Structure-property relationships of chain-extended thermoplastic polyurethane elastomers

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Structure-Property Relationships of Chain-Extended Thermoplastic Polyurethane Elastomers

by
Paul A. Sykes

A doctoral thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of Loughborough University 1999

Supervisor: Professor D. J. Hourston
Institute of Polymer Technology and Materials Engineering

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I would like to thank my parents for their encouragement and enthusiasm throughout my academic studies.

Finally, I wish to thank my wife Lisa for her support and patience, and to whom I would like to dedicate this thesis.
Abstract

The effect of chain extender chemical structure on the physical and mechanical properties of thermoplastic polyurethane/urethaneurea elastomers was systematically investigated.

Several series of materials were synthesised using 4,4'-diphenylmethane diisocyanate (MDI) and poly(tetramethylene oxide) glycol (PTMG), each series incorporating a particular class of chain extender compound. Elucidation of the influence of chain extender structural variations within each series was the principal objective of the investigation.

The groups of compounds used as chain extenders were C₄ α,ω-diols, hydroxyamine compounds (and the equivalent dihydroxy compounds), aromatic diamines, 2,4-pentanediol stereoisomers and benzenedimethanol isomers. In addition, the effect of processing conditions (reaction process and cure temperature) on the properties of the materials containing C₄ α,ω-diols was studied.

The properties of these materials and the morphologies giving rise to them were characterised using such techniques as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), modulated-temperature differential scanning calorimetry (M-TDSC), dynamic mechanical thermal analysis (DMTA), wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), tensile testing and swelling studies.

In the case of the C₄ diol chain-extended polyurethanes it was found that increased linearity and structural regularity of the diols increased the extent to which phase separation and domain formation occurred. It was also noted that the presence of a racemic mixture of diols impaired phase separation. In addition, it was found that either employing a two-stage reaction process rather than a one-stage scheme, or applying an increased cure temperature resulted in more perfectly ordered domain structures.
It was observed that the use of hydroxyamine chain extender compounds resulted in the formation of polyurethaneureas which possessed significantly more phase separated hard/soft segment domain morphologies than the equivalent dihydroxy compound chain-extended polyurethanes.

The chemical structure of the link group between the aromatic structures of the aromatic diamine chain extenders was found to strongly influence elastomer properties. Polar groups and groups which were thermodynamically incompatible with the soft segment structures resulted in the formation of the most phase separated domain morphologies.

For chain extension with 2,4-pentanediol stereoisomers, it was discovered that increasing the number of enantiomers/stereoisomers in a composition from one to three caused a significant reduction in the level of phase separation achieved.

In the case of chain extension with isomers of benzenedimethanol it was discovered that the linearity of the isomer influenced the degree of phase separation and domain formation attained. It was also found that the use of mixed isomers as chain extenders reduced the tendency for phase separation to occur.

It was generally concluded from the results of the investigations performed that the morphologies and properties of the polyurethanes/urethaneureas were predominantly determined by the presence of cohesive interactions between hard segments and, therefore, the degree of hard/soft segment thermodynamic incompatibility. It was also inferred that the structural regularity of the hard segment structures significantly influenced the ability of such interactions to occur.
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<td>TDI</td>
<td>Toluene diisocyanate</td>
</tr>
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<td>H₁₂MDI</td>
<td>4,4'-Dicyclohexylmethane diisocyanate</td>
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<td>PTMG</td>
<td>Poly(tetramethylene oxide) glycol</td>
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<td>DETDA</td>
<td>3,5-Diethyl toluene 2,4-/2,6-diamine</td>
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<td>Proton nuclear magnetic resonance spectroscopy</td>
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<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Hard segment domain melting temperature</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Enthalpy of melting</td>
</tr>
<tr>
<td>Tan δ</td>
<td>Loss factor</td>
</tr>
<tr>
<td>E'</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>2θ</td>
<td>Scattering angle</td>
</tr>
<tr>
<td>S</td>
<td>Reciprocal repeat distance</td>
</tr>
<tr>
<td>σ&lt;sub&gt;s, Q&lt;/sub&gt;</td>
<td>Volume fraction of solvent in swollen elastomer</td>
</tr>
<tr>
<td>δ</td>
<td>Solubility parameter</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction


1.1 Polyurethanes

Polyurethanes are an extremely diverse and versatile class of polymeric materials which include plastics, elastomers, rigid and flexible foams, coatings, fibres and adhesives\(^{(1)}\). Consequently, they find application in a very broad range of fields. They are generally characterised by the presence of the urethane, or carbamate group.

![Urethane group](image)

Figure 1.1. The urethane group.

The diversity of the physical and mechanical properties exhibited by polyurethanes arises from the ability to incorporate other chemical structures into these polymers. Such structures may be inherently rigid or flexible, or may have the ability to result in crystallinity or chemical crosslinking.

The original work which resulted in the development of polyurethanes was initiated by Otto Bayer and his co-workers of I. G. Farbenindustrie in Leverkusen, Germany in 1937\(^{(2)}\). This was in response to the work by Carothers of DuPont in the USA on the polyamides or ‘nylons’. The earliest commercialised polyurethanes were prepared from the reaction of low molecular weight aliphatic diols and diisocyanates\(^{(3)}\) and displayed properties similar to those of the analogous polyamide thermoplastics. However, these materials are currently of little practical significance since polyamides are less expensive high-volume plastics. Subsequent developments resulted in the synthesis of polyurethanes with polymeric diols. These materials possessed elastomeric properties and a significant proportion of the polyurethanes in current use are of this type.

Polyurethane elastomers are generally composed of an alternating segmental structure\(^{(4)}\) with the segments being linked by the characteristic urethane linkage. This structure is itself usually formed from three basic chemical constituents. These are a
diisocyanate, an oligomeric ‘polyol’ and a chain extender. It is the enormous chemical variety of these constituents which results in the ability of polyurethane elastomers to possess such a broad range of properties.

1.2 Objectives of the Research

An understanding of the structure-property relationships of polyurethane elastomers may facilitate the use of appropriate molecular architecture to achieve optimised properties for particular applications. A knowledge of the influence of processing conditions on properties can also assist in the process of tailoring materials to applications. Such optimisation may result in improved levels of performance and also financial advantages.

