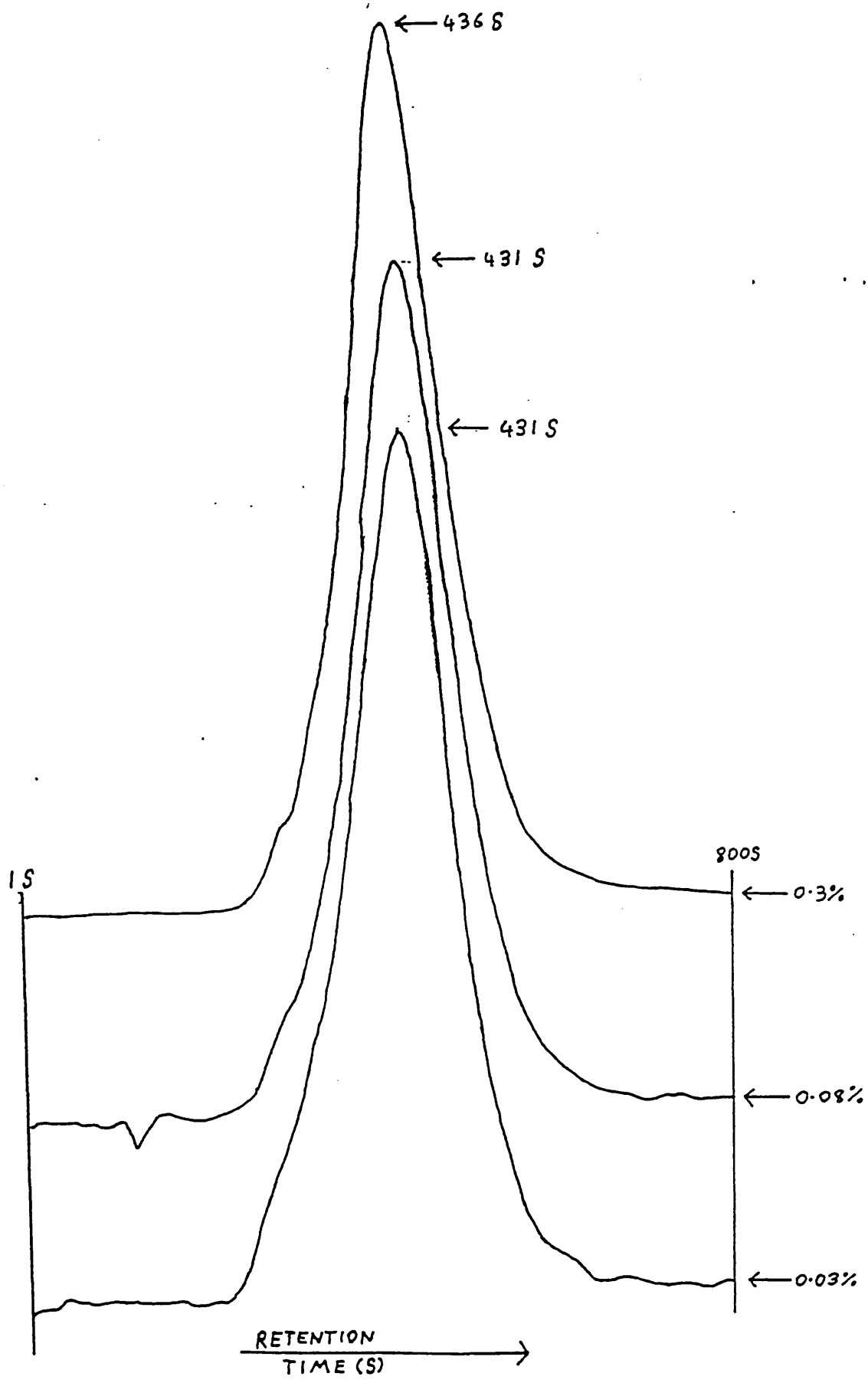


Figure 8.14
Gel Permeation Chromatograms
of PE-0-Th/BD at
varying Concentrations

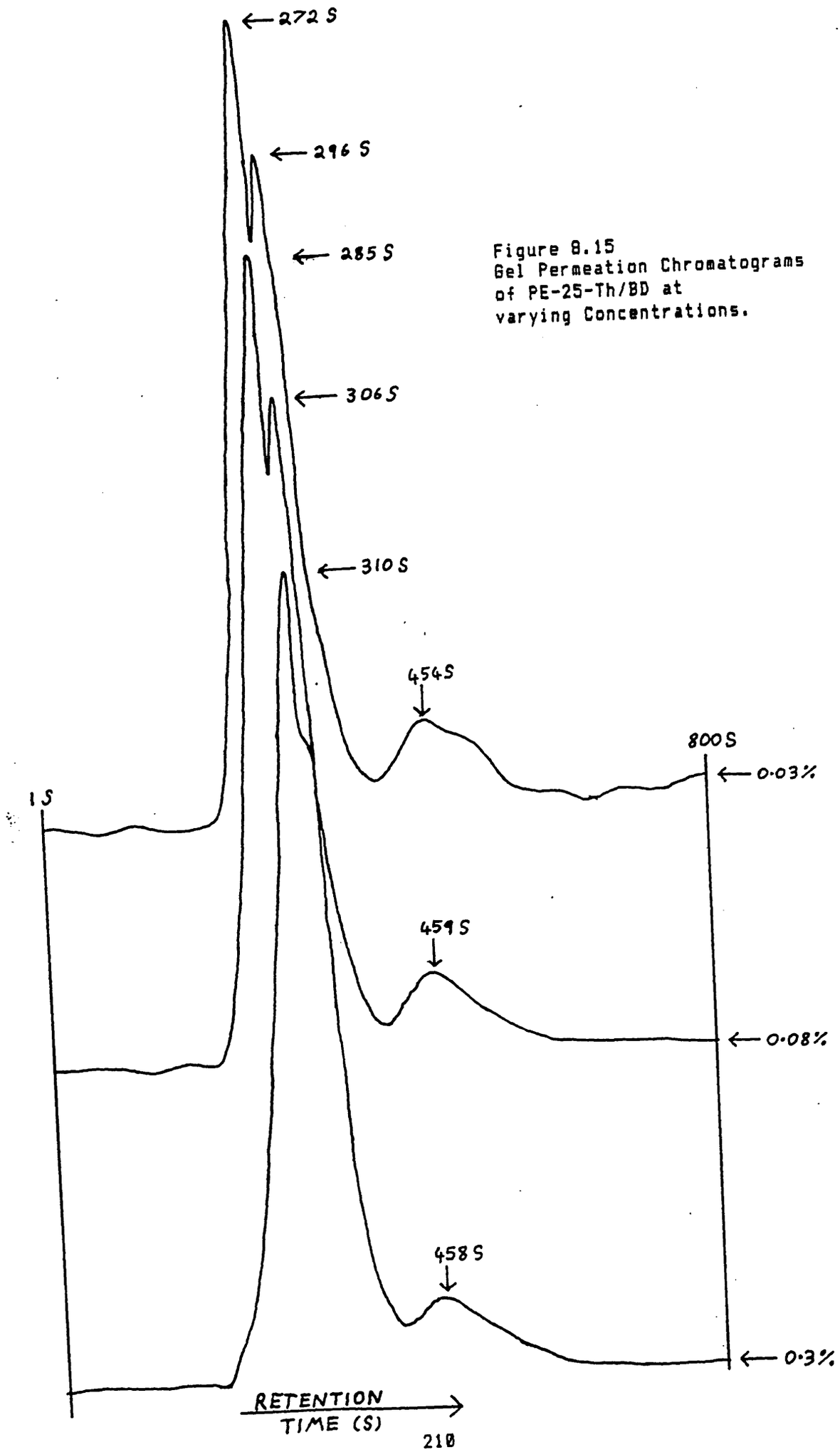


Figure 8.15
Gel Permeation Chromatograms
of PE-25-Th/BD at
varying Concentrations.

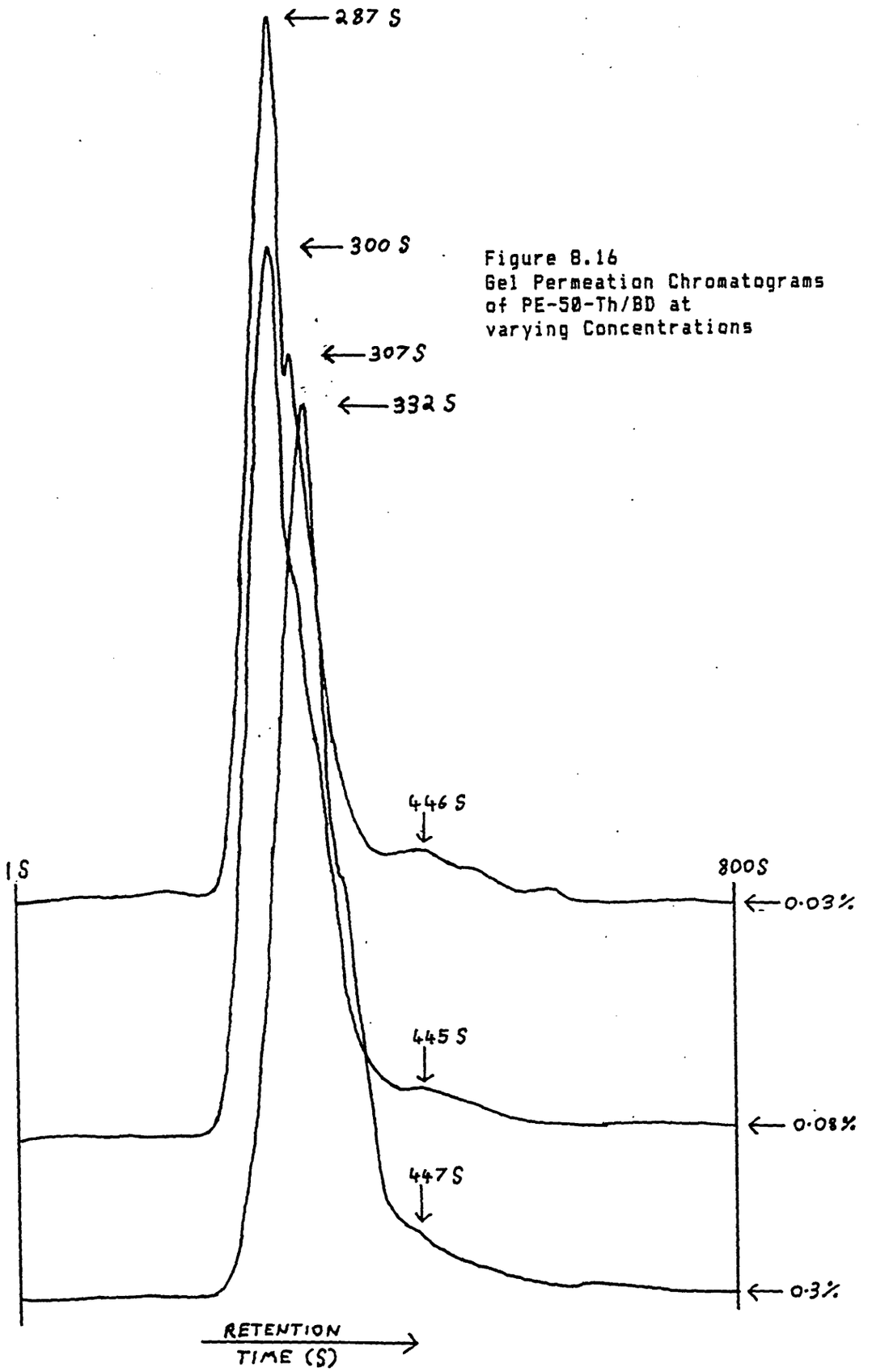


Figure 8.16
Gel Permeation Chromatograms
of PE-50-Th/BD at
varying Concentrations

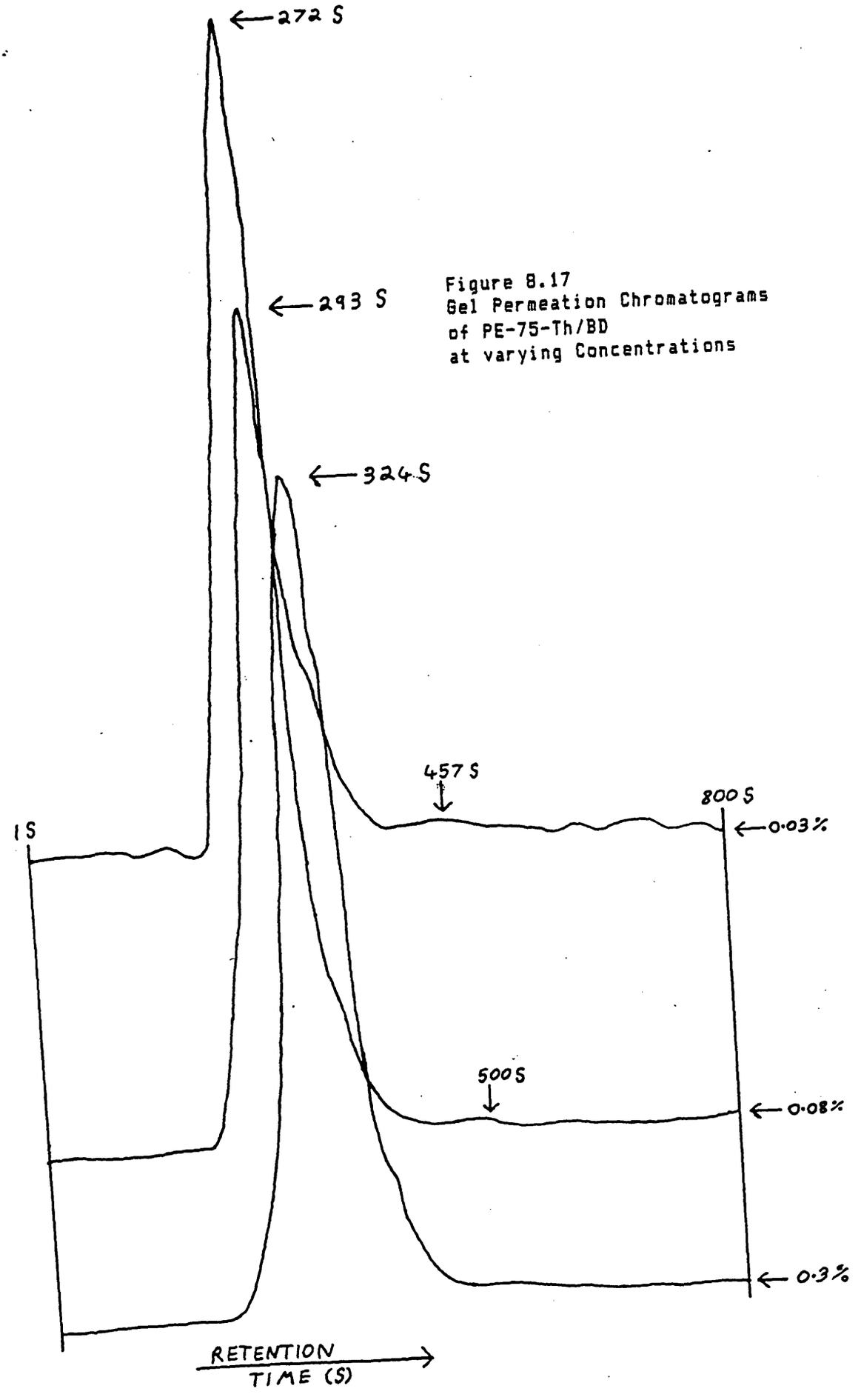


Figure 8.17
Gel Permeation Chromatograms
of PE-75-Th/BD
at varying Concentrations

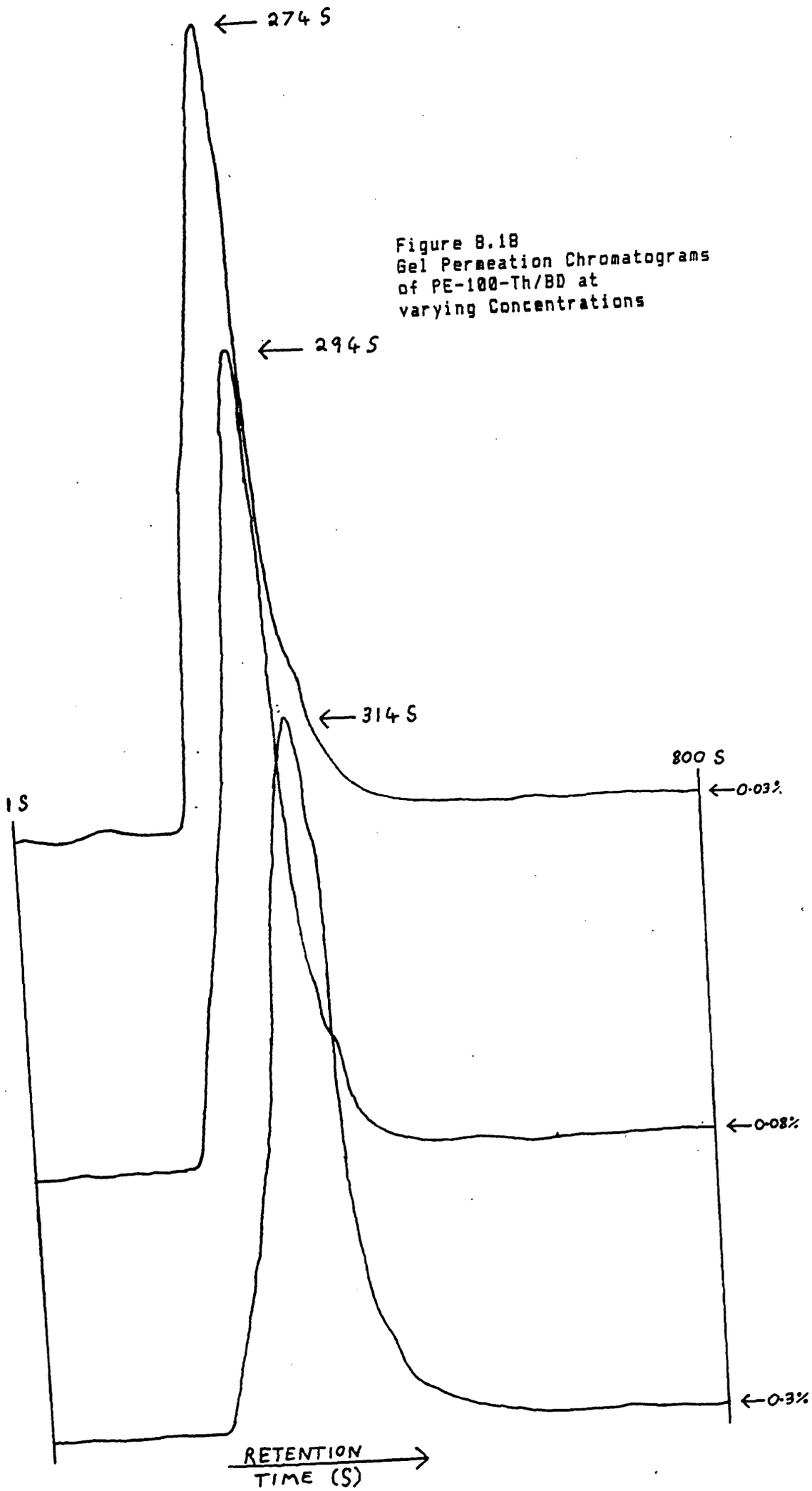


Figure 8.18
Gel Permeation Chromatograms
of PE-100-Th/BD at
varying Concentrations

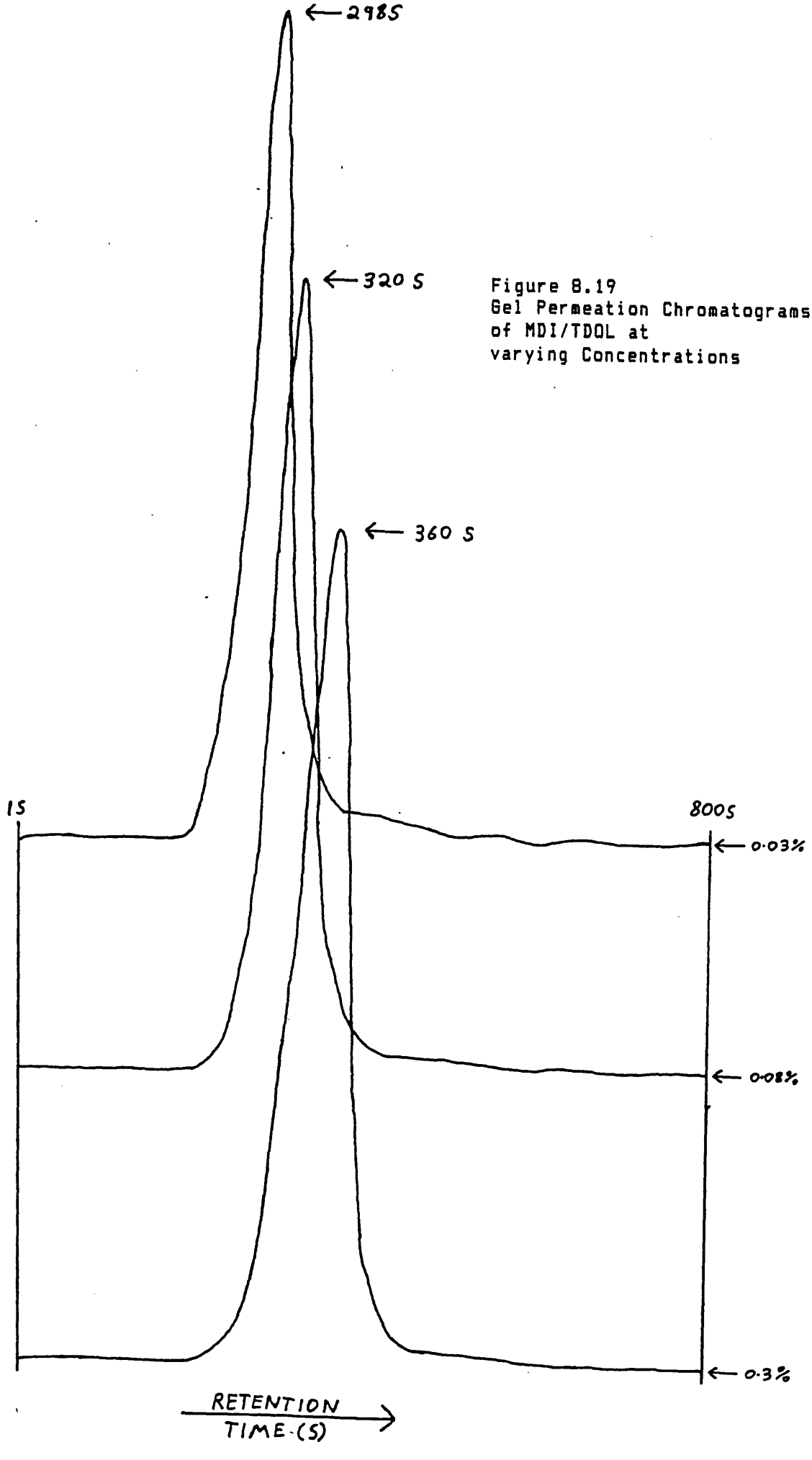


Figure 8.19
Gel Permeation Chromatograms
of MDI/TDOL at
varying Concentrations

dependent on the ionic strength of the solution and the ionic strength is, in turn, dependent on the polymer concentration.

At low ionic strengths, the DMF solution behaves as a poor solvent for the ionomer molecules with their highly polar ionic groups and a high degree of short range intermolecular association takes place between these groups. This gives rise to aggregate species, formed from several molecules, of high molecular weights. Once formed, such aggregates are stable to further dilution, as this lowers the ionic strength further and increases the stability of short range associations.

At higher ionic concentrations, the solution behaves as a more polar solvent and short range associations become less favourable. Molecular motion is therefore able to dissociate larger aggregates. Hence, the species present at higher concentrations are of lower molecular weight and show longer retention times in the chromatograms.

Short range intramolecular associations between ionic groups also take place and the polymer will tend to be in highly coiled conformations. Thus, only a proportion of the ionic groups will be available for intermolecular interactions as many groups will be inaccessible to another molecule. This is the key to the multiple peaks seen for PE-25-Th/BD and PE-50-Th/BD.

For these materials, the number of points of interaction holding a molecule in an aggregate is quite low (in comparison to the high ionic content materials) and an uneven distribution of stable aggregate sizes results. Also, material of retention time similar to the non ionic polymer is seen and this must correspond

to single molecules that are either not able to take part in aggregate formation because their conformation shields the ionic groups from other molecules or have broken free of aggregates and been unable to easily re-associate with an aggregate. It should be noted that, even for PE-25-Th/BD, such material is clearly very much in the minority.

It is clear that, in general, the higher the number of potential interaction points, the more uniform and stable are the aggregates.

The second, minor effect is not visible in the chromatograms in figures 8.14-8.19 and became apparent only by observation of a large number of chromatograms.

In general, for the ionomers, there appeared to be a tendency for the usually sharp front of the chromatogram to be marginally less sharp than is usual. The rear of the chromatograms appeared to be subject to slightly less tailing than is usual. These observations may be explained as follows.

As the sample flows through the equipment, the material at the front becomes slightly more dilute and tends to aggregate more. In the column these aggregates flow away from lower molecular weight material, becoming more stable as they move away from the region of highest ionic strength. Hence, these species are seen as a very slight broadening of the high molecular weight front of the chromatogram.

At the rear of the sample, material also becomes diluted during flow and aggregates. These aggregates then accelerate in the column, catch up with the bulk of the sample and dissociate again in this region of highest ionic strength. Thus, the tailing

normally seen in chromatograms is fractionally reduced.

8.4.4 Some Visible Viscosity Trends.

Owing to lack of time, a viscometric investigation was not possible, but visible differences were observed during preparation and manipulation of solutions for the casting of films. DMF solutions of 10% w/v were used for this purpose and a trend of increasing viscosity with falling ionic content was noted.

As has been discussed in section 8.4.3, multimolecular aggregates are formed at low concentrations where the ionic strength is low. At the high ionic strengths present in the 10% w/v solutions, the forces involved in ionic interactions are probably sufficiently weak that the aggregates do not hold together. However, intramolecular interactions, which are not subjected to such large disruptive forces as intermolecular interactions, will still take place. Those molecules with larger numbers of ionic groups will therefore be in coiled conformations more often than molecules with fewer ionic groups.

At these concentrations, intermolecular tangling will affect the viscosity. Those materials whose molecules are most tightly coiled will therefore have lower viscosities as there will be less tangling.

Hence, the higher the ionic content, the lower the viscosity at these concentrations.

Comparison of solutions of polymer PUTDOL in DMF and water at equal concentrations revealed the water solution to be very much more viscous than the DMF solution. A possible explanation

is as follows.

In water, the highly hydrophobic MDI residues in the chains interact strongly and this, coupled with the highly hydrophilic nature of the rest of the chain leads to a large degree of intermolecular interaction and formation of micelle like structures. The level of these interactions is such that a high solution viscosity is produced because of the forces needed to separate the molecules during flow of the solution.

8.4.5 Addition of Salts to Aqueous Ionomer Solutions.

Addition of salt crystals to aqueous solutions of PUTDOL (a polymer similar to PE-100-Th/BD, see chapt 9) led to an unusual phenomenon.

The salt crystal was immediately surrounded by a sticky white precipitate. This entity proceeded to slowly expand into a clear sphere with an extremely fine, but visible, boundary membrane. The sphere continued to grow until finally dissapearing into solution. Spheres of 0.5-1 cm diameter were observed. If burst (by being suddenly pressed with a spatula) the contents of the sphere formed a small quantity of white precipitate which formed a new sphere.

Such behaviour was observed for sodium and potassium chloride, sodium and potassium acetate and the disodium salt of azo bis cyanopentanoic acid.

The likely course of events is as follows.

Upon addition the salt crystal starts to dissolve, giving an extremely high local ionic strength that "salts" out a small quantity of polymer as the sticky precipitate. This precipitate acts as a barrier to the ions of the salt but allows water to

flow into the region of high ionic strength by osmosis. This is the point at which the sphere is formed and starts to grow.

As the water diffuses into the region bounded by the precipitate, this region becomes more dilute and the majority of the precipitate dissolves into it. A very fine layer is left at the interface between the bulk solution and the local solution.

This boundary layer continually dissolves into the "inner" solution of the sphere as it grows and is replaced by a fresh layer of polymer precipitated from the bulk solution at the interface. See Figure 8.20. The cause of this continual precipitation of a fresh boundary layer is the difference in ionic strength between the inner solution and the bulk solution. The interface region can be regarded as the region where the polymer is out of equilibrium with its surroundings as it adjusts from conformations suitable at lower ionic strengths to those suitable at higher ionic strengths.

Eventually, the inner solution becomes so dilute that no fresh material is precipitated and the boundary disappears leaving a homogeneous solution.

If a sphere is violently ruptured, its contents are ejected into the surrounding solution resulting in a dramatic increase in surface area over which precipitate may form. Sufficient precipitate is formed so that it aggregates as a small quantity of white precipitate. The growth pattern of the sphere then recommences.

Repeated rupture of the spheres ultimately results in sufficient mixing of the two solutions to the point where no

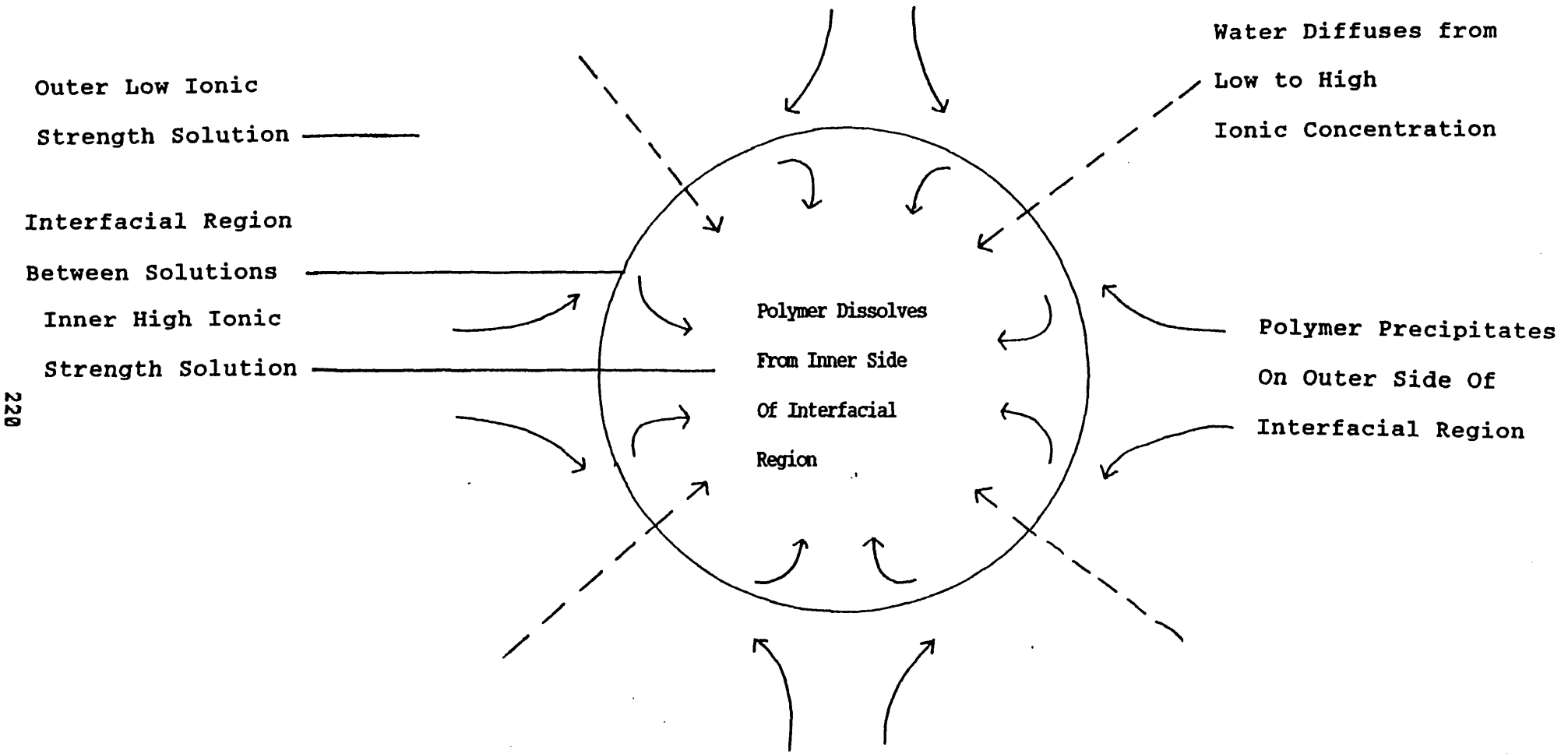


Figure 8.20
Micellar Sphere Growth after addition of Salt

material is precipitated and only a single homogeneous solution remains.

The rate of swelling of the spheres was clearly seen to be influenced by the common ion effect. Spheres formed from potassium salts took much longer to dissolve than those formed from the sodium salts due to the presence of potassium ions in solution as the counter ions of the anionomer.

Salts with polyvalent cations were not studied as the ionomers are polyvalent anions and combination of the two would lead to extremely complex behaviour.

8.5 Some General Properties of the Ionomers.

8.5.1 Equilibrium Solvent Uptakes.

Interest in solvent selective membranes for ethanol/water separations and alcohol sensors for fermentation applications prompted the measurement of the equilibrium uptake of the ionomers for these two solvents.

The percentage uptake is defined as :-

$$\frac{\text{Increase in Sample Weight X 100\%}}{\text{Dry Sample Weight}}$$

The results given are average values from duplicate samples of each polymer.

8.5.1.1 Water Uptake.

Equilibrium water uptakes were only possible for PE-0-Th/BD, the non ionomer, and PE-25-Th/BD, the lowest ionic content ionomer. All the other ionomers were water soluble. A graph of percentage uptake with time for these two materials is shown in figure 8.21.

Both samples had approached equilibrium after approximately

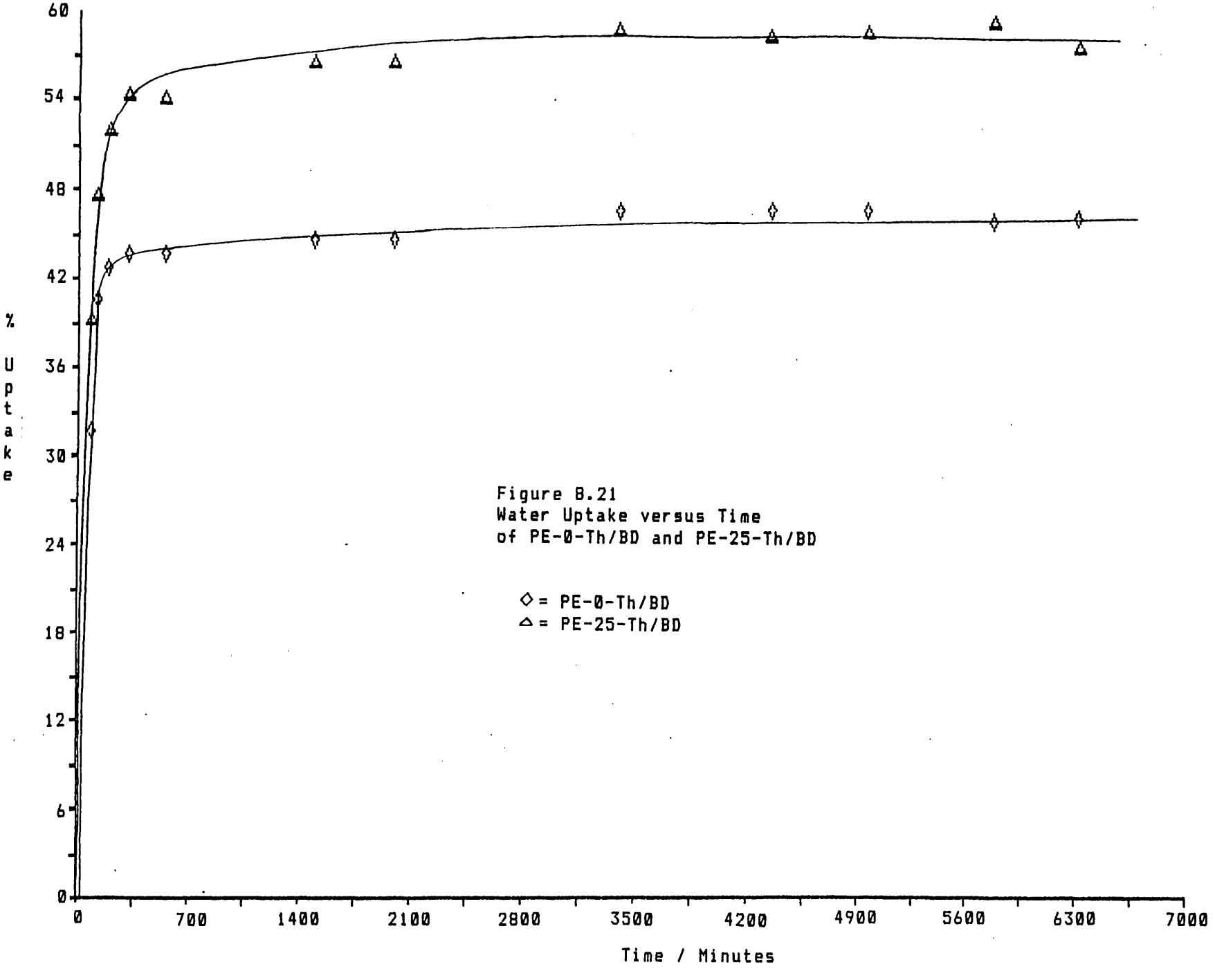


Figure 8.21
Water Uptake versus Time
of PE-0-Th/BD and PE-25-Th/BD

2.5 days and PE-0-Th/BD and PE-25-Th/BD took up 49% and 61% respectively. Between 2.5 and 10 days, the samples were stable in mass to ±1%. As can be seen in fig 8.21, initial water uptake was very rapid for both samples during the first 4 hours but, subsequently, equilibrium was achieved much more slowly over the next 2 days.

There are two reasons for this initial rapid uptake. Firstly, the outer regions of the sample takes up water quickly because they are in direct contact with the water. The inner regions of the sample take up water by diffusion of the water through the outer regions at a slower rate.

Secondly, the highly hydrophilic polyether phase formed from the soft segments of the polymer chains rapidly takes up water. The subsequent slower approach to equilibrium is due to the much smaller uptake by the hydrophobic hard domains. For PE-0-Th/BD, uptake of water by the hard domains is entirely due to the urethane linkages present in these domains.

The effect of inclusion of ionic groups is strikingly illustrated both by the 12% increase in water uptake for PE-25-Th/BD over PE-0-Th/BD and the solubility all the higher ionic content materials. The ionic group achieves this effect in three ways. Firstly, it is a bulky group and disrupts the regular packing of the benzene rings present in the hard domains. Secondly, it is highly polar and alters the pattern of hydrogen bonding that usually helps maintain the regular structure of the hard domain. Both of these effects increase the accessibility of polar groups in the hard domain to water and allow greater swelling of the domain. The third and by far the most important

effect is the large increase in overall hydrophilicity of the hard domain caused by the inclusion of salt groups in it. It is this final effect that boosts the uptake so dramatically and, for the higher ionic contents, solubilises the hard domains in water.

8.5.1.2 Ethanol Uptake.

Graphs of ethanol uptake with time could not be obtained for the ionomers as the samples became plasticised, tacky and lost all mechanical strength within 1 hour of immersion and repeated weighings of the samples became impossible. The samples were therefore left for 44 days to reach equilibrium. The results are given in table 8.3. Duplicate samples of the same materials gave good agreement, differing by less than 0.5% uptake, except for PE-25-Th/BD, samples of which differed by 2% uptake.

Since the non ionomer reached equilibrium after 3 days, 44 days should be more than sufficient time for all the samples to have reached equilibrium. A graph of ethanol uptake with time for the non iomomer is shown in figure 8.22. This material was not plasticised by ethanol.

Polymer	% Uptake
PE-0-Th/BD	22.7
PE-25-Th/BD	20.8
PE-50-Th/BD	11.8
PE-75-Th/BD	7.3
PE-100-Th/BD	5.6

Table 8.3 % Equilibrium ethanol uptake of PE-X-Th/BD samples.

The equilibrium ethanol uptake falls as ionic content increases. In addition, the degree of plasticisation was observed to lie in the order 50 >> 75 > 25 > 100 > 0 for the PE-X-Th/BD series of samples.

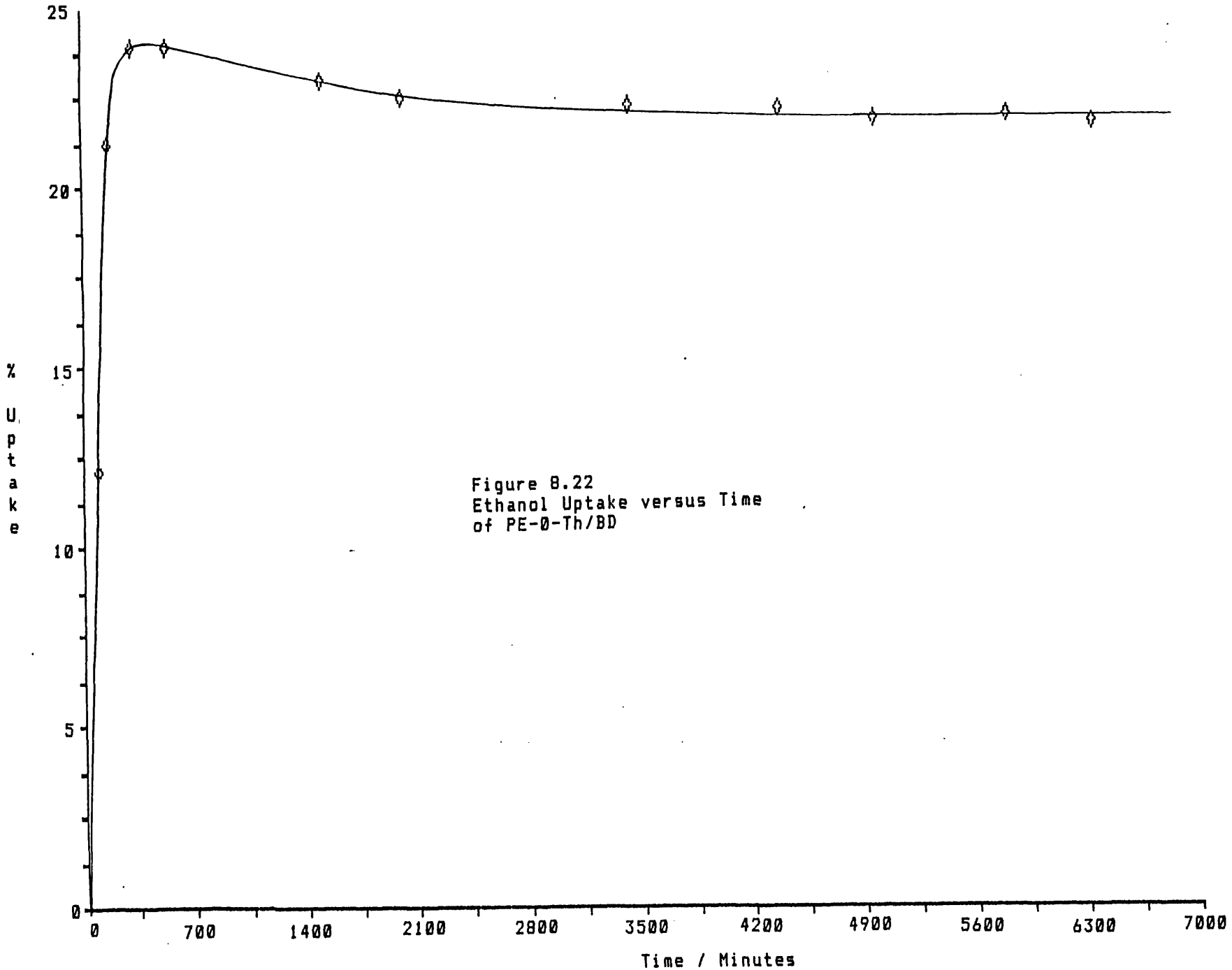


Figure 8.22
Ethanol Uptake versus Time
of PE-0-Th/BD

These observations may be explained by considering the effects of the ionic groups in the hard domains and in the bulk of the sample.