The general objective of the work reported in this thesis was to elucidate the effects of chain extender chemical structure on the morphology and properties of several generic groups of chain-extended thermoplastic polyurethane/polyurethaneurea elastomers. Each of these generic groups incorporated a particular class of chain extender compound, and the effect on properties of systematic variations in the structure of these compounds was investigated. The study was performed with the more specific aim of identifying structural features which may result in enhanced levels of physical and mechanical properties. In addition, the effect of processing conditions on the morphology/properties of elastomers was investigated in the case of one of the generic groups. The groups of elastomers studied are described below.

(a) A series of polyurethanes chain-extended with C₄ α,ω-diol compounds was prepared and characterised in order to evaluate the effects of unsaturation (carbon-carbon double and triple bonds) and also halogen substituents in the chain extender component on elastomer properties. The presence of carbon-carbon double bonds also enabled the effect of chain extender isomerism to be studied.
In addition, the effects of variations in the processing technique employed to prepare these materials were investigated. The effect of a ‘one-shot’ reaction process in which all of the chemical constituents are reacted simultaneously was compared to that of a ‘two-shot’ process which involves chain extension of a previously formed prepolymer. The effect of differing cure temperatures was also investigated.

(b) The morphology and properties of polyurethaneureas chain-extended with hydroxyamine compounds were investigated and compared to those of similar polyurethanes incorporating the equivalent, dihydroxy-functionalised compounds.

(c) A number of polyurethaneureas were synthesised with aromatic diamine chain extender compounds. These were studied with the intention of elucidating the effect on properties of chemically different link groups between the aromatic ring structures.

(d) Polyurethanes chain-extended with single enantiomers, a racemic mixture and a combination of three stereoisomers of 2,4-pentanediol were prepared and characterised in order to ascertain the effect on morphology and properties of these variations in chain extender structure.

(e) A series of polyurethanes were chain-extended with two different benzenedimethanol isomers, and also with combinations of these isomers in varying proportions, in order to determine the effects of these compositional changes on the properties of the resulting elastomers.

The effects of the imposed chemical and processing variations on the morphologies and properties of these groups of materials were characterised by the techniques of Fourier transform infrared spectroscopy, differential scanning calorimetry, modulated-temperature differential scanning calorimetry, dynamic mechanical thermal analysis, wide angle X-ray scattering, small angle X-ray scattering, tensile testing and swelling measurements.
Chapter 2

The Chemistry of Polyurethanes
2.1 Isocyanate Chemistry

The urethane group may be obtained via such synthetic routes as the reaction of chloroformic esters with amines, or of carbamic esters with alcohols.

\[ \text{RNH}_2 + \text{CICOOR'} \rightarrow \text{RNHCOOR'} + \text{HCl} \]

\[ \text{ROH} + \text{R'OOCNHR''} \rightarrow \text{ROOCNHR''} + \text{R'OH} \]

However, commercially the reaction between isocyanates and alcohols is the only one of significance. In practice, polyurethanes may also incorporate a variety of other functional groups. Consequently, the chemistry of polyurethanes is generally based on the ability of the isocyanate functional group to react with compounds containing active hydrogen atoms, i.e. compounds having hydrogen atoms which are replaceable by sodium.

2.1.1 Reactions of Isocyanates with Active Hydrogen-Containing Compounds

The reactivity of the isocyanate group with active hydrogen compounds can be explained by the relative electronegativities of the groups constituent atoms and the resulting resonance structures.\(^{(5)}\)

\[ \text{N} \rightleftharpoons \text{N} \rightleftharpoons \text{N} \]

These may be summarised by the general form shown below.

\[ \delta^- \delta^+ \delta^- \]

\[ \text{N} = \text{C} = \text{O} \]
This structure indicates that the electron density is greatest on the oxygen atom and least on the carbon atom. Thus, the oxygen atom carries the greatest net negative charge and the carbon atom a net positive charge. The nitrogen atom carries an intermediate net negative charge. Reactions of isocyanates with active hydrogen compounds, therefore, proceed via the attack of nucleophilic centres on the electrophilic carbon atom. In such reactions the active hydrogen compound acts as an electron donor.

It should be noted that the presence of electronegative substituents in the active hydrogen compounds tends to reduce electron density at the reactive site and decreases the rate of reaction with isocyanates. In contrast, electron withdrawing substituents in isocyanate compounds tend to increase the positive charge on the electrophilic carbon atom and cause increased reaction rates with electrophilic groups.

The reaction of most importance is that with alcohols and is responsible for the formation of the urethane group.

\[
\text{RNCO} + \text{R'OH} \rightarrow \text{RNHCOOR'}
\]

The reaction of isocyanates with amines results in the formation of ureas.

\[
\text{RNCO} + \text{R'NH}_2 \rightarrow \text{RNHCONHR'}
\]

Isocyanates react with water and result in the formation of amines and the liberation of carbon dioxide. The formation of carbon dioxide can be exploited in the formation of cellular materials, the gas acting as a blowing agent. The reaction proceeds via the formation of an unstable carbamic acid derivative.

\[
\text{RNCO} + \text{H}_2\text{O} \rightarrow \text{RNHCO}_2\text{H} \rightarrow \text{RNH}_2 + \text{CO}_2
\]
The amines formed may then react with additional isocyanate to form a symmetrical urea.

\[
\text{RNCO} + \text{RNH}_2 \rightarrow \text{RNHCONHR}
\]

The reactions of isocyanates with carboxylic acids also results in the liberation of carbon dioxide. These reactions, depending on conditions, may lead to amides via thermally unstable anhydrides.

\[
\text{RNCO} + \text{R'CO}_2\text{H} \rightarrow \text{RNHCO}_2\text{COR'} \rightarrow \text{RNHCOR'} + \text{CO}_2
\]

Alternatively, the products may be carboxylic anhydrides and ureas.

\[
\text{RNCO} + 2\text{R'CO}_2\text{H} \rightarrow \text{RNHCONHR} + (\text{R'CO})_2\text{O} + \text{CO}_2
\]

If di- or polyfunctional reagents are employed in any of these reactions the formation of polymeric structures can occur. The use of purely difunctional compounds leads to the formation of linear products, while higher functionality results in branched or crosslinked materials.