Firstly, the incompatibility of the ionic groups with ethanol steadily depresses the equilibrium uptake.

Secondly, the disruption of hard domain packing and hydrogen bonding, coupled with the steady increase of ionic interactions in the hard domain as ionic content increases, gives rise to the observed order of plasticisation. The disruption of the conventional structure allows increasing accessibility and plasticisation by ethanol in the hard domains. However, increasing ionic interactions and ionic content give rise to a domain less easily penetrated and plasticised by ethanol. Hence, a maximum degree of plasticisation is seen for PE-50-Th/BD.

The conventional hard domain is less susceptible to plasticisation than an ionic domain because of its excellent packing of MDI residues and hence PE-25-Th/BD is less affected by ethanol than PE-75-Th/BD as the former has a greater content of conventional groups. Similarly, but more clearly seen, is the difference between PE-100-Th/BD and PE-0-Th/BD. The latter is not at all plasticised.

In conclusion, both ethanol and water uptakes show the changeover from a highly ordered domain to a less ordered domain held together by ionic interactions. In both cases, the overall level of uptake is dominated by the presence of the highly polar ionic group. The potential for selectivity between solvents of differing polarity was also clearly shown.

8.5.2 Long Term Stability.

Although no specific investigation was carried out on the stability of the ionomers, some signs of both thermal and photochemical degradation were observed.

Storage at room temperature and/or exposure to sunlight for extended periods (several months) gave rise to a sulphurous odour and a yellow opaque material appeared within the polymer, which was formerly transparent orange in colour. In addition, the material became insoluble. The decomposition was more significant for higher ionic contents. Identical observations were noted for samples used in differential scanning calorimetry, though much higher temperatures and shorter timescales were involved.

The yellow opaque material is almost cetainly elemental sulphur and the smell may be either H_2S or SO_2. The decomposition of alkyl thiosulphates is known to give rise to thiols and disulphides[105]. The latter would act as crosslinks in the material and render it insoluble.

These ionomers would therefore seem unsuitable for applications requiring long term exposure to UV light or elevated temperatures. However, short term exposure to UV light (4 hours under a 250 watt Hg vapour lamp) did not lead to any noticeable signs of degradation.

8.5.3 Differential Scanning Calorimetry.

Differential scanning calorimetry, DSC, was performed with a heating rate of $10^{o}C$ per minute and the temperature ranges -100 to $30^{o}C$ and 30 to $170^{o}C$ were studied. Each sample was run twice through the temperature ranges.

The upper limit of $170^{o}C$ was chosen as rapid urethane

decomposition can occur at higher temperatures[6].

8.5.3.1 The Low Temperature Region.

The DSC trace for PEG1000, Fig 8.23, shows a glass transition at -21°C, a melting endotherm for absorbed moisture at 0°C and the onset of the polyether melting endotherm can be seen at 20°C.

The traces for the segmented polymers PE-0-Th/BD to PE-100-Th/BD, Figures 8.24 - 8.28 respectively, all show clearly defined soft phase glass transitions. The start, end, and centre of these transitions are given in table 8.4.

MDI/TDOL, which does not possess a soft phase, did not display any features in this region. See Fig 8.29 for the trace obtained from this material.

Polymer		start of transition (°C)	centre of transition (°C)	end of transition (°C)
PEG1000		-24	-21	-18
PE-0-Th/BD	Run 1	-18	-11	-3
	Run 2	-11	-4	+4
PE-25-Th/BD	Run 1	-9	+2	+14
	Run 2	-9	+2	+12
PE-50-Th/BD	Run 1	-8	+3	+14
	Run 2	-12	0	+12
PE-75-Th/BD	Run 1	-13	-1	+12
	Run 2	-22	-10	+1
PE-100-Th/BD	Run 1	-11	0	+11
	Run 2	-24	-12	0

Table 8.4 Soft phase glass transitions of PE-X-Th/BD Samples.

The transition temperature is taken as being the temperature at the centre of the transition and the width of the transition is an indication of the width of the interfacial region that forms the boundary between the hard and soft phases.

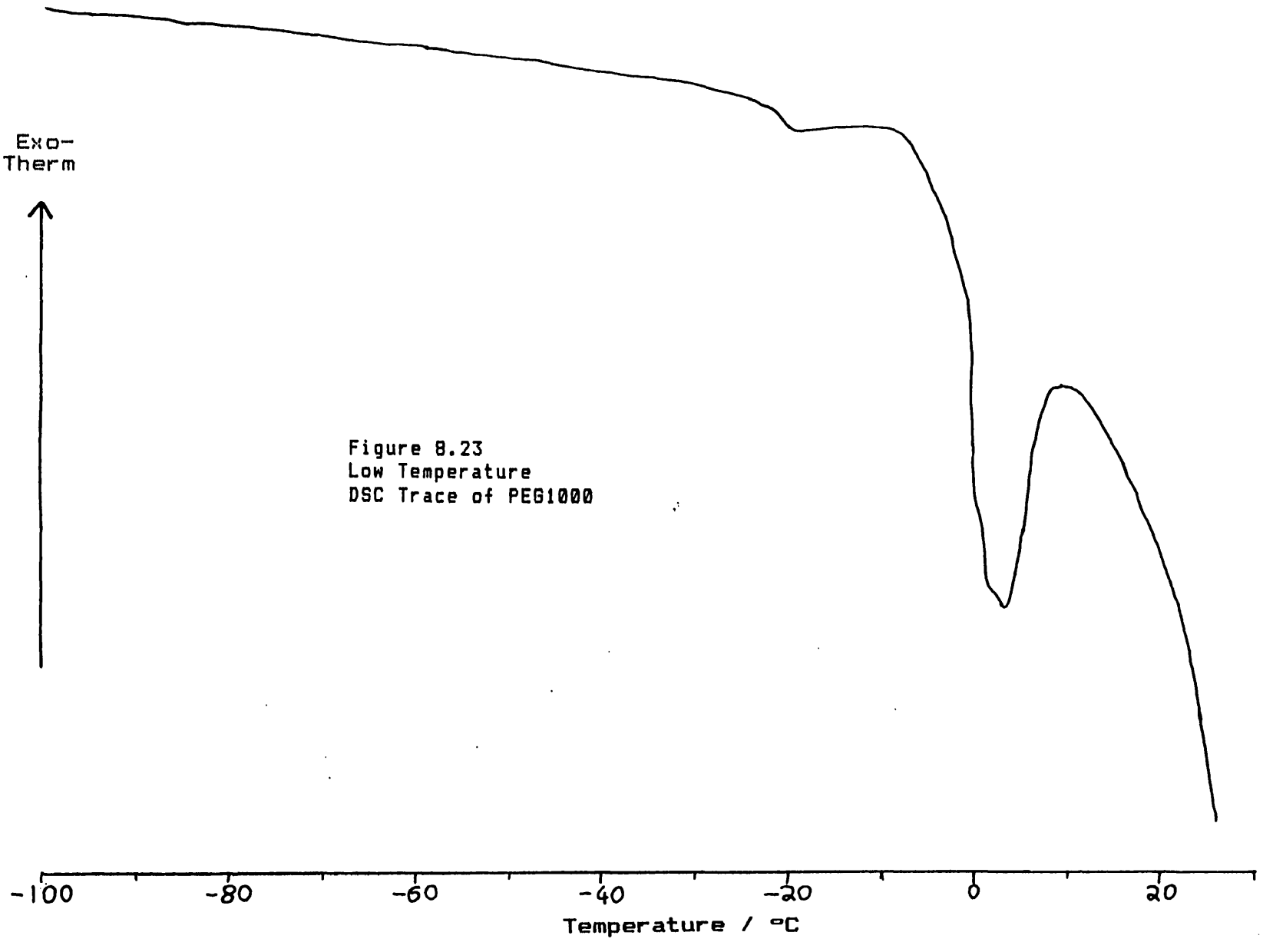


Figure 8.23
Low Temperature
DSC Trace of PEG1000

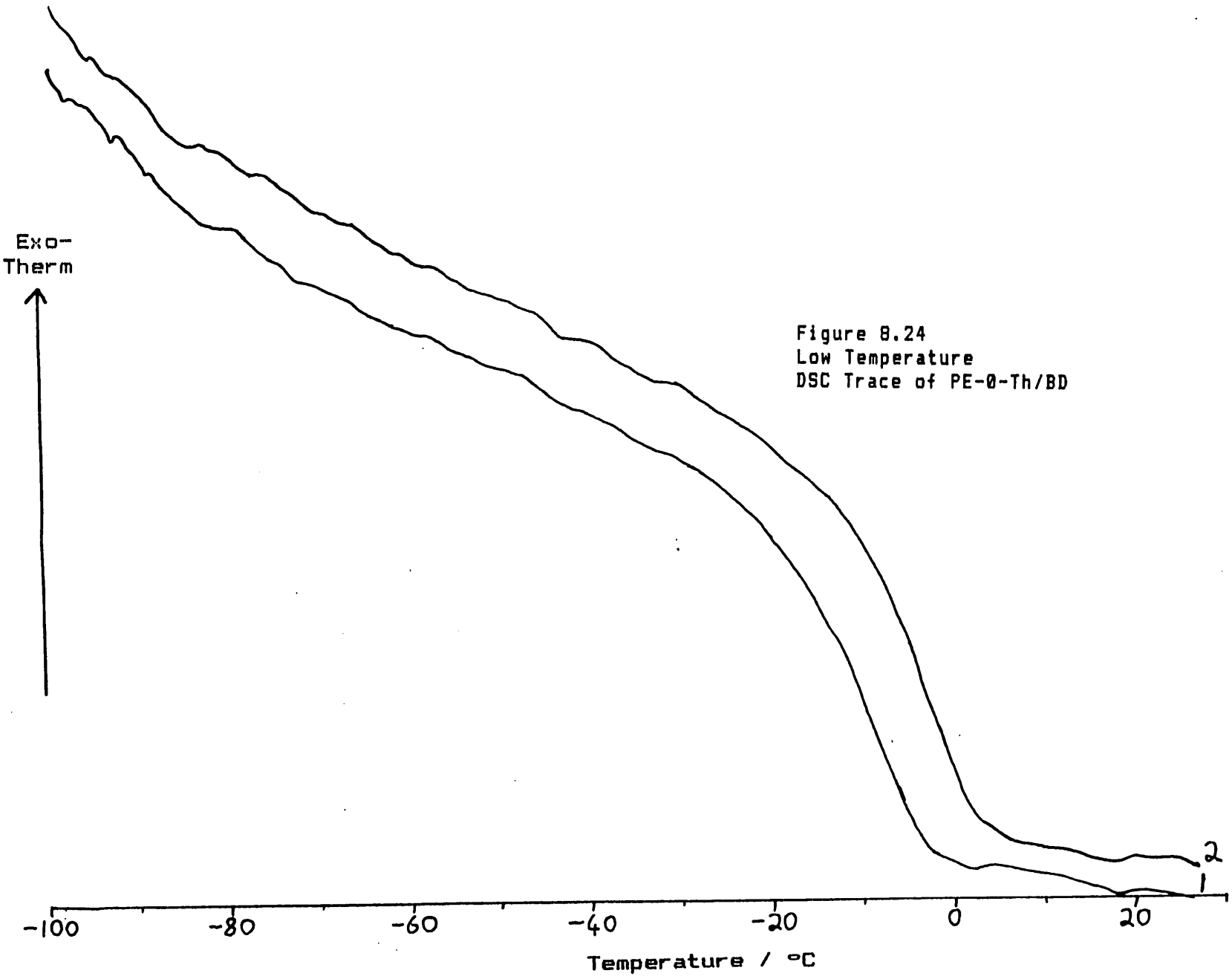


Figure 8.24
Low Temperature
DSC Trace of PE-0-Th/BD

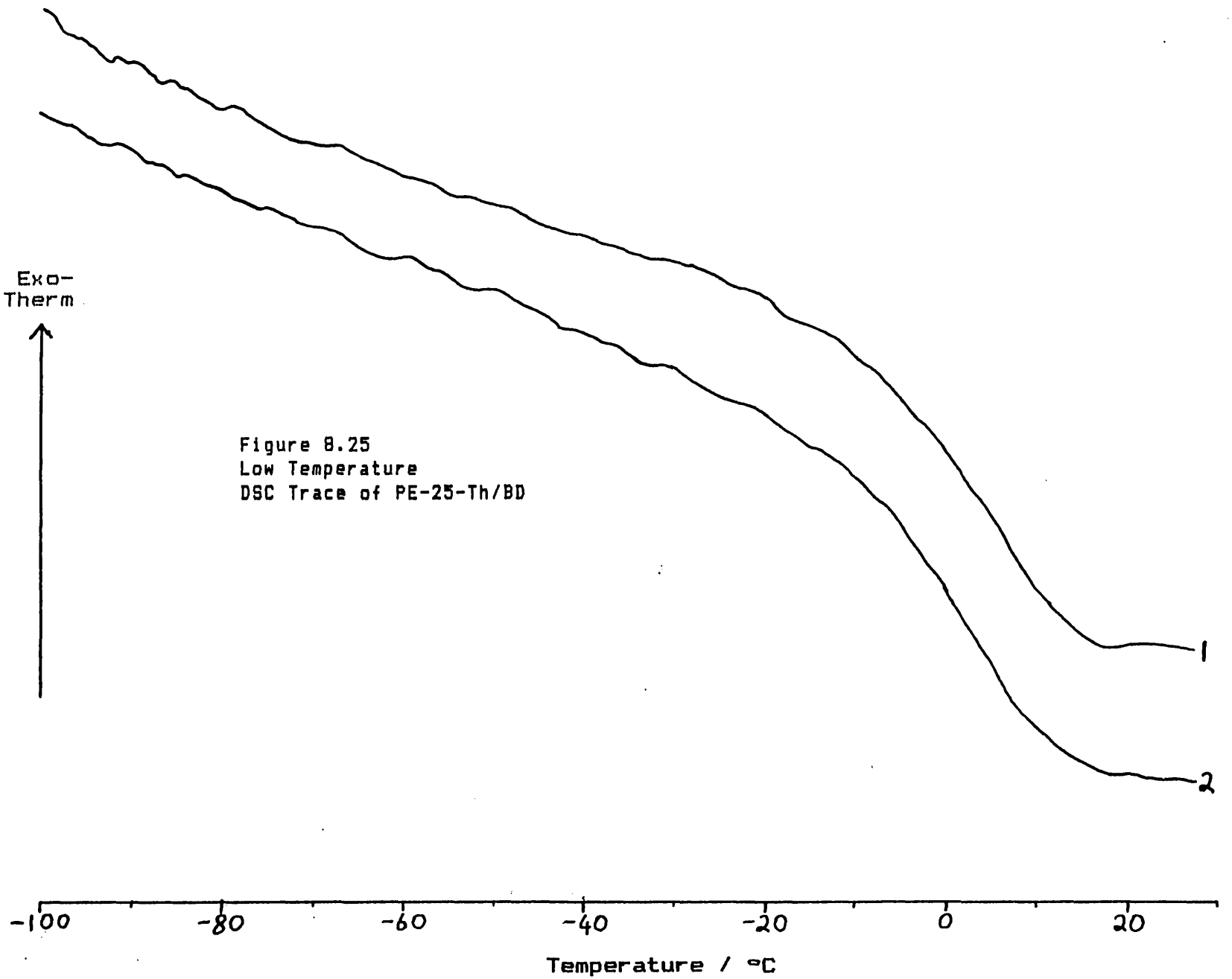


Figure 8.25
Low Temperature
DSC Trace of PE-25-Th/BD

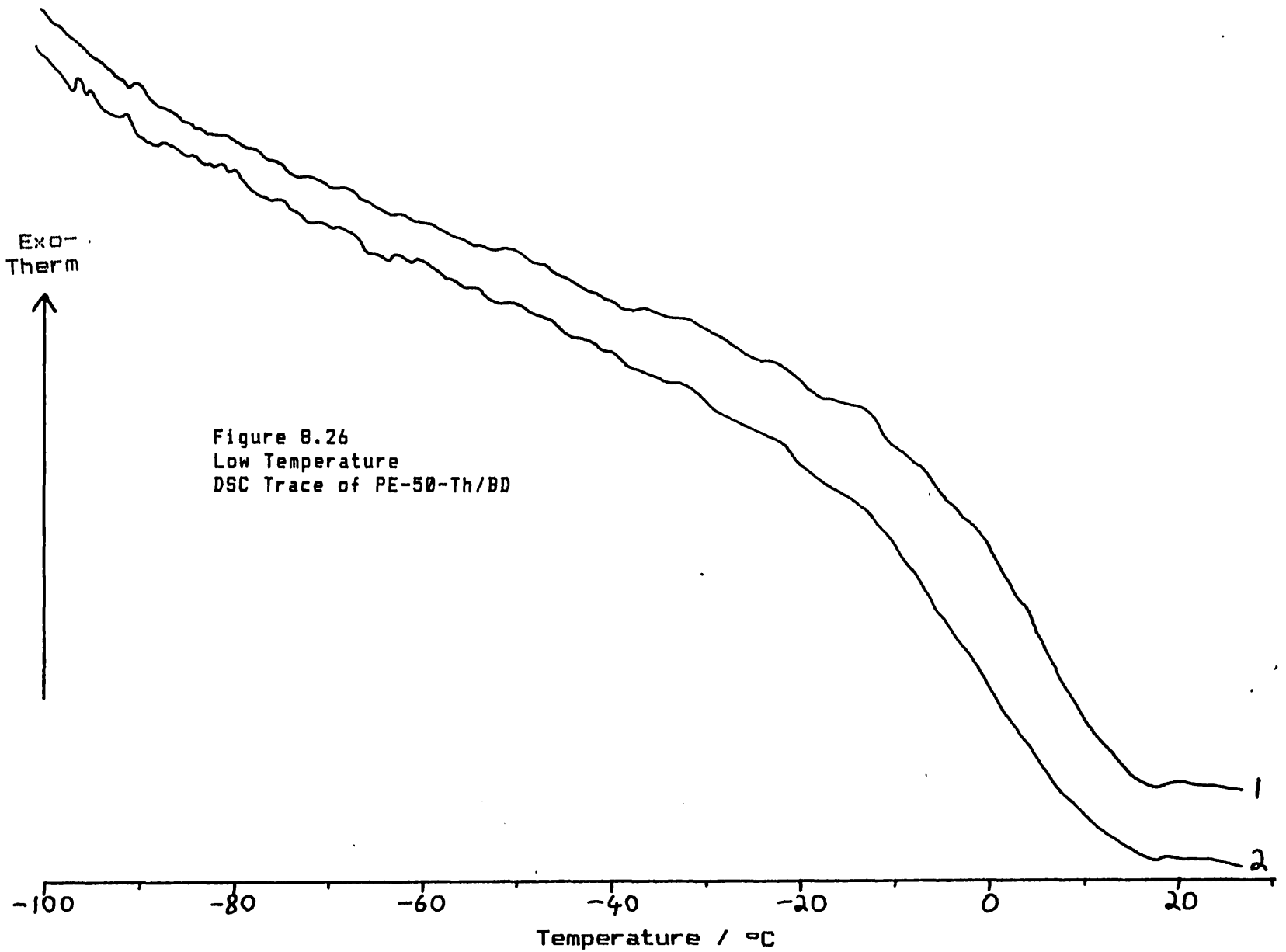


Figure 8.26
Low Temperature
DSC Trace of PE-50-Th/BD

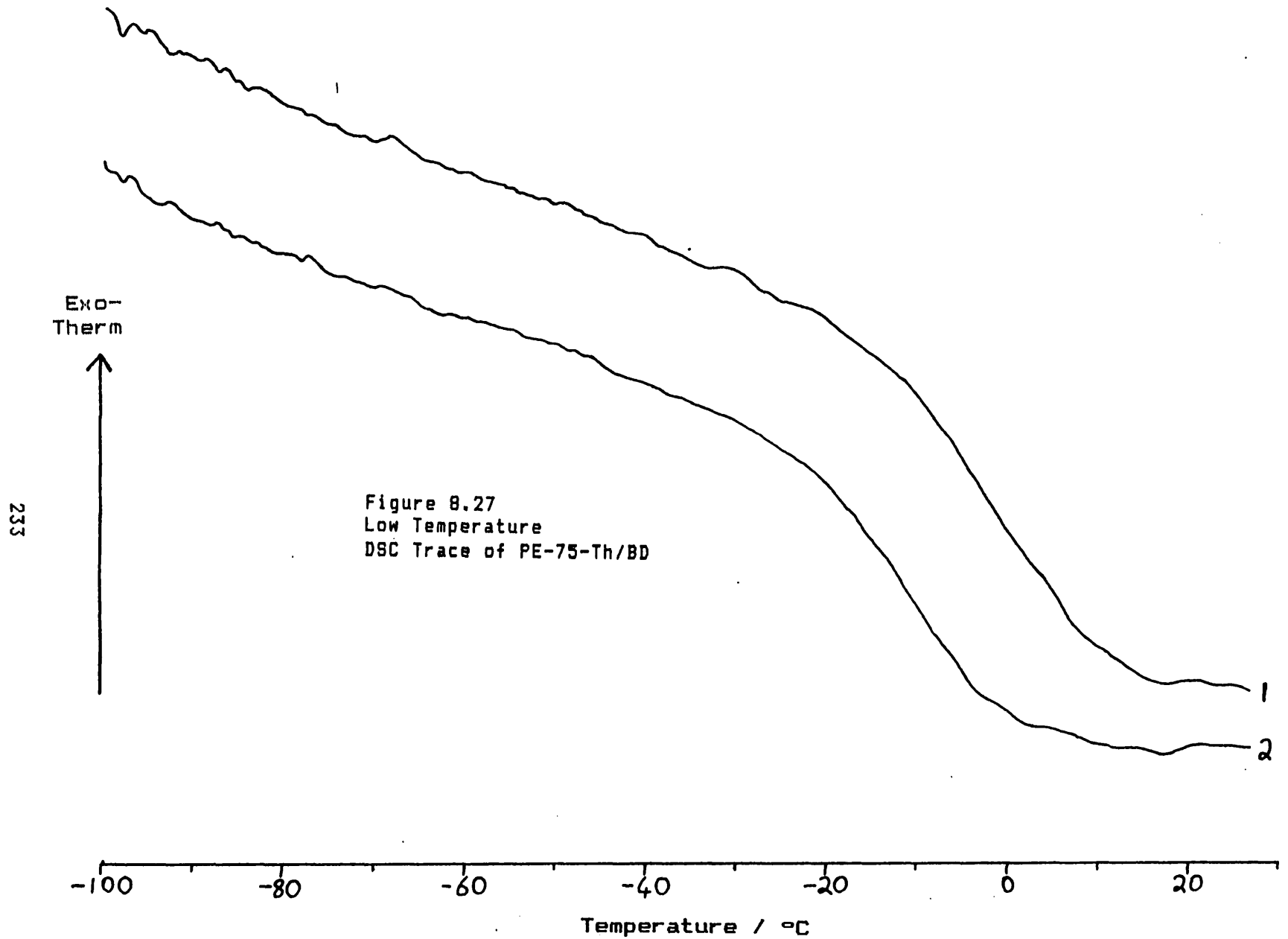


Figure 8.27
Low Temperature
DSC Trace of PE-75-Th/BD

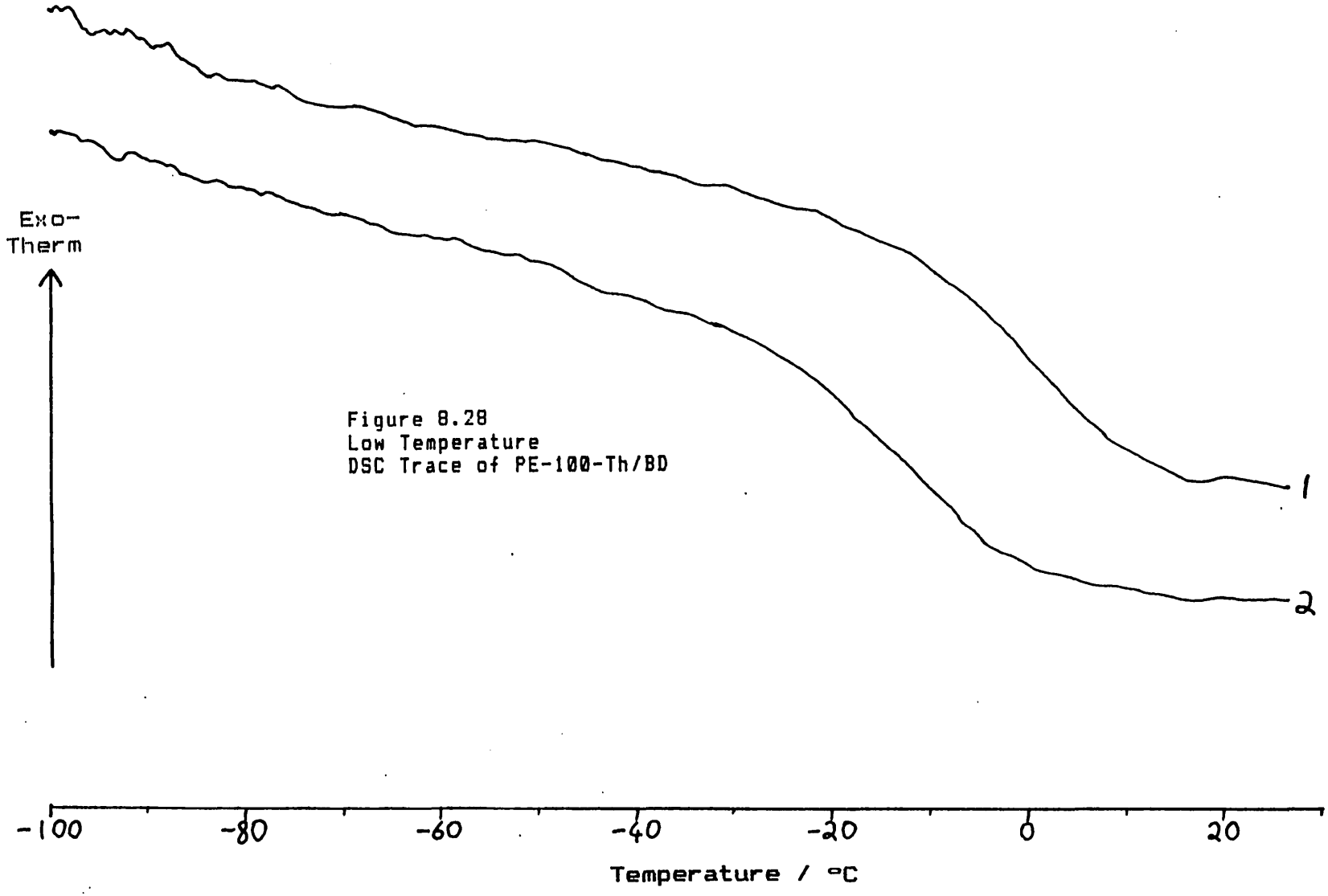


Figure 8.28
Low Temperature
DSC Trace of PE-100-Th/BD

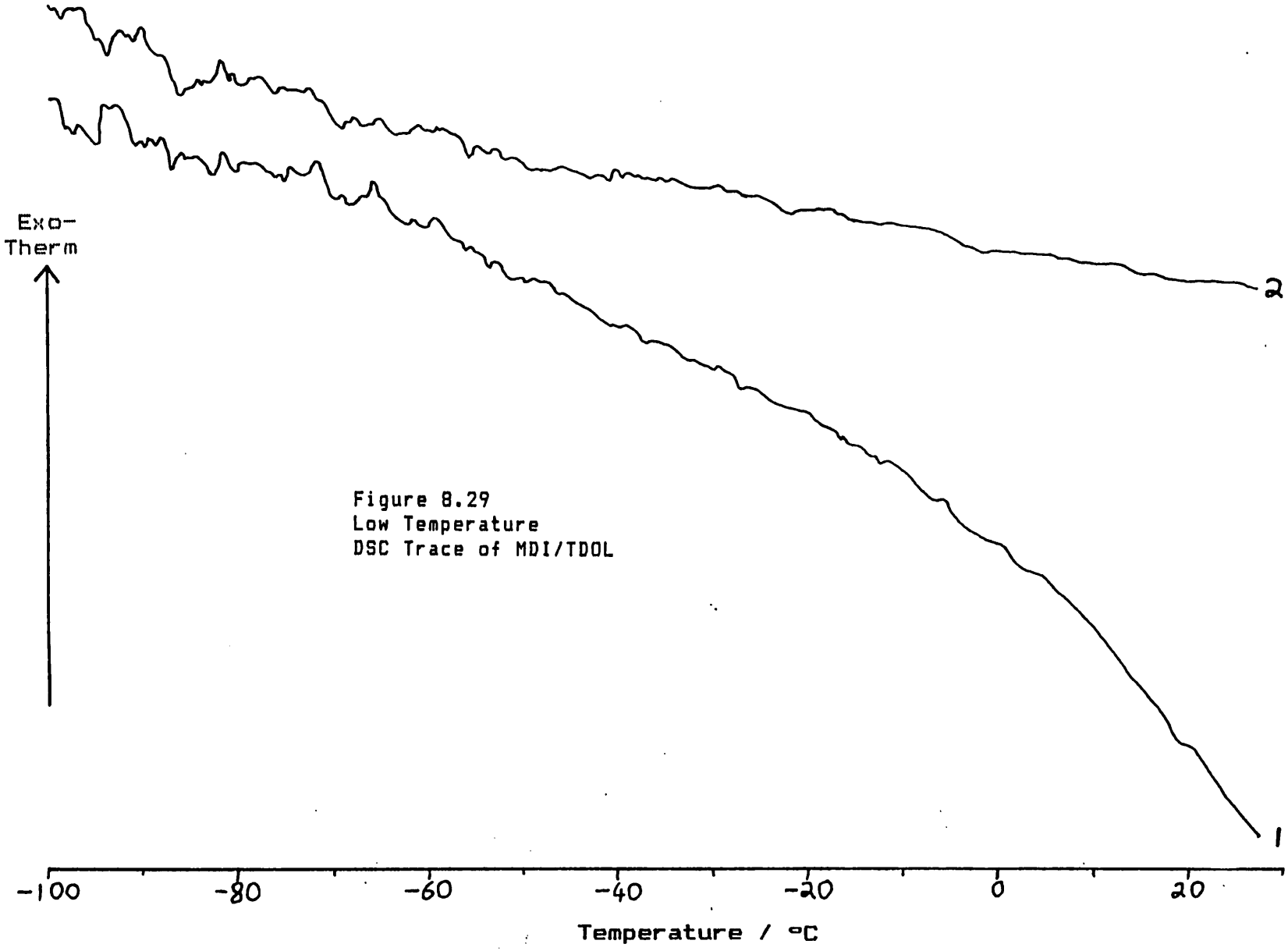


Figure 8.29
Low Temperature
DSC Trace of MDI/TDOL

Two trends are visible in the data.

Firstly, during its first run, the non ionic sample posesses a much higher degree of phase separation than any of the ionic samples. The ionomers all have a very similar transition width, of approximately 25^{o}C, and transition temperature, approximately +1^{o}C, on their first run. This compares with a width of 15^{o}C and a temperature of -11^{o}C for the non ionomer, indicating a smaller interfacial region and purer soft phase material.

At first sight, this appears to contradict the results of a number of workers, all of whom have reported improved phase separation with increased ionic content (see chapt 2.2.3). However, only one of these workers used a polyethylene glycol soft segment[39]. Furthermore, this literature example was a zwitterionomer in which the cation was a quaternary ammonium group on the polymer backbone and such a cation will not be complexed by a polyether. The literature thus contains no examples of polyurethane ionomers where an interaction opposing phase segregation can occur to a significant extent.

In the ionomers reported here, a proportion of the potassium counter ions of the ionic groups probably become complexed by the polyethylene glycol chains during the last stages of the film casting process, as the ionic groups are exposed to an increasingly non polar environment. This reduces the final degree of phase separation. Hence, an increased interfacial zone and a higher glass transition temperature are seen for the ionomers in their first run.

After the first run, samples were cooled and rerun. A consistent pattern for the second run was seen. The width of the

interfacial region remained unaltered for all the samples. The soft phase Tg fell with increasing ionic content, the non ionomer actually showing an increased Tg.

The increase in soft phase Tg coupled with the absence of any change in transition width seen for the non ionomer suggests that small hard domains have dissolved in the soft phase. Larger domains may have lost material into the soft phase, but continue to be surrounded by a fairly constant interfacial layer. This change most probably occurred at high temperature when the hard domains were near their melting transitions. Quenching for the second run was sufficiently fast to prevent re-separation of the dissolved hard segments.

Sample PE-25-Th/BD does not appear to show any change in Tg on the second run. This implies that no overall change in phase separation has occurred.

The remaining higher ionic content samples show increasing falls in soft phase Tg with ionic content.

Two mechanisms are probably operating within the ionomers. The first is the dissolution of conventional hard segments in the soft phase at high temperature as seen for the non ionomer.

The second is probably a migration of ionic groups from the soft phase towards the hard domains where the majority of the ionic groups have aggregated. This again will be temperature dependent as the groups will migrate more rapidly when there is more overall movement in the system. This effect will be larger with higher ionic content as there will be more ionic aggregates to attract the ionic groups in the soft phase and fewer

conventional non ionic hard domains. Hence, the higher ionic content materials gain better phase separation.

This ionic attraction of groups to the hard domains is almost exactly balanced by the dissolution of conventional hard block material in PE-25-Th/BD and is dominant in the other ionomers.

The interfacial region, as indicated by the width of the glass transition, does not change in width or composition to any great degree. This can be explained by considering the behaviour of the region as new ionic groups arrive.

The new groups arrive and their counter ions are initially still complexed by polyether chains. Their arrival, however, results in groups already in the region being shielded from the bulk of the soft phase allowing them to settle into the ionic aggregate. As they enter the increasingly polar ionic hard domain, the counter ion loses its complexing polyether chain, which moves towards the outer regions of the interface.

The regions can be regarded as a dynamic system where the arrival of new groups shifts the equilibrium of existing groups causing them to become a part of the bulk of the hard domain. The new groups form the new interfacial region. The region as a whole thus stays approximately constant in composition and width while the inner domain grows.

One further factor complicates the behaviour of the ionomers. This is the thermal decomposition of some of the thiosulphate groups at high temperatures. It is clear that substantial decomposition occurs (see sect. 8.5.3.2) giving a "precipitate" of sulphur in the polymer and rendering it

insoluble by disulphide crosslinking.

The crosslinking would be expected to reinforce the ionic hard domains and prevent their possible dissolution at high temperatures. The decomposition of the ionic groups in the soft phase would be expected to give some shift in the Tg. However, the higher ionic content materials would give rise to greater quantities of decomposition products including potassium salts which would be left in the soft phase. This would tend to reduce any fall in Tg caused by loss of the ionic group on the polymer chain and the increasing falls in Tg with increasing ionic content would not be seen. Also, the range of compositions across the interfacial region would be dramatically changed. Since no change in transition width was seen, it seems likely that, while important, the decomposition is not dominant in determining the rearrrangement occurring at high temperature. This would also imply that the rate of migration is significantly faster than the rate of decomposition. In the absence of further information on the rates of migration versus decomposition, no further conclusions can be drawn on the effects of the two processes.

8.5.3.2 The High Temperature Region.

The high temperature region (30 to 170^{o}C) gives little information when compared to the low temperature region, but gives some indication of the decomposition of the polymers.

Pure TDOL shows a strong endotherm peaking at 108^{o}C (Figure 8.30), probably due to the dissolution of TDOL in residual water of crystallisation followed by loss of this water. These two

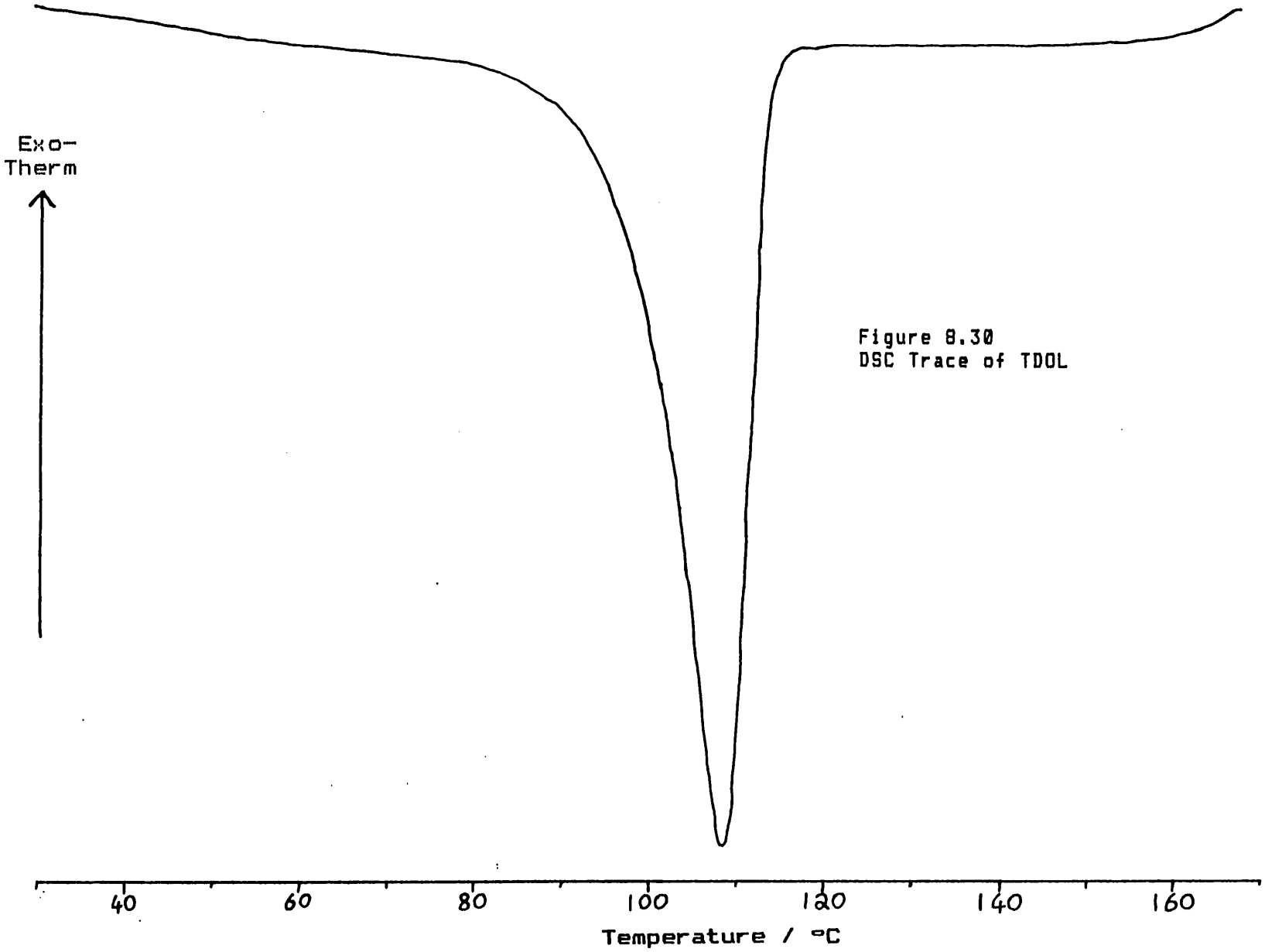


Figure 8.30
DSC Trace of TDOL

stages are reflected in the broad start of the peak, 85 to 108°C followed by the sharp cessation of the endothern at 115°C.

An exotherm starting at 155°C and rising sharply at 158°C may be the start of decomposition of the diol.

The high temperatures traces of the iomomers are all quite similar (Figures. 8.31-8.35)

PE-0-Th/BD, the non ionomer, shows only a very weak exotherm from 120 to 160°C.

PE-25-Th/BD shows a small exotherm between 150 and 170°C, peaking at 162°C.

PE-50-Th/BD displays a notable exotherm between 142 and 160°C with a broad peak top at 159°C.

PE-75-Th/BD has a strong exotherm from 129 to 159°C with peak maxima at 141 and 148°C.

PE-100-Th/BD shows a very strong exotherm from 135 to 170°C with two peaks at 147 and 155°C.

Upon being rerun, no features were visible for any of the samples.

The very weak exotherm seen for the non ionomer may represent decomposition of traces of allophanate in the material, such groups being less stable than urethane units.

The ion containing materials all display significant exotherms, the strength of which varies with ionic content. These almost certainly reflect the energy release from one or more complex decomposition mechanisms. There may also be a contribution from the rearrangement of ionic groups.