Reactions of isocyanates with urethane, urea and amide groups already introduced into polymeric systems are possible due to the fact that they also contain active hydrogen atoms. These reactions lead to chain branching and crosslinking and the formation of allophanates, biurets and acylureas, respectively.

\[
\text{RNCO} + \text{R'NHCOOR''} \rightarrow \text{R'NCOOR''} \quad \text{Allophanate}
\]

\[
\text{RNCO} + \text{R'NHCOOR''} \rightarrow \text{R'NCOOR''} \quad \text{CONHR}
\]
Chapter 2  The Chemistry of Polyurethanes

\[
RNCO + -R'NHCONHR''- \rightarrow RNCONHR'' + CONHR
\]

\[
RNCO + -R'NHCOR''- \rightarrow R'NCOR'' + CONHR
\]

2.1.2 Self-Addition Reactions

Other useful basic reactions of isocyanates are those which involve reaction with themselves. These can lead to the formation of dimers, trimers and polymeric structures. Dimerisation of isocyanates to form uretidiones provides a means to 'block' isocyanates, with dissociation leading to the isocyanate function becoming available at elevated temperatures.

\[
2RNCO \rightarrow R-N=N-R
\]

Isocyanates may also react with themselves to form carbodiimides and liberate carbon dioxide.

\[
2RNCO \rightarrow RN=C=NR + CO_2
\]

The resulting carbodiimides may then react with excess isocyanate to form uretoneimines, a reaction used for the modification of isocyanates, for example to reduce their melting point.
The trimerisation of isocyanates results in the formation of the isocyanurate ring structure. In the case of diisocyanates a trifunctional derivative is the product, which is capable of introducing chain branching and crosslinking into polyurethanes.

Under certain conditions (at low temperatures with catalysts) isocyanates may also undergo polymerisation.

2.2 Polyurethane Intermediates

A large proportion of polyurethanes possess an alternating segmental structure and display elastomeric properties. The structure of polyurethane elastomers is usually the
result of the reaction between three basic chemical constituents\(^{(6)}\). These are isocyanates, polyols and chain extenders/crosslinkers.

2.2.1 Isocyanates

Although polyfunctional isocyanates are available a significant proportion of the isocyanate compounds used in the synthesis of polyurethanes are difunctional. The most commonly used diisocyanates for the commercial production of elastomers are the aromatic isocyanates 4,4’-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI). TDI is usually used as an 80%/20% isomeric mixture of 2,4- and 2,6-toluene diisocyanate.

Alternative aromatic diisocyanates commercially available include 1,5-naphthalene diisocyanate (NDI), 3,3’-toluene-4,4’-diisocyanate (TODI), 4,6-xylylene diisocyanate (XDI), 1,1,3,3- and 1,1,4,4-tetramethylxylylene diisocyanate (m-TMXDI and p-TMXDI) and para-phenylene diisocyanate (PPDI).

\[
\begin{align*}
\text{OCN} & \quad \text{NCO} \\
\text{CH}_3 & \quad \text{NCO} \\
\text{NCO} & \quad \text{NCO} \\
\text{OCN} & \quad \text{NCO}
\end{align*}
\]

4,4’-Diphenylmethane diisocyanate (MDI)

2,4- and 2,6-Toluene diisocyanate (TDI)

1,5-Naphthalene diisocyanate (NDI)
Chapter 2  The Chemistry of Polyurethanes

3,3'-Toluene-4,4'-diisocyanate (TODI)

4,6-Xylene diisocyanate (XDI)

$m$- and $p$-Tetramethylxylylene diisocyanate

$(m$- and $p$- TMXDI)

para-Phenylene diisocyanate (PPDI)

Figure 2.1a. Aromatic diisocyanates used in the synthesis of polyurethane elastomers.

Although aromatic diisocyanates are the most widely used, aliphatic diisocyanates are also of importance in certain applications. Unlike aromatic diisocyanates these compounds result in polyurethanes which do not turn yellow on exposure to light. Examples of aliphatic diisocyanates are 1,6-hexamethylenediisocyanate (HDI), 1,4-cyclohexyl diisocyanate (CHDI), 4,4'-dicyclohexylmethane diisocyanate ($H_2$MDI) and isophorone diisocyanate (IPDI).

$OCN(CH_2)_6NCO$  

1,6-Hexamethylenediisocyanate (HDI)
1,4-Cyclohexyl diisocyanate (CHDI)

4,4'-Dicyclohexylmethane diisocyanate (H₁₂MDI)

Isophorone diisocyanate (IPDI)

Figure 2.1b. Aliphatic diisocyanates used in the synthesis of polyurethane elastomers.

2.2.2 Polyols

Polyols are usually hydroxy-functionalised oligomeric materials with molecular weights in the approximate range 200-12000 (typically 1000-6000) and with functionalities of 1-10 (commonly 2-4). The vast majority of polyols belong to one of two classes, polyether polyols and polyester polyols. Examples of commercially available polyether polyols are poly(ethylene oxide) glycol (PEG), poly(propylene oxide) glycol (PPG), poly(ethylene-co-propylene oxide) glycol and poly(tetramethylethylene oxide) glycol (PTMG).
Polyether polyols generally exhibit improved hydrolytic stability in comparison to polyester polyols due to their less polar nature. However, poly(ethylene glycol) is seldom used in pure form due to its hydrophilic nature. It is usually copolymerised with poly(propylene glycol) to improve its properties in this respect and also to inhibit soft segment crystallisation (cold hardening).

The reactivity of poly(propylene glycols) may be modified by the use of ethylene oxide. The end-capping of a PPG with ethylene oxide replaces the secondary terminal hydroxy groups with primary hydroxyl functionalities, thereby increasing their reactivity with electrophiles such as isocyanates\(^7\).

Examples of polyester polyols are poly(alkylene) adipates, sebacates and benzoates, poly(caprolactones) and poly(carbonates). The latter two groups result in elastomers with improved resistance to hydrolysis.

\[
\text{HO-R}\bigg[O\text{--CO--R'--CO--O--R}\bigg]_n\text{OH}
\]

Poly(alkylene) ester

\[
H\bigg[O\bigg(\text{CH}_2\bigg)_5\text{CO}\bigg]_n\text{--O--R}\bigg[O\bigg(\text{CH}_2\bigg)_5\text{O}\bigg]_m\text{H}
\]

Poly(caprolactone) ester

\[
H\bigg[O\bigg(\text{CH}_2\bigg)_6\text{O--CO}\bigg]_n\text{--O--}(\text{CH}_2\bigg)_6\text{OH}
\]

Poly(hexamethylene carbonate)

Figure 2.2a. Polyether polyols used in the synthesis of polyurethane elastomers.

Figure 2.2b. Polyester polyols used in the synthesis of polyurethane elastomers (R represents an alkyl substituent).
The use of co-polyester polyols which introduce structural irregularity can reduce the sometimes undesirable tendency for cold hardening to occur in the case of higher molecular weight polyols.

Alternative types of polyol finding mainly specialised applications include hydroxyl-terminated polybutadienes, fluorinated polyols and also amine-functionalised polyethers. Polybutadiene polyols impart superior hydrolysis resistance to polyurethanes while fluorinated polyols result in enhanced chemical resistance. Amine-terminated polyols find application in the area of reaction injection moulding (RIM) due to their relatively high rates of reactivity \(^8\). Recent interest in polyols such as those derived from poly(isobutylene) \(^9\), poly(ethylene) \(^10\) and poly(siloxanes) \(^11\) has also arisen due to their potential resistance to hydrolysis and oxidation.

2.2.3 Chain Extenders and Crosslinkers

Chain extender compounds are generally relatively low molecular weight difunctional alcohols or amines with the ability to link isocyanate structures. Crosslinkers are similar compounds but with functionalities of greater than two.

Examples of frequently used diol chain extenders are 1,2-ethanediol, 1,4-butanediol, 1,4-cyclohexanediol, 1,4-dihydroxybenzene and hydroquinone bis(hydroxyethyl ether) (HQEE), while a commonly used crosslinker is trimethylol propane (TMP).

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{OH} & \quad 1,2\text{-Ethanediol} \\
\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \quad 1,4\text{-Butanediol} \\
\text{HOCH}_2\text{-CH}_2\text{OH} & \quad 1,4\text{-Cyclohexanediol} \\
\end{align*}
\]
Figure 2.3a. Diol chain extenders used in the synthesis of polyurethane elastomers.

Examples of diamine chain extenders are ethylene diamine, 4,4'-methylenebis(3-chloro-2,6-diethyl aniline) (M-CDEA) and 3,5-diethyl toluene 2,4-/2,6-diamine (DEDTA). MOCA (4,4'-methylenebis(ortho-chloroaniline)) was an extensively used diamine chain extender in elastomer synthesis, although toxicity effects led to its demise and replacement.

\[
\text{HOCH}_2\text{CH}_2\text{O} - \text{OCH}_2\text{CH}_2\text{OH} \quad \text{Hydroquinone bis(hydroxyethyl ether) (HQEE)}
\]

\[
\text{CH}_2\text{CH}_2\text{OH} \quad \text{CH}_2\text{CH}_2\text{OH} \quad \text{Trimethylolpropane (TMP)}
\]

\[
\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \quad \text{1,2-Ethanediamine}
\]

\[
\text{H}_2\text{H} - \text{CH}_2 - \text{NH}_2 \quad \text{4,4'-Methyleneedianiline}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{H}_2\text{H} - \text{CH}_2 - \text{NH}_2 \quad \text{4,4'-Methylenebis(ortho-chloroaniline) (MOCA)}
\]

\[
\text{H}_5\text{C}_2 \quad \text{Cl} \quad \text{Cl} \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{H}_2\text{H} - \text{CH}_2 - \text{NH}_2 \quad \text{4,4'-Methylenebis(3-chloro-2,6-diethyl aniline) (M-CDEA)}
\]
Figure 2.3b. Diamine chain extenders used in the synthesis of polyurethane/urethaneurea elastomers.

The greater basicity of primary amines in comparison to alcohols generally results in diamine chain extenders having significantly increased rates of reaction with electrophilic isocyanate groups. The introduction of sterically hindering groups such as alkyl structures or electron withdrawing substituents such as chlorine atoms may be employed to reduce their reactivity\(^{(12-16)}\). The reactivity of secondary amine functionalised chain extenders have been found to display reduced rates of reactivity in comparison to similar primary amines\(^{(17)}\).

### 2.3 The Synthesis of Polyurethanes

Two basic mechanisms are employed for the synthesis of polyurethanes, the ‘two-shot’, or ‘prepolymer’ method and the ‘one-shot’ technique.

#### 2.3.1 The Two-Shot Process

The two-shot, or prepolymer method for the preparation of polyurethanes proceeds in two distinct stages. The first stage involves the reaction of the polyol component with a stoichiometric excess of diisocyanate to form an isocyanate end-capped prepolymer. These are usually viscous liquids or low melting point solids. The second stage of the process involves conversion of the prepolymer to a high molecular weight polymer by reaction with a diol or diamine chain extender compound. The two-shot process for the preparation of polyurethanes is represented in figure 2.4 (overleaf).
A process known as a quasi-prepolymer reaction can also be employed. This involves reaction of the isocyanate with part of the polyol in the first stage and reaction with the remaining polyol and chain extender in the second.

\[
\begin{align*}
\text{Diisocyanate} & \quad \text{Diisocyanate} \\
\text{+} & \\
\text{Polyol} & \\
\text{Prepolymer} & \\
\text{Diol Chain Extender} & \quad \text{Diamine Chain Extender} \\
\text{Polyurethane} & \quad \text{Polyurethaneurea}
\end{align*}
\]

*Figure 2.4. The two-shot method for the synthesis of polyurethane elastomers.*

### 2.3.2 The One-Shot Process

The one-shot method for the preparation of polyurethanes is a single stage process and involves the simultaneous addition of the polyol, diisocyanate and chain extender components. The one-shot process for the preparation of polyurethanes is represented in figure 2.5 (overleaf).
It should be noted that the rates of a significant proportion of the reactions employed to prepare polyurethanes are controlled by the use of catalysts. Catalysis is of particular importance in one-shot systems where the control of simultaneous reactions is desired.

\[ \text{Polyol} + \text{Diisocyanate} + \text{Chain Extender} \rightarrow \text{Polyurethane} \]

*Figure 2.5. The one shot method for the synthesis of polyurethane elastomers.*

2.4 The Classification of Polyurethanes

Although their basic chemical constituents are very similar, minor variations result in solid polyurethane elastomers being classified into three basic groups according to their processing characteristics. These are castable, millable and thermoplastic elastomers.

2.4.1 Castable Elastomers

Prior to curing, castable polyurethane elastomers are liquid systems. They may be processed by such techniques as casting into open or closed moulds, compression or transfer moulding, spray coating or reaction injection moulding (RIM). The range of properties that can be exhibited by castable elastomers is very broad.
2.4.2 Thermoplastic Elastomers

Thermoplastic polyurethane elastomers are chemically very similar to castable elastomers, but due to their linear nature are able to be processed using conventional thermoplastic processing techniques such as extrusion, injection moulding and blow moulding. A small excess of isocyanate is often incorporated to enable the formation of a lightly crosslinked structure during a post-cure stage.