It is worth noting that the ionic groups appear to be much less stable in the polymer than in pure TDOL. They may undergo

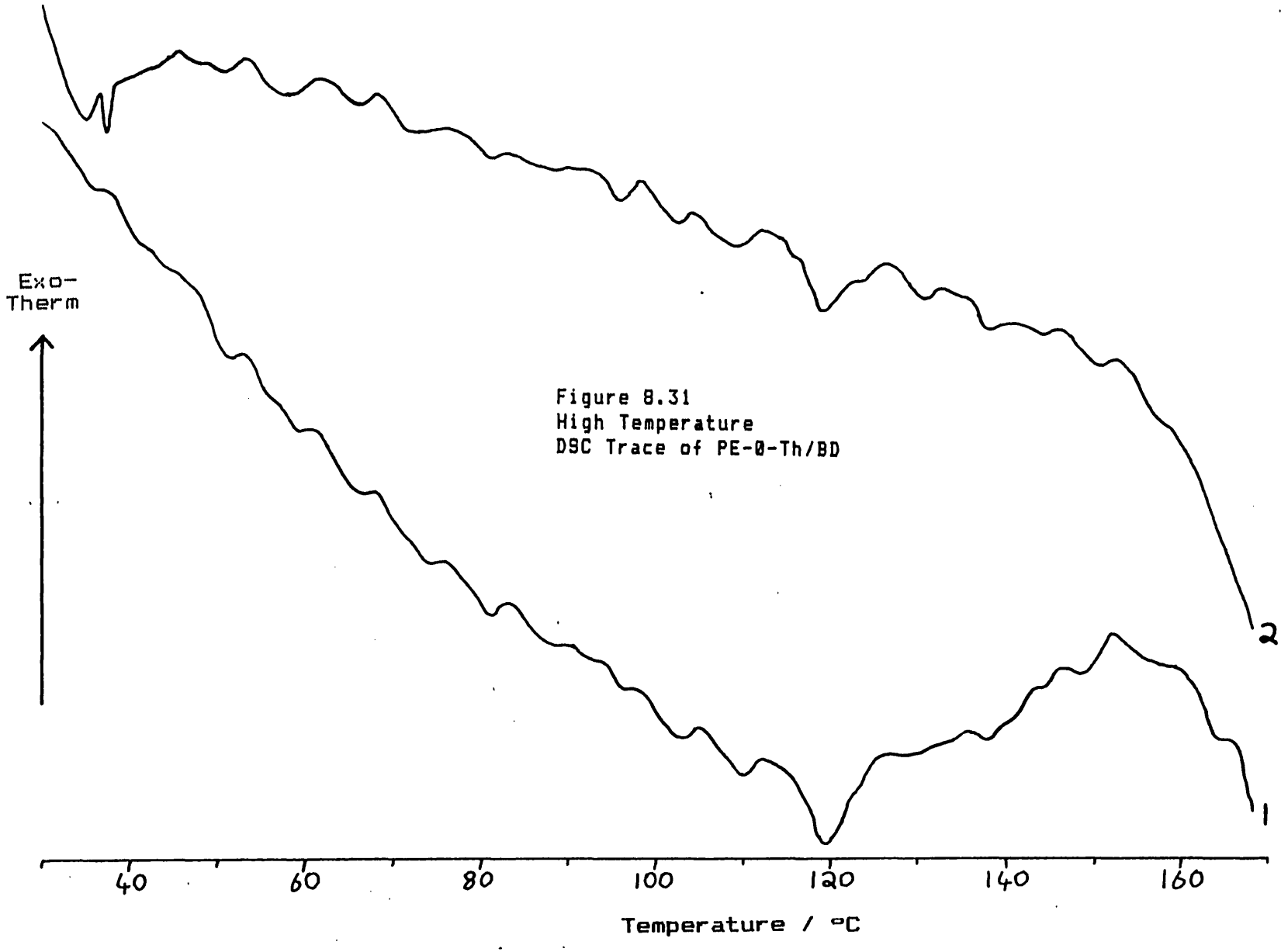


Figure 8.31
High Temperature
DSC Trace of PE-0-Th/BD

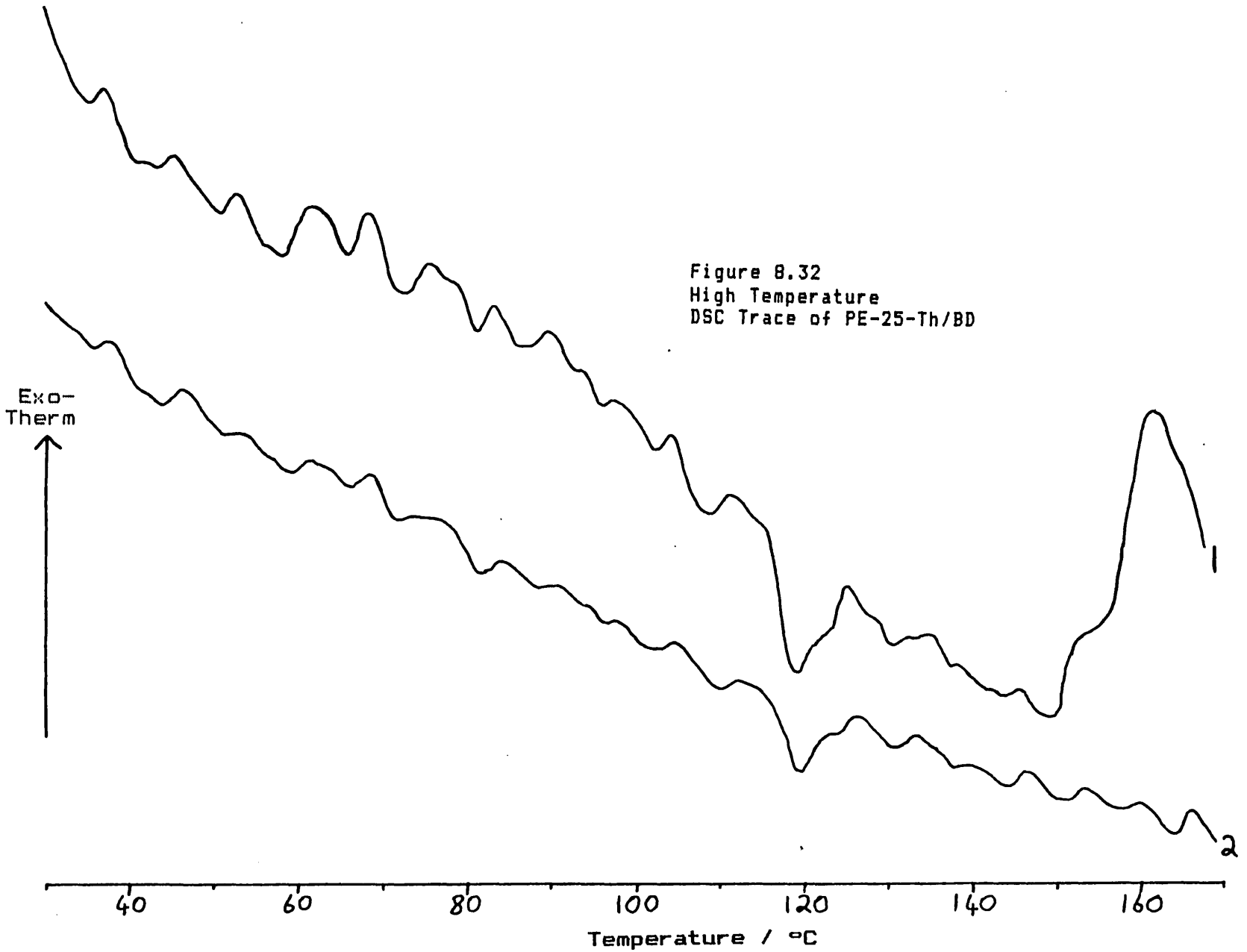


Figure 8.32
High Temperature
DSC Trace of PE-25-Th/BD

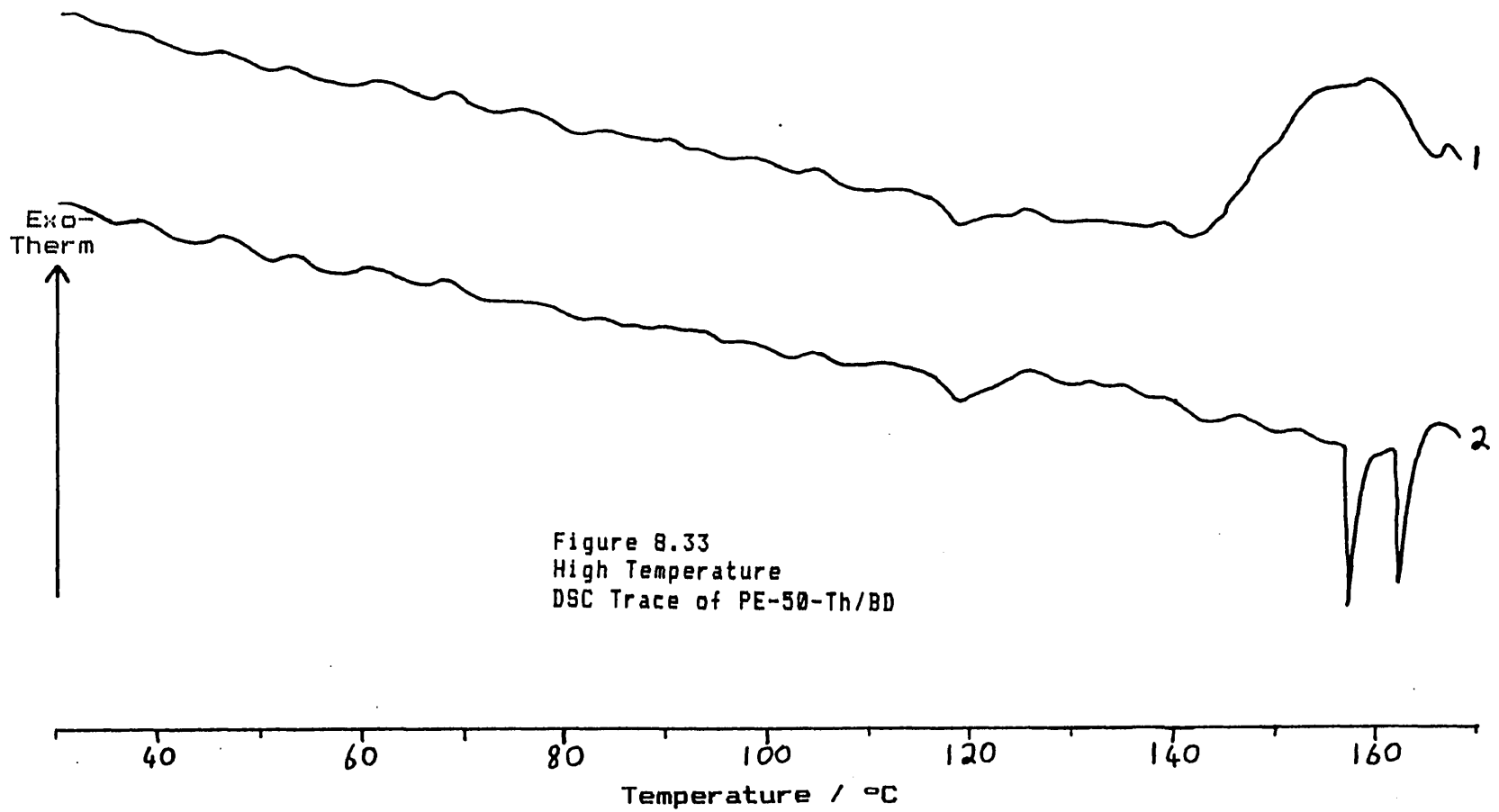


Figure 8.33
High Temperature
DSC Trace of PE-50-Th/BD

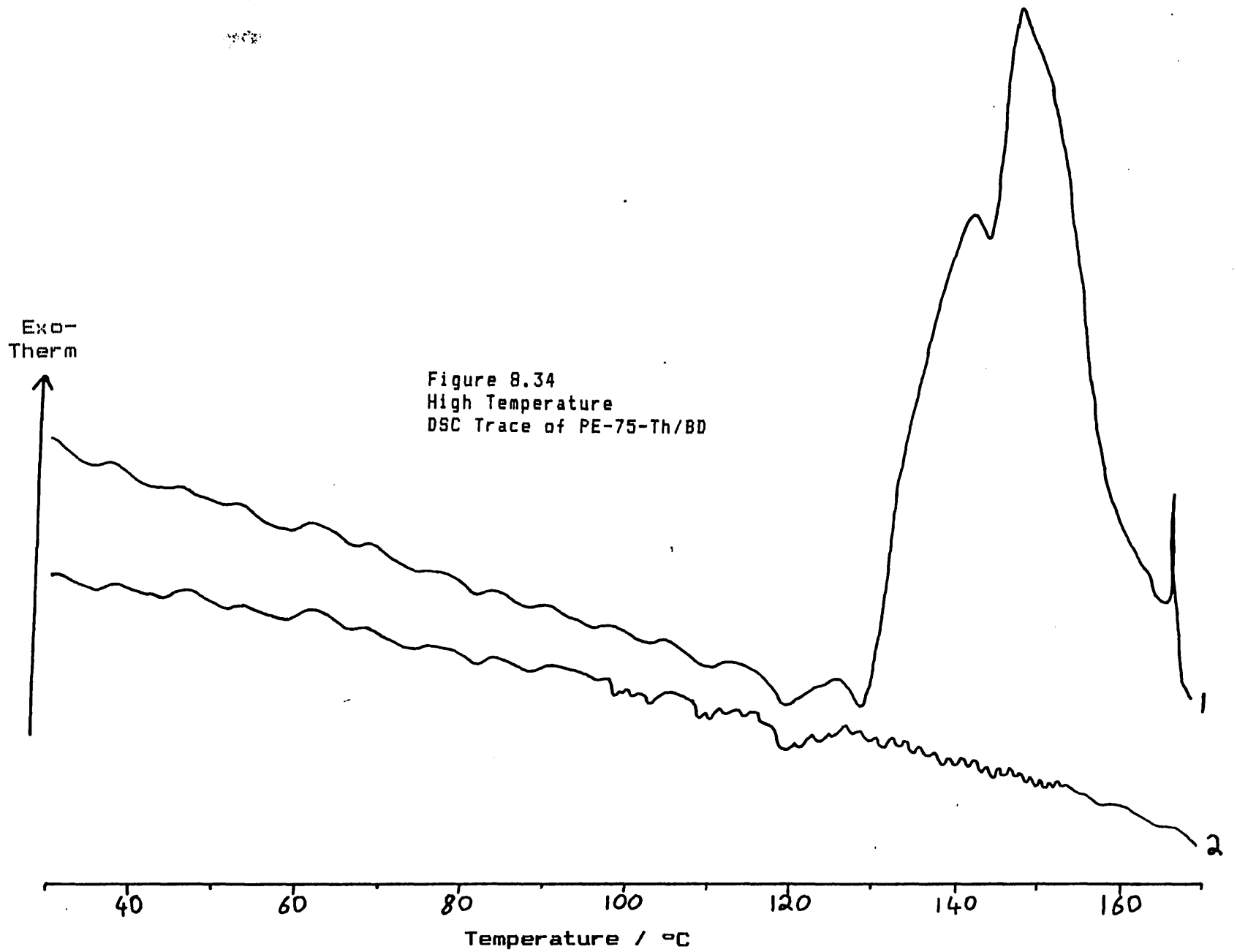


Figure 8.34
High Temperature
DSC Trace of PE-75-Th/BD

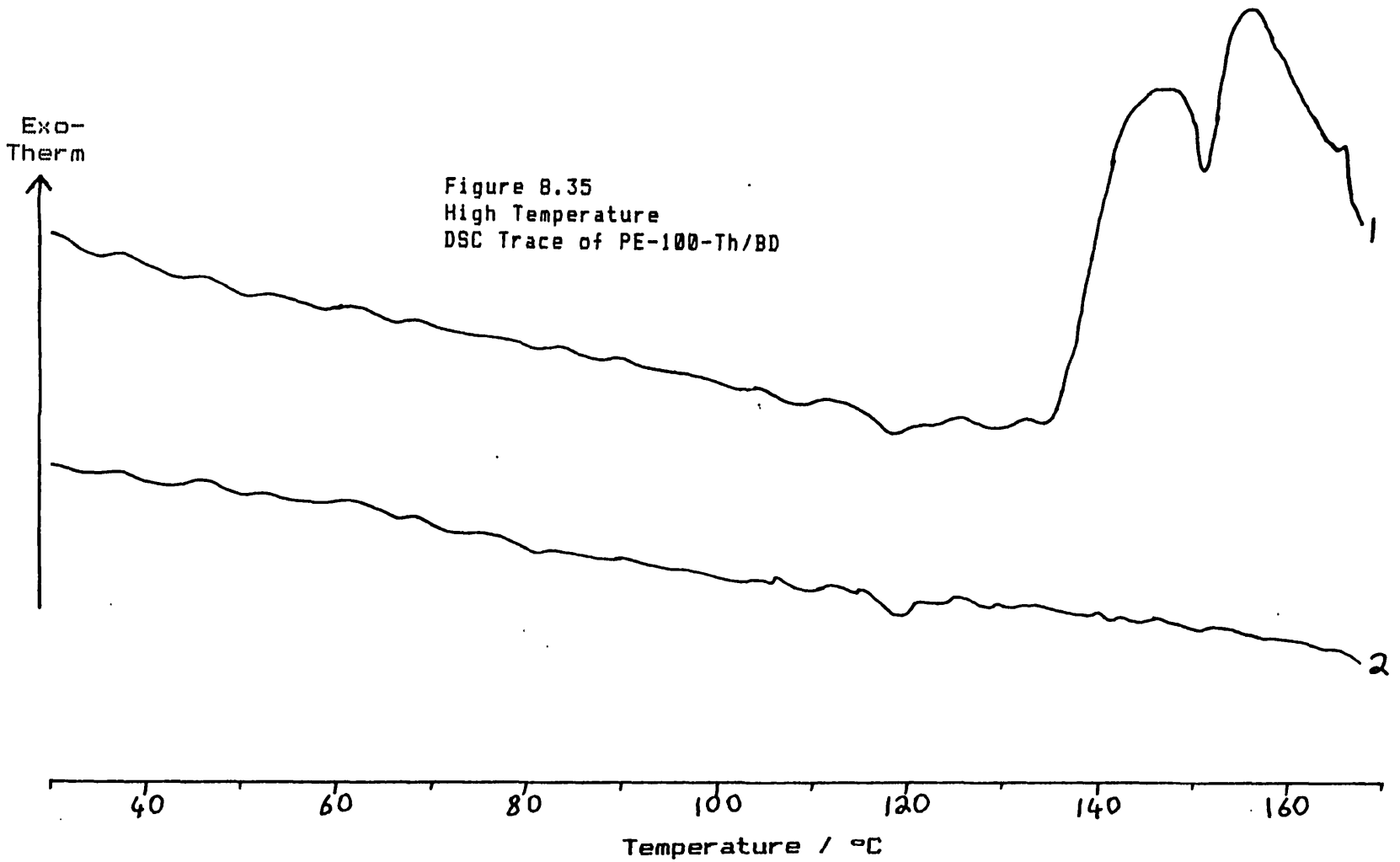


Figure 8.35
High Temperature
DSC Trace of PE-100-Th/BD

reaction with urethane groups or the environment may catalyse the decomposition. The exotherm shows two peaks, and varies in width, suggesting a number of different temperature dependent steps are occurring. There is no other evidence to allow identification of any of the steps.

The absence of any exotherm in the reruns of the samples suggests that any process has gone to completion during the first run. Whether all the ionic groups have decomposed or only those in particular surroundings is not clear. However, the materials were insoluble and did not swell greatly in water, indicating a considerable loss of ionic content. The materials PE-75-Th/BD and PE-100-Th/BD were also insoluble in DMF suggesting introduction of a fair number of crosslinks, probably by formation of disulphide bonds.

The high temperature trace of MDI/TDOL (Fig. 8.36) shows a decomposition exotherm from 148 to 170^{o}C with a peak at 163^{o}C and a shoulder at 155^{o}C. This is similar to the exotherms seen for the other ionomers and is absent on the rerun.

A very broad endotherm is present, with its minimum at 89^{o}C and may be due to some form of rearrangement or transition. It is replaced by an exotherm from 93 to 141^{o}C in the rerun. The cause of these features is not clear. They may reflect changes in ordering or possibly some form of motion allowing shifts of side groups to give more favourable orientations.

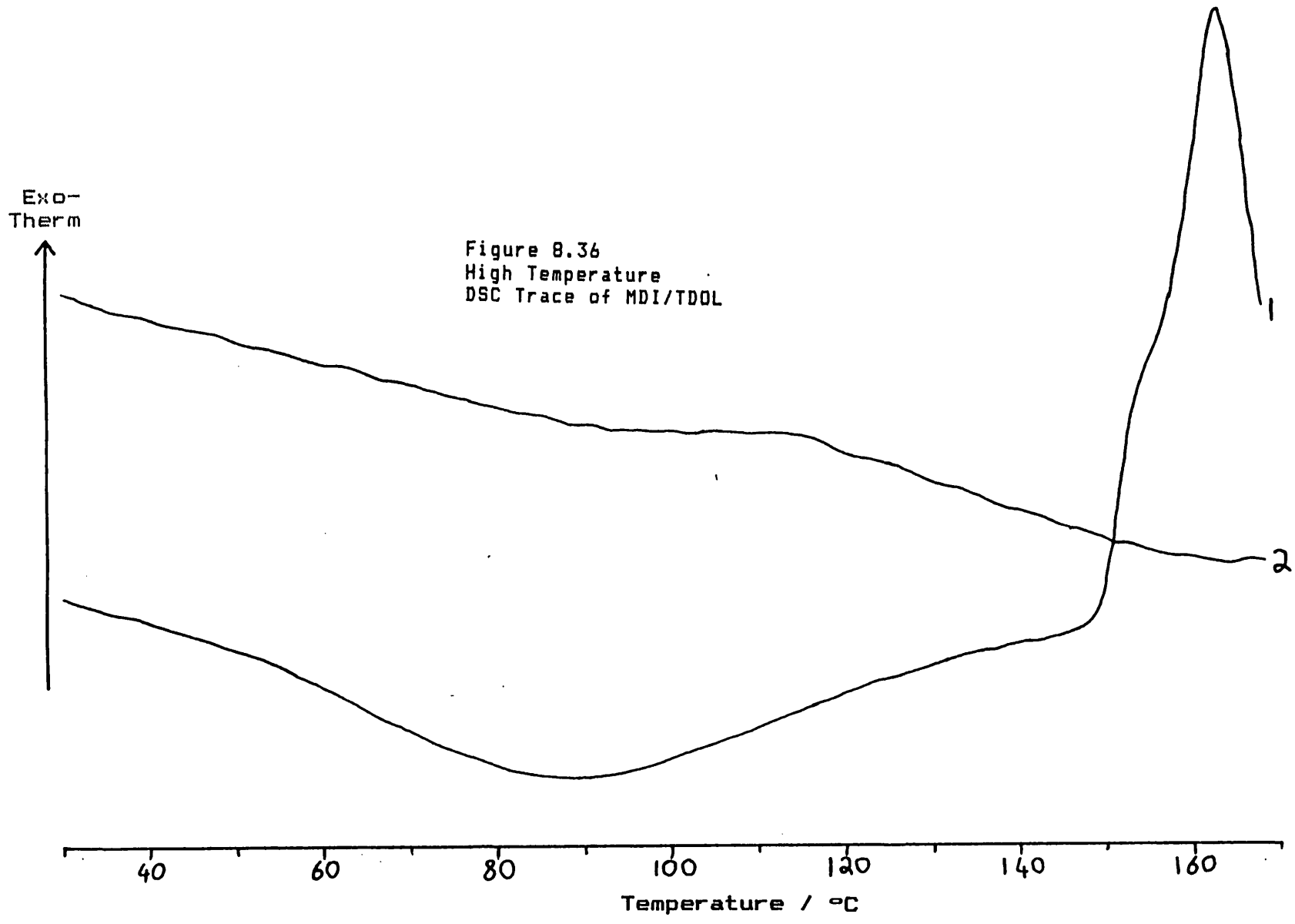


Figure 8.36
High Temperature
DSC Trace of MDI/TDOL

8.5.4 Tensile Testing.

The stress-strain curves of the PE-X-Th/BD series of polymers were all very similar in appearance, with an initial sharp rise in stress followed by a long shallow near linear region ended by failure of the sample. The initial rise and the region close to the failure point are shown in Figures 8.37 to 8.41 for PE-0-Th/BD to PE-100-Th/BD respectively, and the values for Youngs modulus at zero extension (calculated from the gradient of the curve at zero extension), ultimate tensile strength and elongation at break are given in table 8.5.