2.4.3 Millable Elastomers

Millable polyurethane elastomers are processed by conventional rubber processing methods such as milling, internal mixing, extrusion, calendering and moulding etc. They are initially produced as hydroxyl-terminated prepolymers and are subsequently crosslinked using isocyanates, sulphur or peroxides.
Chapter 3

Structure-Property Relationships of Polyurethanes
3.1 Introduction

The ability of isocyanates to participate in a wide variety of reactions in addition to that which produces the urethane group, enables the incorporation of many different chemical structures into polyurethanes. This provides the possibility of synthesising chemically diverse materials with correspondingly diverse properties. This is enhanced by the existence of large numbers of compounds containing the isocyanate functional group and other functional species such as hydroxyl and amine groups.

3.2 Unsegmented Polyurethanes

Polyurethanes synthesised from low molecular weight diisocyanates and diols such as 1,6-hexane diisocyanate and 1,4-butanediol exhibit properties which correspond to those of structurally similar polyamides\(^6\). With a high degree of crystallinity and extensive hydrogen bonding these materials are polymers with high strength and hardness. Similar but amorphous polyurethanes result from, for example, compounds such as toluene diisocyanate and ethylene glycol.

Conversely, polyurethanes synthesised from high molecular weight, non-crystalline hydroxy-functionalised polyethers or polyesters, and stoichiometric quantities of diisocyanates are soft, relatively weak elastomeric materials. With a much lower percentage of urethane groups the dominant intermolecular interactions are Van der Waals forces between the polyols, and properties depend on the chemical structure, chain length and degree of branching of the polyol. The introduction of crosslinking results in stiffer, less elastomeric networks but as for the linear materials these products are single-phase systems. Polyurethanes of technical importance in this class are highly crosslinked, hard products such as rigid foams and coatings.
3.3 Segmented Polyurethanes

A large proportion of polyurethanes are segmented polyurethanes\(^6\). In terms of chemical structure these materials are intermediate between the extreme types of unsegmented polyurethanes described previously. Segmented polyurethanes are usually formed from the reaction of three basic polyurethane constituents, a diisocyanate, an oligomeric 'polyol' and a chain extender compound. They are regarded as possessing an alternating, \((\text{AB})_n\) type block copolymeric structure, where \(A\) represents a relatively flexible 'soft' segment and \(B\) represents a comparatively rigid 'hard' segment. The soft segments are comprised of the polyol constituent while the hard segments are derived from the isocyanate structures linked by the chain extender component. The idealised primary chemical structure of a linear segmented polyurethane derived from two moles of diisocyanate, one mole of polyol and one mole of chain extender is represented in figure 3.1.

![Figure 3.1. Idealised chemical structure of a segmented polyurethane elastomer.](image)

As a result of their constituents, the chemical structures of the two segmental types are quite distinct. The hard segments possess a relatively high proportion of polar groups such as urethane and urea linkages, while the soft segments contain less polar structures such as methylene and ether groups. Consequently, particularly cohesive
interactions such as hydrogen bonding and dipole-dipole interactions may occur between the hard segments\textsuperscript{(18-31)}, as indicated schematically in figure 3.2.

![Diagram of inter-hard segment interactions in a segmented polyurethane elastomer.](image)

Figure 3.2. Inter-hard segment interactions in a segmented polyurethane elastomer.

Empirically determined values for the energy of interaction of a number of common chemical groups are shown in table 3.1\textsuperscript{(5)}.

<table>
<thead>
<tr>
<th>Chemical Group</th>
<th>Cohesive Energy / kJmol\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene</td>
<td>(-\text{CH}_2-) 2.8</td>
</tr>
<tr>
<td>Ether</td>
<td>(-\text{O}-) 4.2</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>(-\text{CO}-) 11.1</td>
</tr>
<tr>
<td>Ester</td>
<td>(-\text{COO}-) 12.1</td>
</tr>
<tr>
<td>Phenyl</td>
<td>(-\text{C}_6\text{H}_4-) 16.3</td>
</tr>
<tr>
<td>Amide</td>
<td>(-\text{CONH}-) 35.5</td>
</tr>
<tr>
<td>Urethane</td>
<td>(-\text{OCONH}-) 36.5</td>
</tr>
<tr>
<td>Urea</td>
<td>(-\text{NHCONH}-) 50-100</td>
</tr>
</tbody>
</table>

Table 3.1. Molar cohesion energies of some common chemical groups.
The existence of polar interactions between the hard segments may be sufficient to result in significant thermodynamic incompatibility with the soft segments. This may then cause phase separation of the two segmental types and the formation of a microinhomogeneous hard and soft segment domain morphology\(^{32-58}\). In this situation the hard segments are physically crosslinked and the hard segment domains act as reinforcing filler particles. Evidence of such dual-phase morphologies in segmented polyurethanes has been obtained by the use of such techniques as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), small angle laser light scattering, solid state NMR spectroscopy and electron microscopy. A two-dimensional schematic representation of such a morphology, as suggested by Estes et al.\(^{(69)}\) is shown in figure 3.3.

![Figure 3.3. Representation of the domain morphology of a segmented polyurethane.](image)
Chapter 3 Structure-Property Relationships of Polyurethanes

It is the existence of such a phase separated, dual-phase morphology which is considered to be responsible for the properties of segmented polyurethane elastomers. The soft segments primarily influence their elastic nature and low temperature performance while the hard segments particularly affect the modulus, hardness and upper-use temperature by their ability to remain associated.

The properties of segmented polyurethanes are dependent on the degree of phase separation and the perfection of the domain morphology attained. These in turn are determined by a number of factors which influence the level of inter-hard segment association and the level of incompatibility of the hard and soft segments. Such factors include the chemical composition of the segments, segmental stoichiometry, segmental size and molecular weight distribution, synthesis procedure and thermal history. These factors are discussed as follows.

3.4 The Effect of the Hard Segment

Other than changes in chemical composition, the most important hard segment variables which have been found to have an effect on the properties of thermoplastic polyurethane elastomers are segmental size and molecular weight distribution.

An increase in hard segment size for a constant soft segment molecular weight results in an increased hard segment content. A number of research groups have investigated the effect on morphology and properties of varying hard segment content for polyurethanes containing such hard segments as those derived from 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol, 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) and 1,4-butanediol, and 2,4-toluene diisocyanate (2,4-TDI) and 1,4-butanediol. Hard segments formed from MDI and chain-extenders such as diethyltoluene diamine (DETDA), diethylene glycol and 1,3-propanediamine have also received attention. Various soft segment structures such as poly(propylene oxide) glycol, poly(ethylene-co-propylene oxide) glycol, poly(tetramethylenepropylene oxide) glycol,

26
oxide) glycol, poly(butylene adipate) and polycaprolactone were employed in the syntheses of these materials. Using characterisation techniques such as DSC, DMTA, SAXS and tensile testing, it was found that an increase in hard segment content in the range 20-80% by weight resulted in increased quantities of hard segment domain formation. Increases in the crystalline perfection of these structures were also evident. These observations were due to the existence of increased inter-hard segment interaction and cohesion, such as that due to inter-urethane hydrogen bonding (as evidenced by FTIR spectroscopy). Thermal stability and tensile properties (strength/moduli) were, consequently, enhanced. Zdrahala et al.(70) noticed a phase inversion from a continuous soft segment phase to a continuous hard segment phase at a hard segment content of approximately 60%. This was coincident with a change in properties from those of a soft elastomer to those of a high-modulus plastic. Similar results have been reported by Hong et al(75).

It should be noted that the increases in hard segment content in these studies have been associated with both unchanged and decreased levels of phase separation. Some results inferred that increased values of soft segment glass transition temperature ($T_g$) and increased proportions of hard/soft segment hydrogen bonding interactions indicated increased phase mixing(74), while others appeared not to show a noticeable effect(75).

Segmented polyurethanes obtained by the reaction of piperazine and bischloroformates have been investigated by Ng et al(77). Despite possessing no capability for inter-hard segment hydrogen bonding interactions to occur, these materials were also found to exhibit increased phase separation, domain perfection, thermal stability and tensile properties with increasing hard segment size/content.

Work performed by Cooper and co-workers(78-80) showed that larger hard segments at a constant hard segment content i.e. in conjunction with higher molecular weight soft segments (poly(tetramethylethylene oxide) glycol or poly(butylene adipate) 2000 rather than 1000) also resulted in increased levels of phase separation and hard segment domain formation. The increase in segmental size was generally accompanied by a
change in morphology from isolated hard segment domains in a soft segment matrix to more interconnected domains.

A consistent effect of hard segment molecular weight distribution on the properties of polyurethane elastomers has been observed\(^{(81,82)}\). The general observation was that a narrower molecular weight distribution resulted in more advanced levels of phase separation. This was attributed to the fact that more regular hard segment structures resulted in more effective inter-hard segment interactions and, therefore, increased degrees of phase separation.

### 3.4.1 The Effect of the Diisocyanate Structure

The chemical structure of the diisocyanate compound used to synthesise hard segments in polyurethanes has been found to strongly influence the properties of these materials.

Wang and Kenney\(^{(83)}\) prepared a number of differently chain-extended elastomers with 4,4'-diphenylmethane diisocyanate (MDI) and the equivalent aliphatic diisocyanate, 4,4'-dicyclohexylmethane diisocyanate (H\(_{12}\)MDI). Using DMTA and tensile testing they established that the polyurethanes incorporating MDI possessed increased levels of phase separation and thermal stability in comparison to the equivalent H\(_{12}\)MDI-containing elastomers. This was ascribed to increased cohesive inter-hard segment interactions between the delocalised \(\pi\)-electrons of the aromatic rings in MDI and also the inherent rigidity of these structures. Similar differences in properties between polyurethanes incorporating MDI and H\(_{12}\)MDI were observed by Van Bogart et al.\(^{(84)}\), in systems chain extended with 1,4-butanediol and with poly(caprolactone) as the soft segment. The reduced levels of phase separation and domain formation found in the elastomers containing H\(_{12}\)MDI were attributed to the presence of \textit{cis-cis}, \textit{cis-trans} and \textit{trans-trans} configurational isomers of H\(_{12}\)MDI. This would tend to reduce structural regularity and inhibit hard segment crystallisation.

WAXS and DMTA studies have been used to compare the morphologies of polyurethanes utilising MDI to those with 2,4-toluene diisocyanate (2,4-TDI)\(^{(85)}\). It
was found that increased phase separation and more thermally stable segment domain morphologies occurred with MDI due to the increased regularity/symmetry of this compound. This resulted in more effective hard segment agglomeration.

Brunette, Hsu and MacKnight(86) synthesised MDI/1,4-butanediol model compounds and found from DSC studies that they were more capable of forming crystalline hard segment aggregates than the equivalent compounds with 2,4- and 2,6-TDI. FTIR spectroscopy revealed that inter-urethane hydrogen bonds of increased strength existed for the MDI-containing compounds. These observations were explained as a consequence of an increased ability of this moiety to become involved in regular packing arrangements. Of the compounds containing 2,4- and 2,6-TDI, the latter were found to possess more perfect crystalline structures with higher melting temperatures and larger melting enthalpies, and also stronger hydrogen bonds in comparison to the former. This was again deemed to be due to increased symmetry which facilitated more effective packing.

Schneider et al.(87) also prepared and characterised elastomers incorporating 2,4- or 2,6-TDI. It was once more found that 2,6-TDI resulted in enhanced phase separation and crystalline domain formation due to its increased structural regularity.

3.4.2 The Effect of the Chain Extender Structure

The chain extender component of a segmented polyurethane has a profound effect on the resulting morphology and properties. The chain extender moiety is responsible for linking isocyanate structures in the formation of hard segments and, therefore, its structure determines the extent to which effective inter-hard segment interactions can occur. Two classes of compound predominate as chain extenders, diols and diamines.

3.4.2.1 Diol Chain Extenders

Diol chain extenders have been the subject of a substantial number of polyurethane elastomer structure-property investigations.
In the case of polyurethanes chain-extended with linear, aliphatic \( \alpha,\omega \)-diols the greatest levels of phase separation and the most perfectly formed domain morphologies have been found to occur when the number of carbon atoms in the diol chain is even\(^{(88-96)}\). This has been shown for different diisocyanate/polyol systems by the results of such characterisation techniques as DMTA, WAXS and tensile testing. It has been explained as a consequence of the conformation of the diol compounds. Such a conformation results in hard segments containing them being able to adopt a fully extended, all-\textit{trans} planar zigzag conformation, which allows hydrogen bonding in opposite directions perpendicular to the main chain axis. This is represented in figure 3.4 for hard segments chain-extended with 1,4-butanediol.