PE-100-Th/BD	Modulus (MPa)	Elongation at Break (%)	Ultimate Tensile Strength (MPa)
PE-0-Th/BD	3.134	983	1.628
PE-25-Th/BD	4.231	1300	1.227
PE-50-Th/BD	9.731	1160	1.884
PE-75-Th/BD	17.78	900	1.444
PE-100-Th/BD	22.33	943	1.229

Table 8.5 Mechanical properties of PE-X-Th/BD samples.

The stress on samples PE-50-Th/BD and PE-100-Th/BD fell slightly just prior to sample failure as the samples began to tear. The maximum stresses were 1.913 MPa at 1153% elongation for PE-50-Th/BD and 1.258 MPa at 933% elongation for PE-100-Th/BD.

No correlation between ultimate strength and elongation at break or between these values and ionic content was seen. This is to be expected as these results are from the testing of only one sample of each material and, more importantly, no sample cutter was available and parallel sided samples had to be cut. This

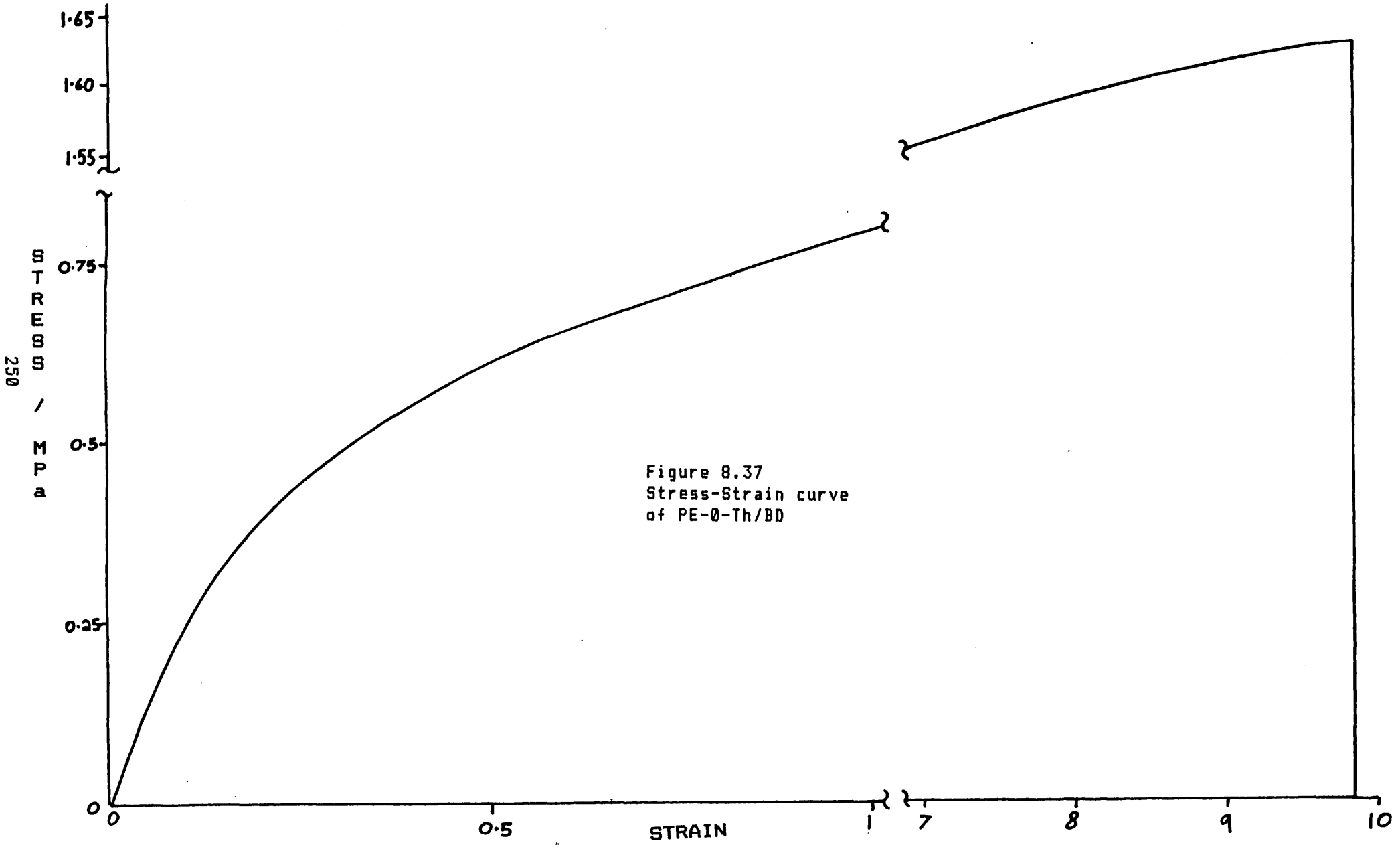


Figure 8.37
Stress-Strain curve
of PE-0-Th/BD

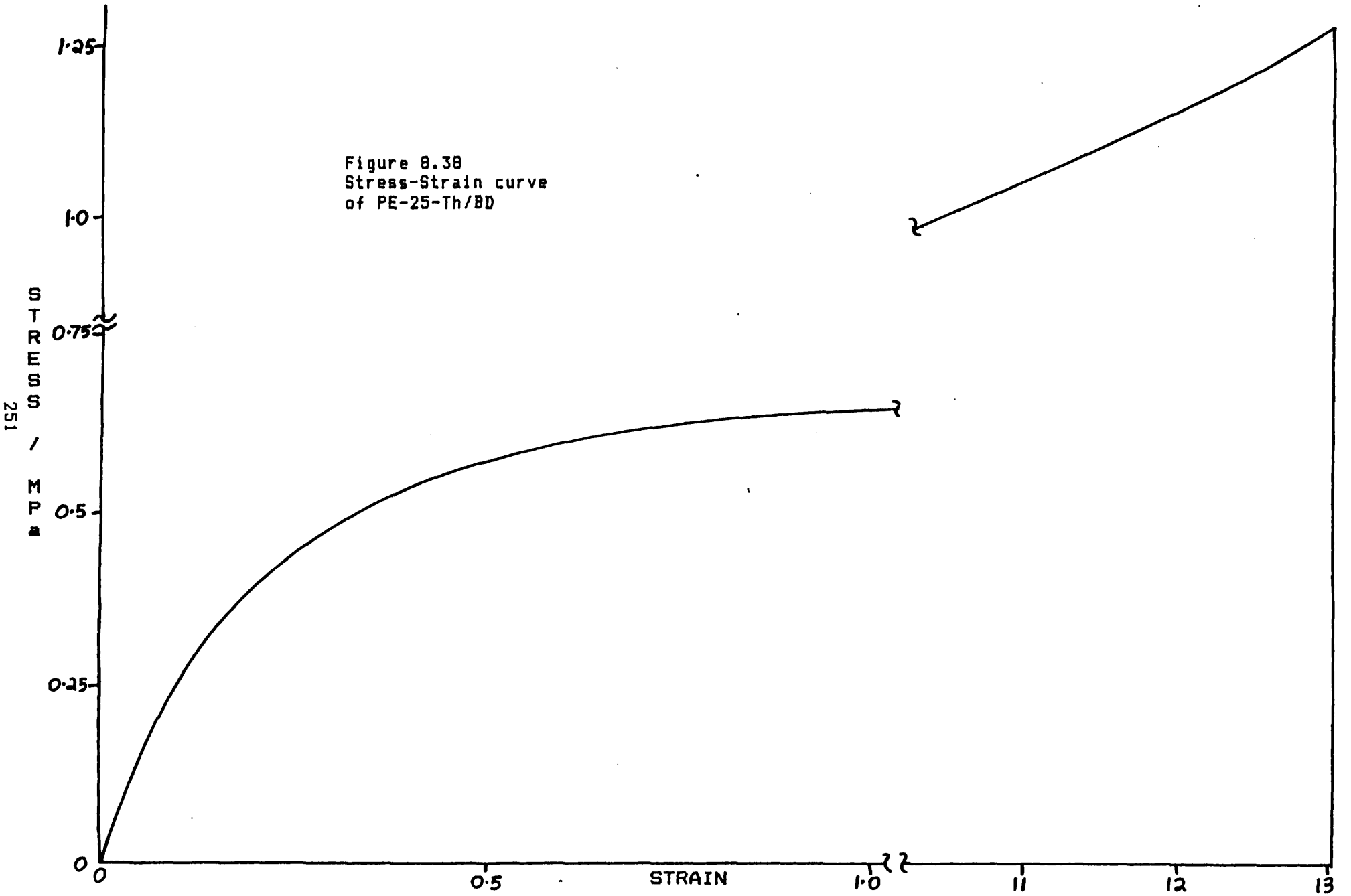


Figure 8.38
Stress-Strain curve
of PE-25-Th/BD

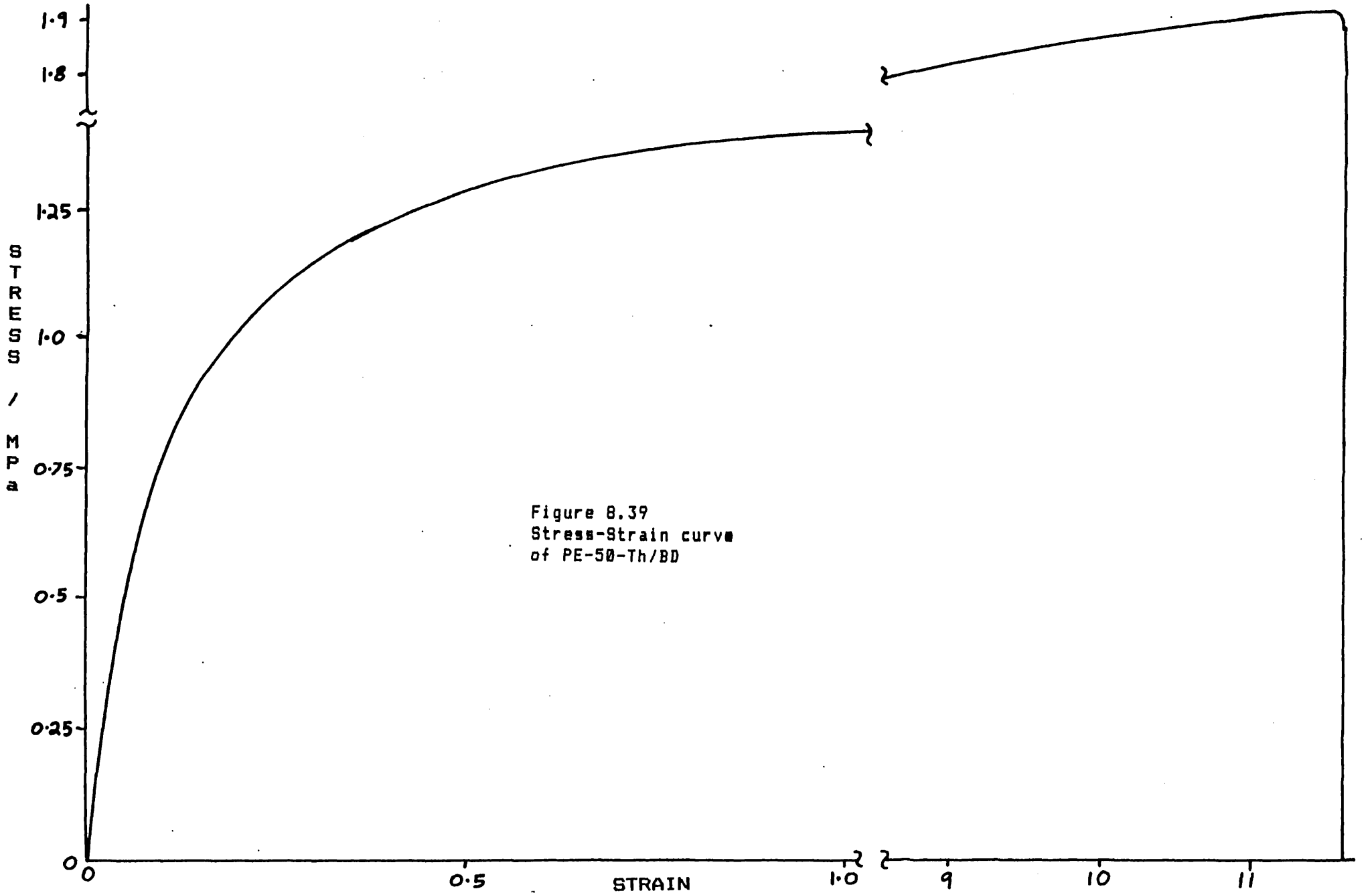


Figure 8.39
Stress-Strain curve
of PE-50-Th/BD

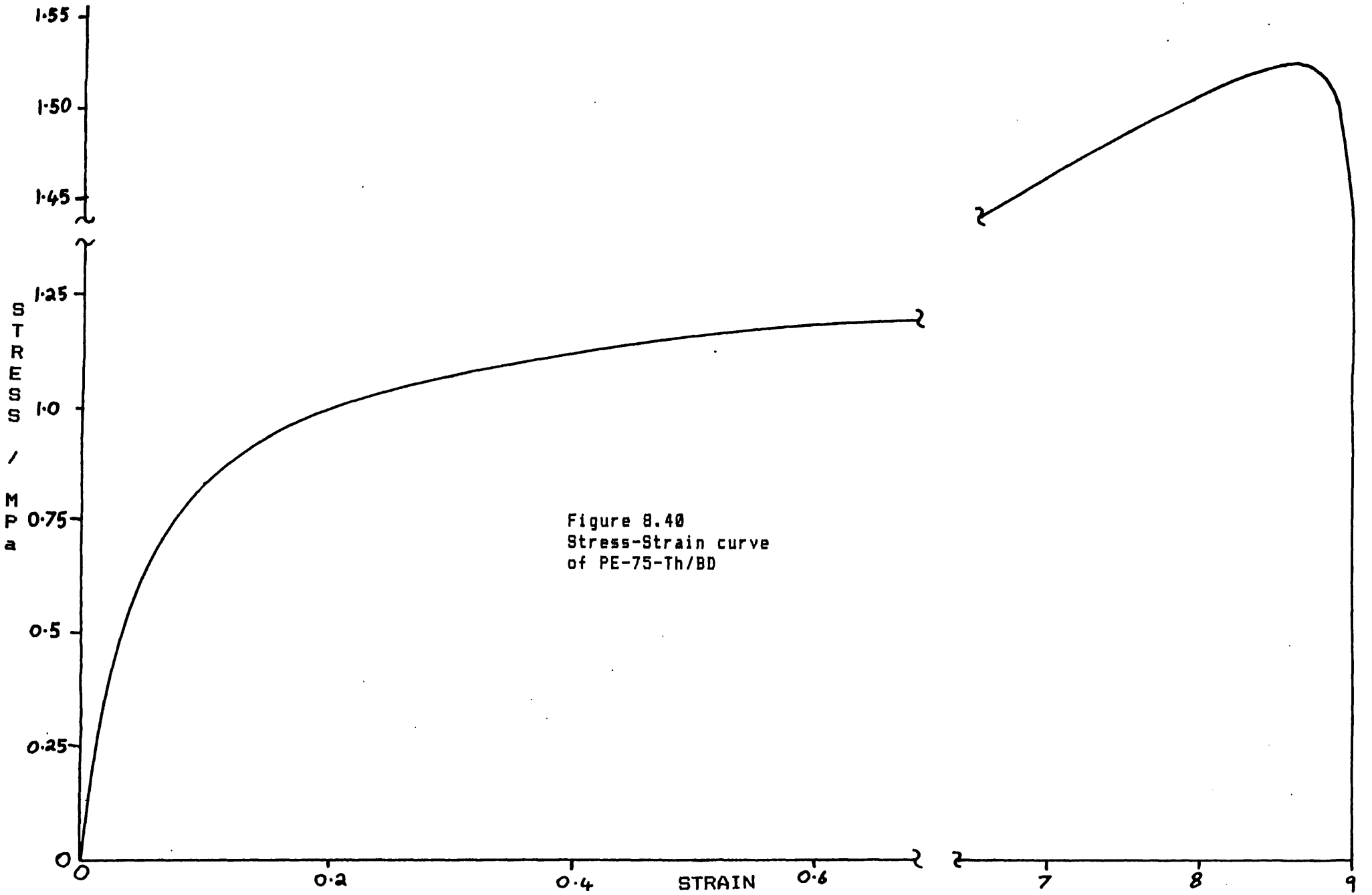


Figure 8.40
Stress-Strain curve
of PE-75-Th/BD

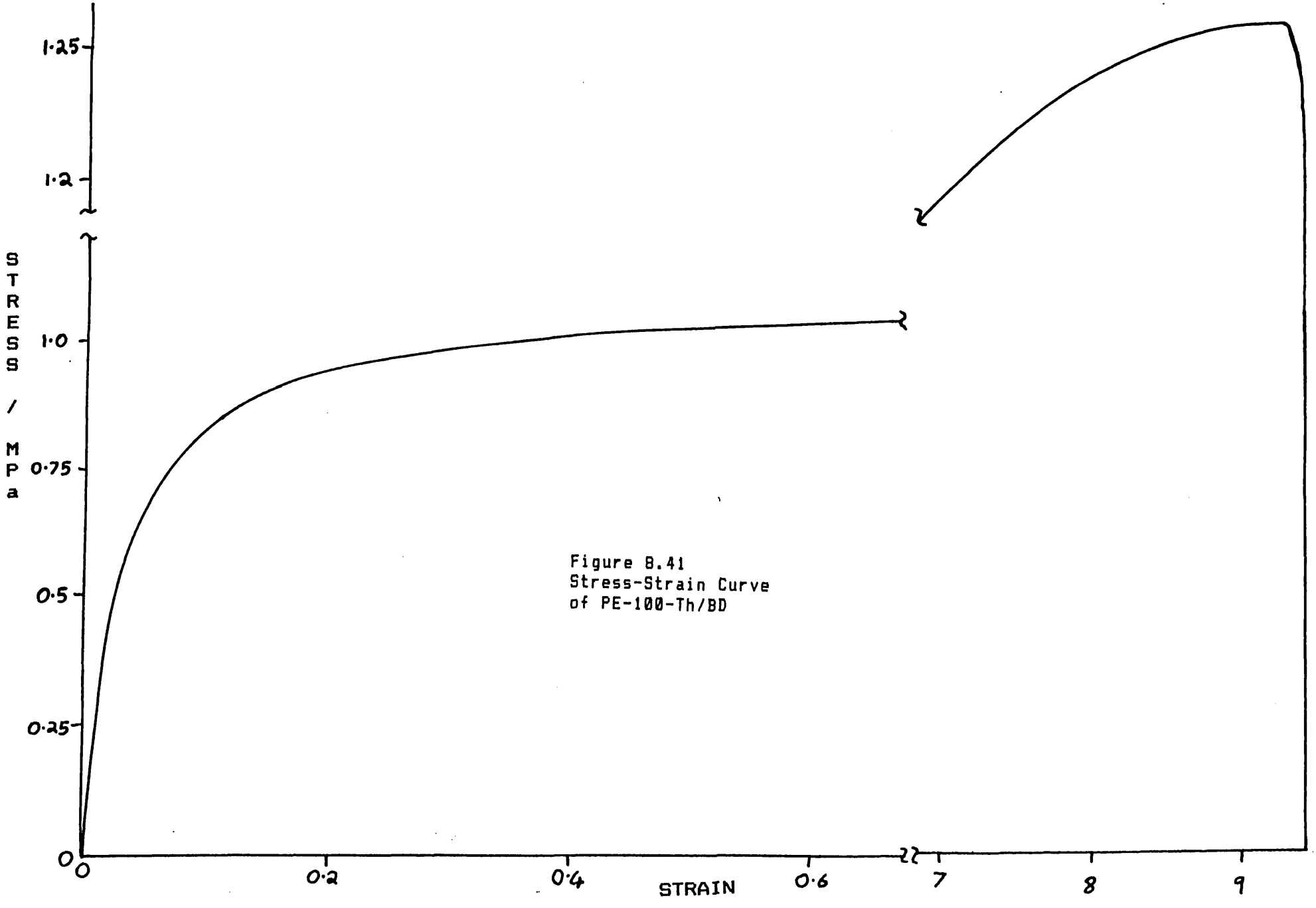


Figure 8.41
Stress-Strain Curve
of PE-100-Th/BD

introduces the likelihood of small nicks in the sample sides acting as weaknesses and centres for tearing to start from. In addition, weaknesses were probably introduced at the points of sample clamping and some of the samples did tear at the point of clamping. Both stress and strain at the breaking point are sensitive to the presence of these types of weaknesses.

Youngs modulus at zero extension is not affected by these problems as it is the gradient of the graph at zero extension and a clear relationship between modulus and ionic content was seen, the modulus increasing with increasing ionic content.

In addition, the region of irreversible extension is reached more rapidly for higher ionic contents. This region represents the end of elastomeric behaviour as hard domains start to be pulled apart and chains slide past each other.

These results are very similar to those obtained by other workers and the link between modulus and ionic content clearly reflects the increased strength of ionic interactions as opposed to hydrogen bonding interactions.

In his extensive work on anionomers and zwitterionomers (see chapt. 2.3.2 and 2.3.3), Cooper has suggested that, rather than discrete hard domains, an interconnected hard phase may exist.

This theory would explain the increased modulus and shorter extension required to reach an irreversible position and it is possible that ionic hard domains interact and become interconnected more readily than their non ionic counterparts. Under this theory, extension of the polymer would immediately stress not only the soft phase but also the hard phase. The more rigid the hard phase, the higher the modulus and the smaller the

extension needed to irreversibly damage it.

An alternative explanation might be that the hard domains act as crosslink sites and filler particles. The stronger the forces holding the domain together, the higher the modulus as extension pulls on the chains linked into the hard domain. In addition, the increased strength with which chains are linked to the domains would reduce the slippage of small numbers of chains as strain increased. This would have the effect of sharpening the divide between elastomeric and irreversible extension.

Finally, one further contibuting factor for the particular ionomers reported here may be the inclusion of ionic groups in the soft phase by polyether complexation of the counter ions. The presence of a small number of ionic groups interacting with each other in the soft phase would increase its strength somewhat. This would only be a minor effect overall when compared to the effects of the hard domain material.

8.6 Conclusions.

The development of a new ionic diol has led to a simple synthetic route to a new class of polyurethane anionomers.

These polmers show evidence of ionic hard domains that are less ordered than conventional hard domains but are held together by stronger forces. This renders the materials more susceptible to plasticisation but also gives very considerable improvements in mechanical properties.

For the first time, some evidence for interaction between the polyethylene glycol segments and potassium cations associated with the ionomer has been seen and the material may find

applications where electrical conductivity is required, either as a solid or in solutions.

These ionomers may be formulated to be water soluble and show complex behaviour in both aqueous and organic solutions and excellent selectivity between liquids of differing polarity is indicated by the solvent uptakes.

Although thermal and photochemical degradation may limit long term applications, the potential for these materials in the future is most promising.

9 Ionic Macromonomers.

9.1 Introduction.

The development of a versatile photocrosslinkable system has been described in chapter 7. This system has one major drawback when used for enzyme immobilisation, namely that it requires the use of an organic solvent or organic/water mixtures. This greatly limits its use with enzymes as many are denatured by the conformational changes that take place in organic as opposed to aqueous solutions. In addition, enzymes may carry a large number of charged groups, rendering them insoluble in organic solvents and making it difficult to obtain a homogeneous distribution of enzyme throughout a membrane.

The creation of a new polyurethane ionomer system, described in chapter 8, has given rise to readily water soluble polyurethanes. The combination of these ionomers with the end-capping process used to synthesise the macromonomers should therefore provide a route to a water soluble photocrosslinkable system.

9.2 Effect of TDOL on Radical Polymerisation.

The first step towards creating a radically reactive polyurethane based on TDOL was to check that TDOL itself had no adverse effects on a radical polymerisation.

A simple experiment consisting of 3 reactive mixtures was set up (see chapt4.6.3), the only difference between the mixtures being the presence of 0, 1 and 10 mole% of TDOL with respect to methyl methacrylate in the solutions.

The gel permeation chromatograms of the polymethyl methacrylate formed in each of the solutions are shown in figure

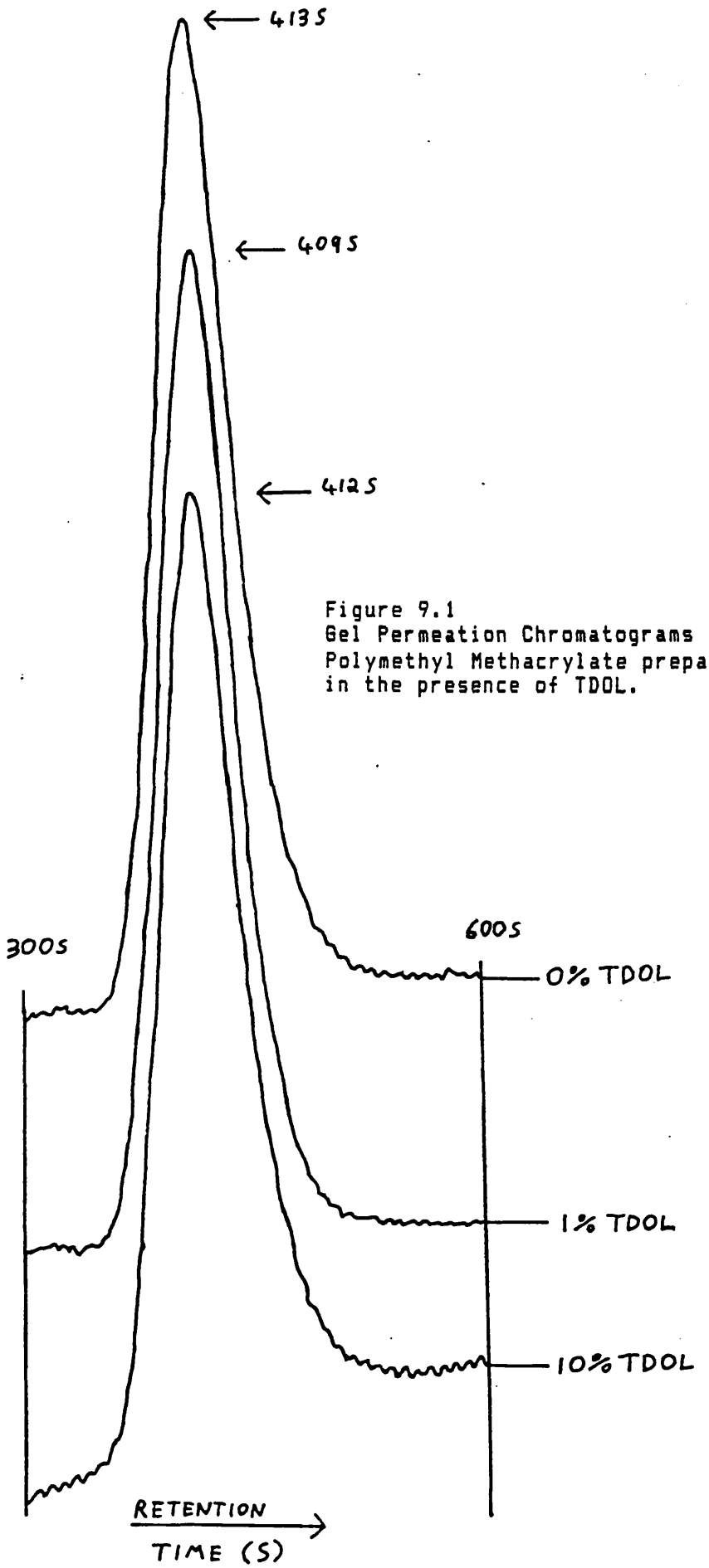


Figure 9.1
Gel Permeation Chromatograms of Polymethyl Methacrylate prepared in the presence of TDOL.

9.1. It is clear that neither the alkyl thiosulphate nor any decomposition products that might have formed under the experimental conditions (65^{o}C for 24 hours) have interfered with the reaction.

Thus, the use of TDOL based macromonomers should not present any problems with regard to unwanted chain transfer or termination steps in a radical polymerisation.

9.3 Polymer Synthesis and Characterisation.

In order to prepare a macromonomer comparable to PUIEM(1000), but with maximum water solubility, a monomer ratio of MDI:TDOL:PEG1000:IEM of 8:6:3:2 was used. Except for the use of TDOL instead of butane diol, this was identical to the formulation of PUIEM(1000). The resultant polymer was designated PUTDOL/IEM.

A control polymer, PUTDOL, of identical formulation except for the absence of the radically reacive IEM units was also prepared. See chapter 4.6.1 for details.

The need for short drying times for the macromonomers, in order to avoid premature crosslinking, was especially difficult for PUTDOL/IEM which, like the other ionomers, retained DMSO and DMF tenaciously. This problem was overcome by isolating the macromonomer by phase separation from dichloromethane. The DMSO or DMF was lost to the bulk of the DCM, which was decanted. The viscous oil, consisting of the polymer and a considerable quantity of DCM, was rapidly dried in vacuo. The rapid rate of boiling of the DCM at room temperature in vacuo caused the oil to foam. As a result, a very high surface area to volume ratio was

obtained and the dry brittle polyurethane foam could be easily crushed and stored after 24 hours.

The foam was observed to be somewhat hydroscopic, becoming sticky after exposure to atmospheric moisture for more than half an hour.

Both PUTDOL and PUTDOL/IEM displayed the same characteristics as PE-100-Th/BD with respect to solution behaviour, spectroscopy and GPC. PUTDOL/IEM also displayed spectral details due to its unsaturated units. The DSC thermograms of a PUTDOL film cast from DMF were identical to those of PE-100-Th/BD. DSC traces of PUTDOL/IEM were not run as reactions involving the unsatuated groups and effects due to the changing and uncertain degree of crosslinking would have given uninterpretable results.

The reader is referred to chapter 8 for an in depth discussion of the properties of these types of ionomer.

9.4 Test Polymerisations of PUTDOL/IEM.

9.4.1 Photochemical Polymerisation in DMF.

An attempt was made to prepare a crosslinked sample of polyPUTDOL/IEM that would be directly comparable with polyPUIEM(1000). The experimental details are given in chapter 4.6.6.

No samples suitable for testing were obtained due to the strong retention of DMF in the gel, the material remaining plasticised despite several weeks drying in vacuo. The approach of swelling the material in THF to allow the DMF to diffuse out and the removal of the volatile THF by evaporation, which was used for the non-ionic crosslinked samples, could not be used

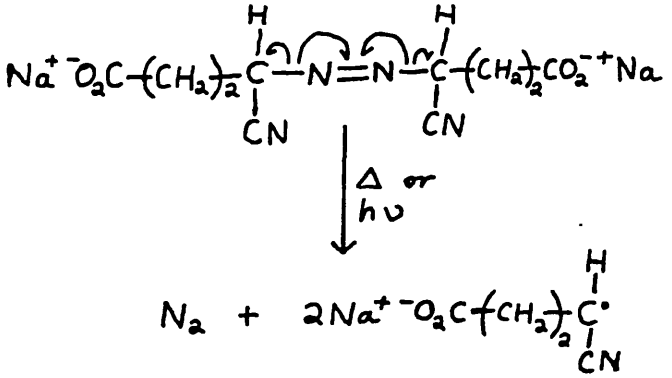
because of the incompatibility of the ionic groups with THF.

9.4.2 Thermal Polymerisation in Water.

A quick test on the use of PUTDOL/IEM as a monomer for free radical polymerisation in water was carried out as detailed in section 4.6.5.

A firm gel was obtained and, while somewhat swellable, it showed no inclination to dissolve or break down in either DMF or water. It therefore seems likely that a high degree of crosslinking was obtained.

The gel was observed to contain some entrapped bubbles of gas. These probably arose from liberation of nitrogen from decomposition of the initiator (see equation 9.1). Once the viscosity of the reaction mixture had become high and after gellation, gas bubbles could not escape by rising through the solution. Hence the presence of bubbles "frozen" in the gel.



Decomposition of sodium 4,4'-azo-bis-cyanopentanoate...Equation 9.1

The initiator used was the disodium salt of azo-bis-cyanopentanoic acid and was chosen because of its high solubility in water at neutral or alkaline pH and because it could be used both as a thermal and as a photochemical initiator. It was prepared from the free acid as described in section 4.6.2.

Because of the need to form a homogeneous solution of initiator and macromonomer in a reasonable time (<1 hour), the initiator was dissolved before the macromonomer. Attempts to dissolve the initiator in a solution of macromonomer required excessive lengths of time to form a homogeneous solution. See also chapter 8.4.5 for a description of the effects of addition of salts to aqueous ionomer solutions.

9.5 Photochemically Crosslinked Test Samples.

9.5.1 Sample Preparation.

Following the success of the thermally initiated aqueous solution polymerisation, the preparation of photochemically crosslinked samples was investigated.

Firstly, a macromonomer concentration of 25% w/v in water was selected. This was a compromise between the need for a manageable viscosity and a high monomer concentration. This concentration also allowed sufficient leeway for the effects of adding the comonomers acrylamide and n-vinyl-pyrollidine to the solution. Section 8.4.4 deals with the viscosity trends seen for this type of ionomer.

Three samples were successfully prepared and Na_2ACV was used as the photochemical initiator. These samples were the homopolymer, poly(PUTDOL/IEM), and two copolymers, poly(PUTDOL/IEM-co-NVP) and poly(PUTDOL/IEM-co-ACM). See section 4.6.7 for details. As was the case for thermal initiation using Na_2ACV, small gas bubbles became entrapped in the gel as the reaction progressed.

The gels were dried in a dessicator for 24 hours over silica gel before the sides of the sample were released from the side

walls of the reaction vessel. If attempts were made to release the sample without any drying, there was a risk of tearing and damaging the film. Conversely, extended drying before releasing the sample introduces the risk that the dry brittle sample may shatter. After release, drying of the samples was completed in a dessicator and then in vacuo.

Tensile tests were not performed on any of the samples because of the presence of the small gas bubbles. These major flaws in the samples would have adversely affected the results of such tests.

No results are reported for poly(PUTDOL/IEM-co-NVP) as the sample was lost through accident and there was insufficient time to prepare, dry and test a replacement.

The brittleness of the dry samples is in stark contrast to the elastomeric nature of this type of material when prepared from DMF solutions and must represent a major difference in morphology. This is discussed in section 9.5.3.

9.5.2 Equilibrium Solvent Uptakes.

Equilibrium uptakes of ethanol and water were measured for both the homopolymer and the acrylamide copolymer.

9.5.2.1 Equilibrium Water Uptake.

The rapid uptake of water coupled with the dramatic swelling of the samples and, in the case of poly(PUTDOL/IEM), the loss of all mechanical strength meant that regular weighing of the samples was not possible. Instead, the samples were allowed 7 days to come to equilibrium. In view of the high water solubility of the original macromonomer, this timespan is probably more than

sufficient.

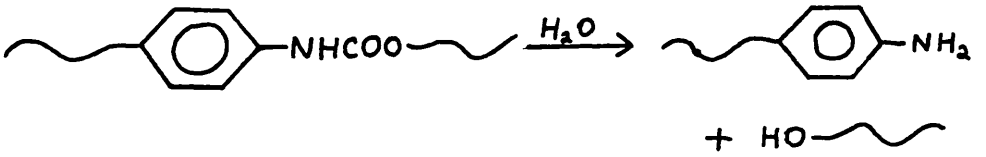
Poly(PUTDOL/IEM) had collapsed into a weak gel after less than an hour and, after a week, had also become slightly orange, as had the surrounding water. The uptakes of the two samples of this material were 586 and 640%. This high uptake value, the poor agreement between the two samples, the weak heavily swollen lumps and the presence of an orangeish tinge in both sample and water suggest a low degree of crosslinking with unreacted macromonomer remaining in the sample. Hence, when the material is immersed in water, it swells massively and the unreacted material starts to diffuse out. The poor agreement in uptake value between the two samples is caused by the differing losses of unreacted material from the two samples and probably also from the loss of small gel particles during the weighing process. The orangeish tinge in the sample occurs only in water and is probably due to hydrolysis of some of the urethane groups. The presence of this tinge in the water as well as the sample indicates the presence of dissolved polyurethane in the water. The existence of the large quantity of insolble gel, however weak, does prove that the crosslinking reaction had taken place to a degree. Higher degrees of conversion and crosslinking could easily be obtained by increasing the initiator concentration.

Poly(PUTDOL/IEM-co-ACM) was synthesised with a higher initiator concentration and, because of the presence of the comonomer, had a higher overall monomer concentration. As a result, a higher degree of crosslinking was obtained. After one week, the sample was heavily swollen but could be handled with care and was elastomeric. The sample was slightly orange in

colour. The water in contact with the sample was colourless. Good agreement was obtained between the two specimens studied (469 and 479%) and the high uptake value reflects the compatibility of the chains of the network with water.

The colouration present in the samples developed during the week the samples were immersed in water and is most probaly due to formation of aromatic amines by hydrolysis. No colouration developed if the samples were immersed in ethanol. The hydrolysis reaction is shown in equation 9.2.

In view of the strength of the colpolymer, it is likely that hydrolysis, which results in chain scission, only occurs to a small degree.



Polyurethane hydrolysis....Equation 9.2

9.5.2.2 Ethanol Uptake.

A graph of ethanol uptake with time for both homo and copolymer is shown in figure 9.2 and the final equilibrium values are 11.1 and 9.8% respectively. This difference in uptake is a reflection of the poor compatibility of the polyacrylamide crosslink chains with ethanol, which depresses the ethanol uptake of the copolymer. A similar effect was seen for the non-ionic crosslinked materials. See chapt 7.4.4.2.

It was noted that poly(PUTDOL/IEM) became plasticised and sticky, whereas poly(PUTDOL/IEM-co-ACM) remained firm although it

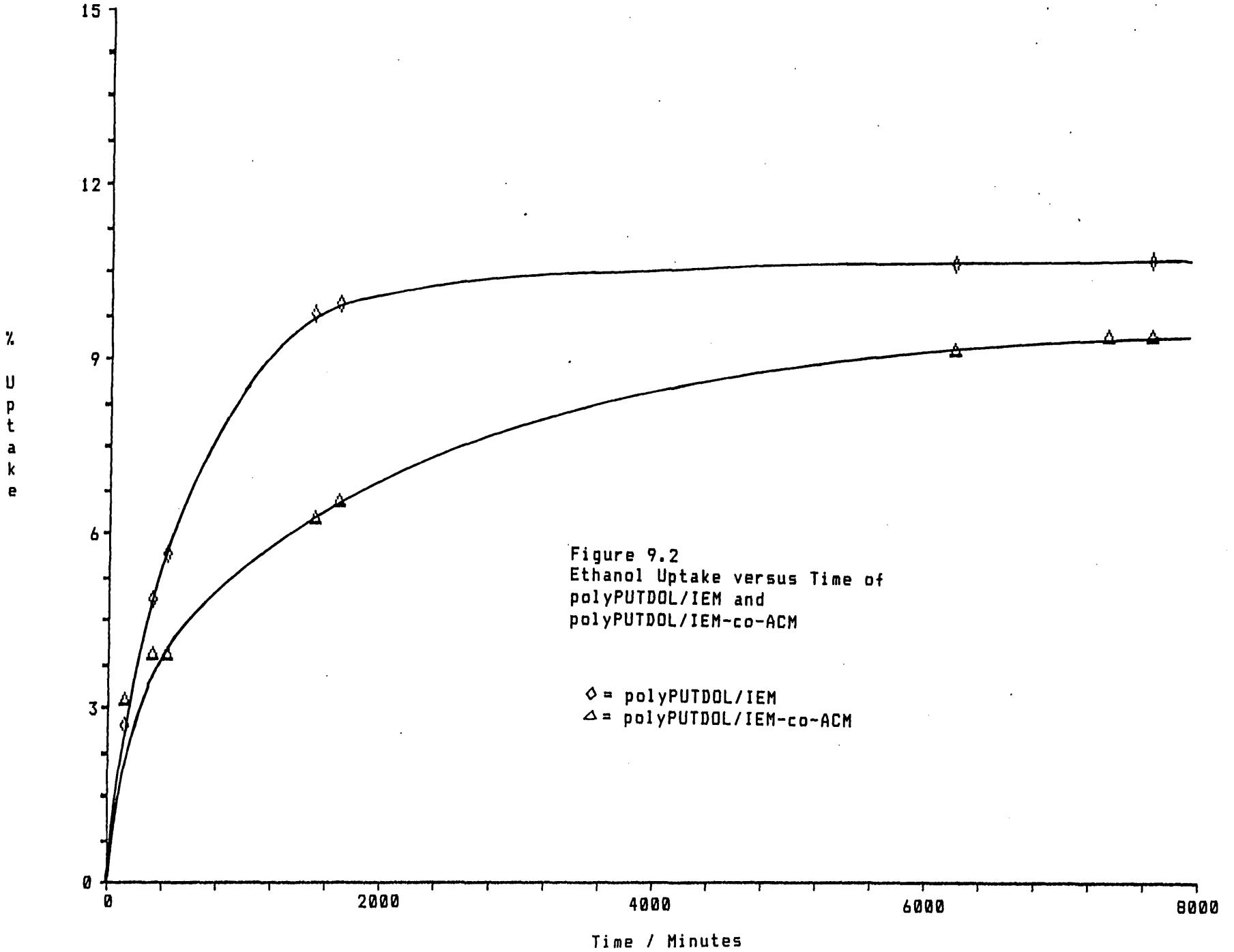


Figure 9.2
Ethanol Uptake versus Time of polyPUTDOL/IEM and polyPUTDOL/IEM-co-ACM

lost its brittleness. This difference has two causes

Firstly, as shown by the water uptakes, poly(PUTDOL/IEM) has a much lower crosslink density than the colpolymer and is therefore less well reinforced by crosslinks.

Secondly, the crosslink chains in the copolymer are formed of polyacrylamide and are not ethanol compatible. Indeed, ethanol is used as a precipitant for polyacrylamides. It is therefore possible that the crosslink chains associate together to reinforce the sample further.

As expected, the uptake of both materials was quite low, but even in the case of the acrylamide copolymer, it is still nearly twice as high as for the similar ionomer PE-100-Th/BD (see chapter 8.5.1.2) which has an uptake of only 5.6%. The cause of this difference is probably twofold. Firstly, the monomer ratios for PE-100-Th/BD and PUTDOL/IEM are MDI:TDOL:PEG of 3.15:2.15:1 and 2.67:2:1 respectively. PE-100-Th/BD contains more materials that are incompatible with ethanol and will thus have a lower ethanol uptake. The second possible cause is the difference in morphology that is apparently produced when water,as opposed to DMF, is removed from a sample. This difference in morphology is also responsible for the brittleness of the dry samples and is discussed in section 9.5.3.