![Hydrogen Bonding](image)

Figure 3.4. Hydrogen bonding in hard segments chain-extended with 1,4-butanediol\(^{(90)}\).
The ability of hard segments to crystallise in such a minimum energy conformation with effective inter-hard segment interactions creates a greater driving force for phase separation and, therefore, leads to a highly hard segment domain reinforced morphology. Such a structure-property relationship has also been observed for materials incorporating linear aliphatic diamine chain extender compounds (97).

For such effective inter-hard segment interactions to occur between hard segments which contain diols with odd numbers of carbon atoms, a contracted conformation containing gauche bonds is required (90). This is energetically unfavourable and, therefore, less likely. As a result polyurethanes chain-extended with these diols do not possess such a strong driving force for phase separation.

It should be noted that although 1,2-ethanediol contains an even number of carbon atoms, hard segments containing it adopt a contracted conformation. This is possibly due to the fact that this diol is too short to permit packing of the diisocyanate structures in the planar zigzag conformation.

Of the polyurethanes chain-extended with aliphatic \( \alpha - \omega \) diols with even numbers of carbon atoms, those incorporating 1,4-butanediol tend to display the most phase-separated domain morphologies and the highest levels of mechanical properties (98,99). This is ascribed to the regularity of the structure of this diol and the ease of formation of an inter-urethane hydrogen bonding network.

Using FTIR spectroscopy, DSC and DMTA, elastomers chain-extended with non-linear aliphatic diols such as 1,2-propanediol, 1,3-butanediol and neopentyl glycol have been found to possess somewhat reduced levels of hard segment domain crystallinity in comparison to the linear diols (85). Consequently, their mechanical properties were also reduced. These results have been explained as a result of the presence of pendant methyl groups which result in less effective hard segment packing arrangements.

The effect of unsaturation in linear diol chain extenders on polyurethane properties has been investigated for the \( \text{C}_4 \) diols, 1,4-butanediol, but-2-ene-1,4-diol and but-2-yne-1,4-diol. These studies have been conducted on elastomers with different
diisocyanates and soft segments and the results obtained varied significantly. In the case of TDI and hexamethylene diisocyanate systems in conjunction with polybutadiene polyols, those incorporating 1,4-butanediol were found to possess the most phase separated domain morphologies and the greatest tensile properties\(^{85,98}\). However, in the case of a TDI/polyester system mechanical properties increased with increasing chain extender unsaturation\(^{99}\). In a system utilising a commercial MDI/polyether polyol prepolymer\(^{100}\), 1,4-butanediol-containing elastomers exhibited the highest levels of phase separation and mechanical properties, while that with but-2-yne-1,4-diol displayed the lowest.

The properties of polyurethanes chain-extended with aromatic diols have been investigated\(^{101-103}\). The general observation from DMTA and tensile testing experiments was that the use of diols such as 1,4-dihydroxybenzene (quinol) and 2,2-bis(4'-hydroxyphenyl) propane (bisphenol A) result in elastomers with higher strength/hardness and greater thermal stability than those chain-extended with aliphatic diols. The rigidity of the aromatic structures and their ability to participate in cohesive interactions were the reasons proposed for these differences.

It was also noted that the substitution of the hydroxy groups in dihydroxybenzene chain extender compounds had a significant effect on properties\(^{102}\). The most phase-separated domain morphologies indicated by the results of DMTA and WAXS analyses, and the highest levels of physical/mechanical properties were observed in the case of 1,4-dihydroxybenzene. Chain extension with 1,3- and 1,2-dihydroxybenzene resulted in progressively less phase separated morphologies and reduced mechanical properties. This sequence of structure-property relationships was attributed to the decreasing linearity of the hard segments and the fact that this reduced their ability to interact and cause phase separation.

A number of diol chain extender compounds have been investigated and shown by DSC and WAXS analysis to be capable of producing polyurethane elastomers with liquid crystalline properties\(^{104-107}\). Examples of such chain extenders are 4,4'-bis(o-hydroxyalkoxy) biphenyls and benzene-1,4-di(4-iminophenol). Interest in these
compounds stems from their rigid (mesogenic) nature and the potential of achieving effective phase separation due to the incompatibility of hard segments derived from them with soft segments.

Another mechanism by which the enhancement of inter-hard segment interactions and phase separation in polyurethanes has been attempted is through the use of ionisable chain extenders\(^{(108-123)}\). Polyurethane cationomers may be obtained by, for example, the neutralisation (quaternisation) of a tertiary amine-containing chain extender such as N-dimethylmethanolamine\(^{(110)}\) by a carboxylic acid such as glycolic acid. Alternatively, the neutralisation of a carboxylic acid-containing chain extender such as dimethylolpropionic acid with a tertiary amine such as triethylamine yields a polyurethane anionomer\(^{(111)}\). Other ionomeric systems include those with halide neutralising ions\(^{(112)}\), and also those with sulphonate\(^{(113)}\) and phosphate\(^{(114)}\) chain extenders with metal neutralising ions.

3.4.2.2 Diamine Chain Extenders

The use of diamine compounds as chain extenders in polyurethanes (polyurethaneureas) has also received substantial research attention.

Primary diamines such as ethylenediamine have been found to result in elastomers with enhanced phase separation, thermal stability and mechanical properties in comparison to those chain-extended with diols of similar chemical structure\(^{(124-133)}\). This has been ascribed to the formation of urea groups from the reaction of amine and isocyanate functionalities. The urea linkage is capable of particularly cohesive interactions and may enable the development of highly cohesive inter-hard segment hydrogen bonding interactions. Such interactions tend to result in higher degrees of phase separation and more perfectly formed hard/soft segment domain structures than those resulting from diol chain extenders.
As with diols, it has been observed that aromatic diamines generally result in elastomers with more ordered and crystalline hard segment structures than aliphatic diamines. This has been observed using DSC to quantitatively determine levels of soft segment crystallinity\textsuperscript{(134)} and, therefore, the degree of hard/soft segment phase separation. The results were explained as being due to the fact that aromatic structures are less compatible with aliphatic soft segment structures.