9.5.3 Differential Scanning Calorimetry.

The samples of crosslinked materials prepared in water and a small sample of PUTDOL cast from water are dramatically different from samples cast from DMF. They are clear, colourless, brittle materials. The properties of ionomer films cast from DMF is discussed in chapter 8.5.3.

This difference can only mean that a different morphology has been obtained and the increased ethanol uptakes over samples cast from DMF may also reflect this difference.

The DSC traces for poly(PUTDOL/IEM) and poly(PUTDOL/IEM-co-ACM) are divided into low temperature regions (-100 to 0^{o}C) and high temperature regions (0 to 170^{o}C) and are shown in figures 9.3 to 9.6.

There are no features in the low temperature region on either the first or second runs. This is a major difference to samples cast from DMF which display a polyether glass transition in this region. See Chapter 8.5.3.1.

The high temperature region contains both endo- and exotherms and is much more complicated than those for samples from DMF. See chapter 8.5.3.2.

The homopolymer shows a large endotherm from 20-62^{o}C with a minimum at 58^{o}C. When rerun, this endotherm has shifted to lower temperature, 0-34^{o}C, centred at 20^{o}C and no longer has a minimum.

An exotherm from 140 to 170^{o}C peaking at 165^{o}C with a shoulder at 158^{o}C was present on the first run but absent on the second run.

The acrylamide copolymer displays a very strong endotherm between 50 and 68^{o}C with a sharp minimum at 61^{o}C. Upon being rerun, the minimum disappears leaving an endotherm with the normal shape of a glass transition, starting at 37^{o}C, ending at 57^{o}C and centred on 46^{o}C.

A small exotherm starting at 163^{o}C was present in the first run. A somewhat larger exotherm starting at 158^{o}C was present on

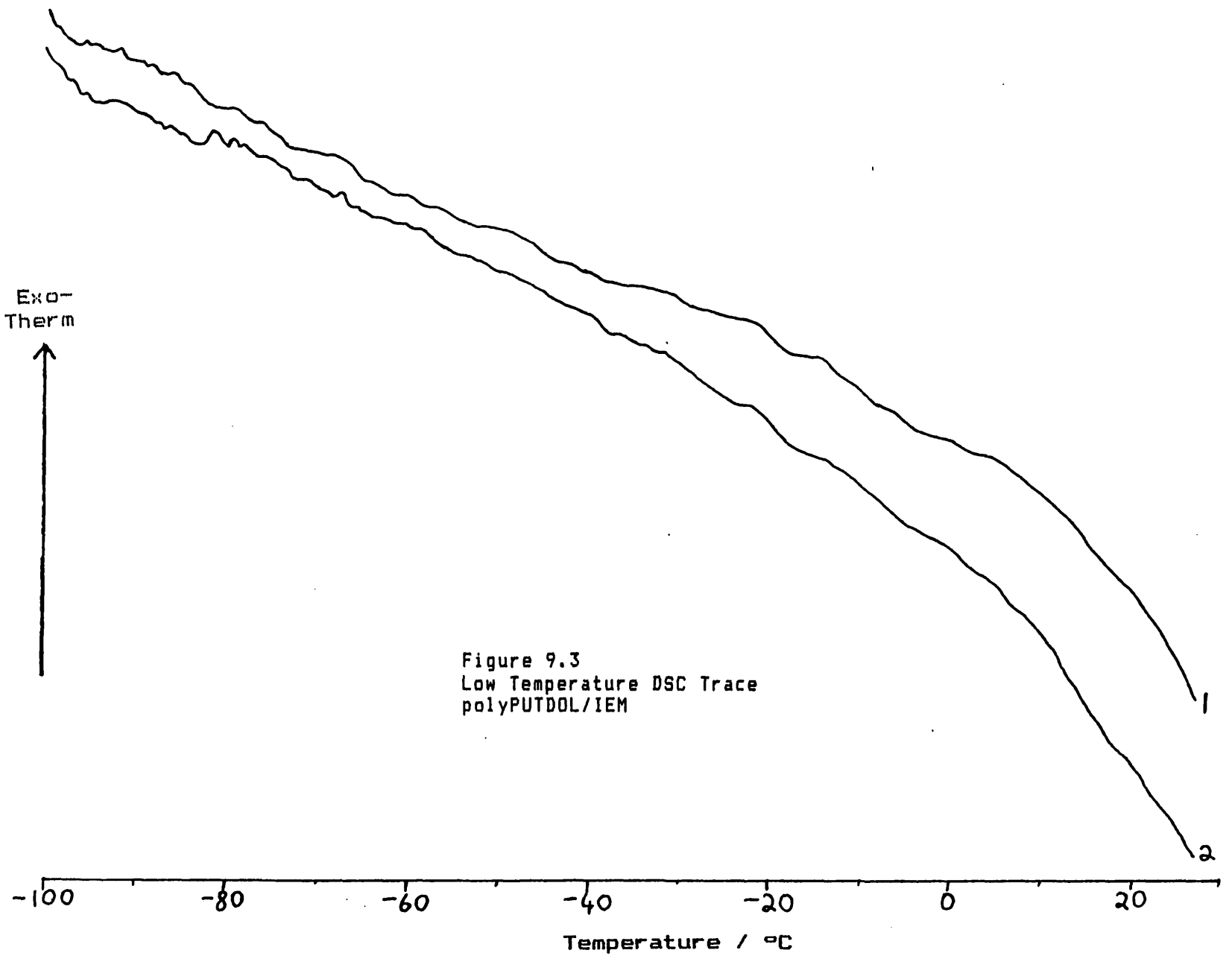


Figure 9.3
Low Temperature DSC Trace
polyPUTDOL/IEM

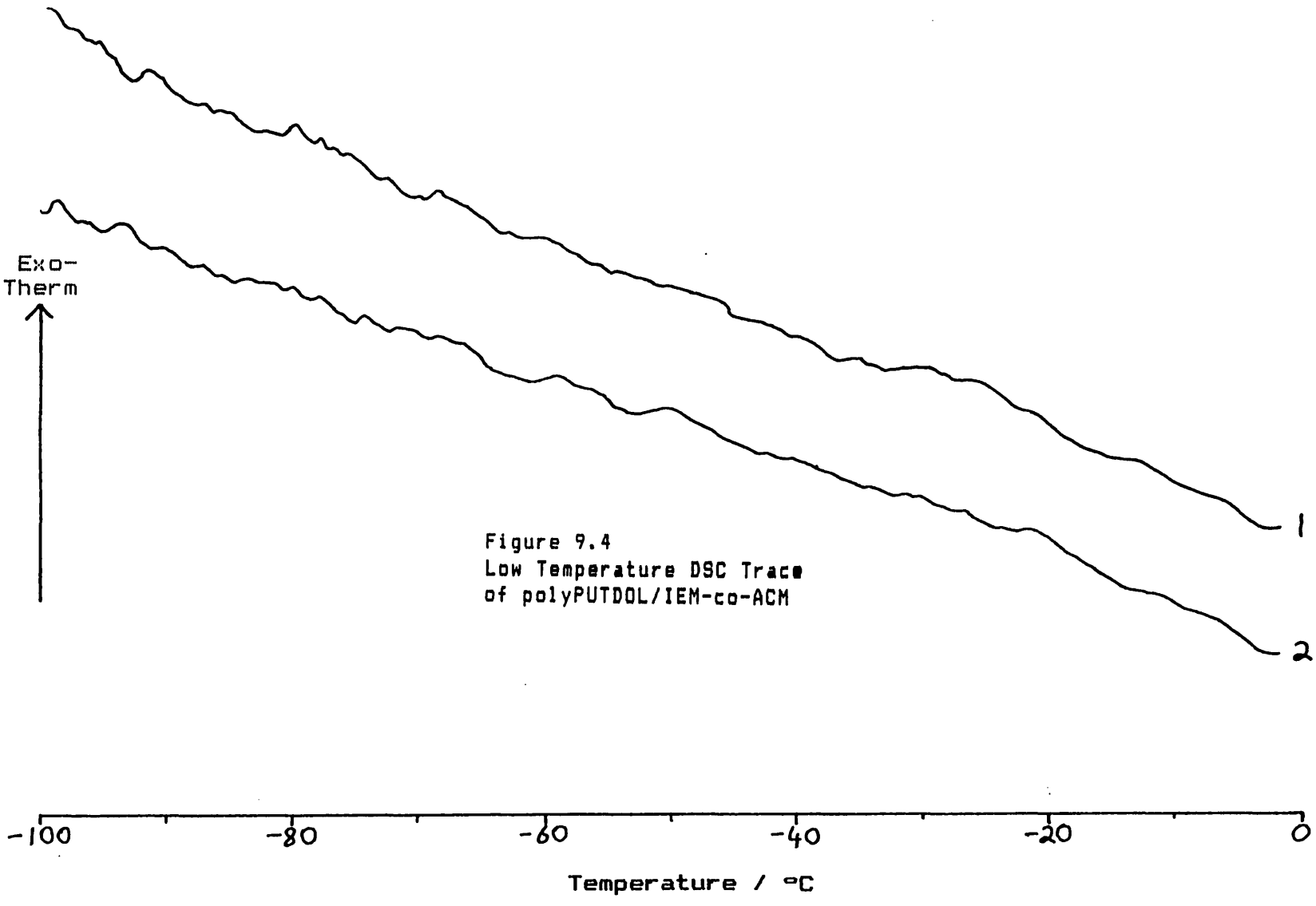


Figure 9.4
Low Temperature DSC Trace
of polyPUTDOL/IEM-co-ACM

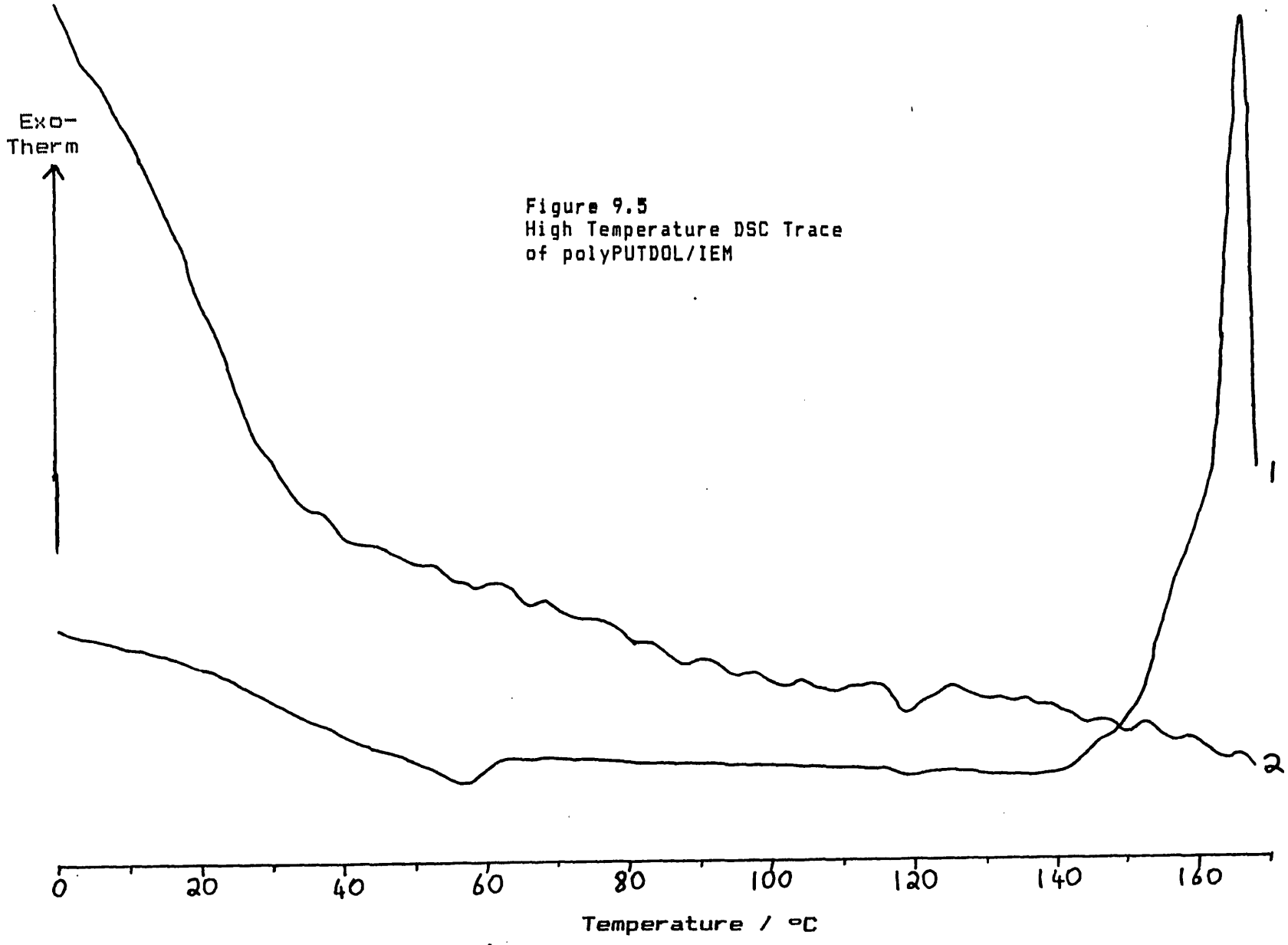


Figure 9.5
High Temperature DSC Trace
of polyPUTDOL/IEM

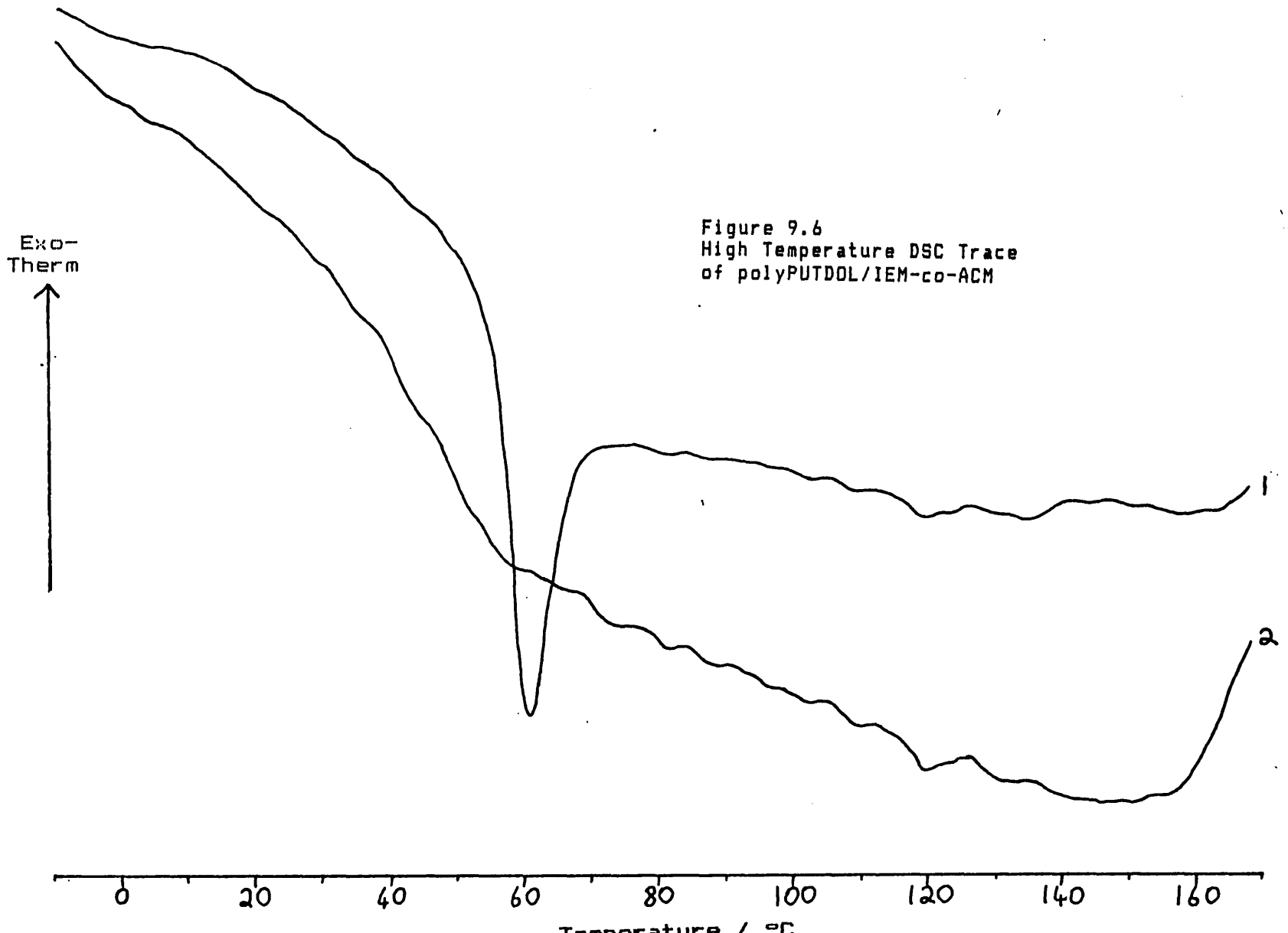


Figure 9.6
High Temperature DSC Trace
of polyPUTDDL/IEM-co-ACM

the second run. No peak or end point was seen in the temperature range studied.

There are two possible explanations for an increase in the brittleness of the samples when going from DMF to water.

The first is that a much more interconnected ionic hard domain is formed, which extends unbroken throughout the sample, making it rigid. However, such a morphology would be expected both to display a low temperature glass transition for a fairly pure soft phase and to reduce the ethanol uptake by physically restricting any swelling of the soft phase.

The second possible explanation is that a very high degree of phase mixing has occurred, with ionic groups distributed throughout the soft phase. The sample would be reinforced by ionic interactions throughout the material. This phase mixing would give a fairly high glass transition temperature, as was observed. In addition, the distribution of the ionic groups throughout the sample, rather than concentrated in ethanol impermeable domains would reduce the volume of sample incapable of taking up ethanol. Hence, an overall increase in ethanol uptake would be expected, as is observed.

The reason for the development of a highly phase mixed morphology is almost certainly the incompatibility of water with the MDI residues in the polymer chain. As metioned in chapter 8.4.2, water does not act as an interface between the highly polar ionic groups and the non-polarbenzene rings of the MDI residues. As the water evaporates, the polyether segments complex the potassium counter ions and provide a medium that eases the incompatibility between the two groups. As a result, a highly

phase mixed morphology comes into existence.

In the case of films cast from DMF, the residual traces of DMF in cast films probably solvate the ionic groups, facilitating hard domain formation and reducing the level of complexation that occurs. By the time the last traces of DMF are removed, the domain structure has formed and is stabilised by the strong short range ionic forces within it.

The fall in Tg when a sample is rerun suggests that heating the sample above its glass transition allows sufficient movement of groups through the material for ionic attraction to start a gradual aggregation and phase separation process. Ionic domains begin to form and the Tg of the soft phase falls as it becomes purer.

It is worth noting that even after the rerun, the Tg of poly(PUTDOL/IEM) is still 32^{o}C higher than the soft phase Tg of PE-100-Th/Bd cast from DMF. This indicates that the rearrangement on heating is a slow process.

It is noticeable that the acrylamide copolymer initially displays a minimum at nearly the same temperature as the homopolymer but has a narrower transition width. In the rerun, the Tg of the copolymer does not fall as much as that of the homopolymer. This is probably due to the presence of polyacrylamide crosslink chains and the higher degree of crosslinking present. These two factors are both likely to maintain a phase mixed system, the latter reducing the mobility of chains in the material and the former by acting as a blending agent. The amide groups and any ammonium carboxylate ion pairs

formed by hydrolysis of amide groups are polar, can increase long range hydrogen bonding and ease the repulsion of the anionic groups for the polyether chains complexing their potassium counter ions. It is this repulsion between the anions and the polyether oxygen atoms which encourages the formation of ionic domains when the sample is heated and the groups more mobile.

The width of a glass transition in a DSC trace is indicative of the size of the interfacial region in a 2 phase system, the larger the width, the bigger the region.

Poly(PUTDOL/IEM-co-ACM) clearly has a much smaller transition width than poly(PUTDOL/IEM). This infers that it has a much smaller quantity of material in the interface between hard and soft phases, indicating that the copolymer is more homogeneous than the homopolymer.

Upon being rerun, the copolymer continues to display a narrower transition width indicating that it is still more homogeneous than the homopolymer.

Further evidence of the degree of dissolution of the ionic groups in the polyether and the homogeneity of the material is seen in the high temperature decomposition exotherm.

For poly(PUTDOL/IEM) this exotherm is strong as ionic groups come close together and the decomposition reaction proceeds and, in the rerun, there is no exotherm as all the groups in close proximity to each other have reacted.

In the copolymer however, there is only a small exotherm in the first run and, in the rerun, only a mild exotherm corresponding to the decomposition of the newly aggregated ionic groups.

While the decomposition reactions are not known and are undoubtedly complex, they result in formation of disulphide crosslinks and elemental sulphur and must therefore require the interaction of two or more ionic groups. Hence, a more phase separated material with higher localised concentrations of ionic groups is more prone to decomposition.

The use of a comonomer thus not only allows variation of the properties, but may also improve the long term stability of the material by rendering it more homogeneous and resistant to phase separation.

9.6 Conclusions.

A new water soluble ionic macromonomer has been prepared and successfully used to form gels with both thermal and photochemical initiation. Aqueous reaction solutions may be used and water soluble comonomers added.

The properties and morphology of these materials are dramatically different to those of ionomers cast from or crosslinked in DMF.

The addition of other monomers allows variation of the properties and may also improve the overall stability of the final polymer.

The main drawback is that the initiator used produces nitrogen as a byproduct and the entrapped gas bubbles in the samples are a major flaw. This is a disadvantage of the initiator rather than the macromonomer and the use of an alternate initiator would overcome it.

This new system should find many uses, both biochemical and

others and further extend the areas in which polyurethanes can be applied.

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