Differences in properties of benzenediamine chain extenders also mirrored findings for the equivalent diols, i.e. para-substitution of the amine functional groups was found to result in the most phase separated domain morphologies due to the symmetry of the resulting hard segments\textsuperscript{(135,136)} and their ability to interact effectively.

The effect on elastomer properties of aromatic diamine chain extenders with different link groups between the aromatic rings has been studied in the case of a TDI/polybutadiene system\textsuperscript{(98)}. Tensile testing suggested that a sulphonyl bridge group caused greater phase separation than an ether group. This in turn appeared to cause greater phase separation than a methylene group. These observations were attributed to the relative polarities of the link groups and the resulting differences in inter-hard segment interactions.

The effect of using mixed chain extender compositions has also been investigated by Ahn et al\textsuperscript{(137)}. This was achieved by synthesising elastomers with a range of compositions in which 1,4-butanediol was progressively replaced by isophoronediamine. It was found that intermediate compositions, i.e. with similar quantities of each chain extender, exhibited reduced levels of phase separation. This was evidenced by the absence of hard segment crystallinity in DSC results and the negative deviation of tensile properties. It was explained as a consequence of reductions in structural coincidence and the resulting effectiveness of the inter-hard segment interactions.
3.5 The Effect of the Soft Segment

The nature of the soft segment/polyol of a polyurethane elastomer also has a significant influence on the morphology and properties of these materials. This is because such variables as the chemical structure, molecular weight and molecular weight distribution of the polyol affect the extent to which phase separation of the soft and hard segments can occur.

For a particular value of soft segment molecular weight and hard segment chemical composition, it has been found that polyurethane elastomers incorporating polyester polyols generally display increased tensile properties (strength/moduli) to those derived from polyether polyols\(^{(137,138)}\). Yuying et al.\(^{(139,140)}\) found this to be the case in a comparison of polyurethaneureas with hard segments composed of MDI/DETDA, and utilising poly(propylene oxide) glycol or poly(butylene adipate) as soft segments. Materials with a range of hard segment contents displayed this behaviour. This general observation was explained as a consequence of increased levels of inter-soft segment interaction in the polyester polyols due to the presence of polar ester groups, and also a greater tendency for such structures to crystallise. Evidence to support this has been provided by work carried out by Morbitzer and Hespe\(^{(141)}\). In the case of poly(hexamethylene adipate) and PTMG polyols, WAXS and deformation calorimetry revealed that the former possessed a significantly greater tendency to undergo strain-induced crystallisation. It was also found that such crystallisation was largely suppressed in copolyester soft segments due to structural irregularity. It should be noted that the enhanced properties displayed by the polyester-containing materials prepared by Yuying et al. were evident despite the presence of reduced levels of phase separation in comparison to those with polyethers. A more perfectly phase separated hard/soft segment domain morphology was observed for the polyether-containing materials using SAXS, while FTIR spectroscopic analysis provided evidence of increased phase separation due to the existence of a greater proportion of inter-urethane (inter-hard segment) hydrogen bonds.
Research by other groups has shown that polyether polyols lead to more advanced degrees of phase separation than polyesters. Increased values of soft segment $T_g$ observed in the case of polyurethaneureas containing poly(ethylene adipate) suggested the presence of less phase separated morphologies than those with polyethers such as poly(propylene oxide) glycol and poly(tetramethylene oxide) glycol$^{(142)}$. Ophir and Wilkes$^{(143)}$, Schneider and Sung$^{(144)}$, and Clough and Schneider$^{(40)}$ employed techniques such as DSC, FTIR spectroscopy and SAXS to show similar differences between polyurethanes containing poly(tetramethylene oxide) glycol or poly(butylene adipate) soft segments, with hard segments derived from MDI/1,4-butanediol or TDI/1,4-butanediol.

The progressive replacement of a polyether polyol (poly(tetramethylene oxide) glycol) with a polycarbonate (poly(hexamethylene carbonate)) in elastomers with mixed soft segments was found to result in reduced phase separation$^{(137)}$. This was deemed to be due to the increased polarity of the carbonate groups in the polyester and their greater thermodynamic compatibility with the hard segments.

Work performed by Chang et al.$^{(145)}$ suggested that the introduction of increasing proportions of methyl side groups onto the backbone chain of polyester polyols may enhance the degree of phase separation and domain formation in the resulting polyurethanes. This was implied by the results of DSC and SAXS analyses and was explained as the result of an increase in free volume of the polyol and, therefore, reduced viscosity.

Amongst other types of polyol it has been found (from quantitative evaluation of the heat capacity change at the soft segment $T_g$) that, for a given hard segment, phase separation is more advanced for hydrogenated polybutadiene than for polybutadiene$^{(146)}$. Phase separation for polybutadiene was in turn found to be more advanced than for poly(tetramethylene oxide) glycol. This progressive reduction of phase separation can be explained on account of the increasing polarity of the soft segments and, consequently, increased compatibility with the hard segments.

The effect of polyol molecular weight on polyurethane elastomer properties has been the subject of numerous investigations$^{(147-154)}$. These have been performed on materials
with such soft segments as poly(tetramethylene oxide) glycol, poly(propylene oxide) glycol, poly(butylene adipate) and poly(caprolactone), and over the range of molecular weights from approximately 650-3000. Various hard segments have been used, including those derived from MDI and ethylenediamine, MDI and propylenediamine, MDI and DETDA, MDI and 1,4-butanediol and TDI and ethylenediamine. The results of these studies, which utilised characterisation techniques such as FTIR spectroscopy, DSC, DMTA, WAXS and SAXS, generally implied that for a given hard segment size increasing soft segment molecular weight resulted in increased levels of phase separation. This was attributed to decreasing hard/soft segment compatibility and was evidenced by reduced degrees of hard-soft segment hydrogen bonding interactions, reduced values of soft segment glass transition temperatures and the advent of hard and soft segment crystallinity.

The molecular weight distribution of the soft segment component of a polyurethane elastomer has been found to influence the resulting properties of these materials. Using DSC, DMTA and tensile testing, Ng et al.\textsuperscript{(77)} and Harrell\textsuperscript{(155)} found that a narrower molecular weight distribution in the case of poly(tetramethylene oxide) glycol resulted in an increase in the perfection of the domain morphology, and caused increased values of mechanical properties such as ultimate tensile strength. It has also been noted that the use of binary and ternary blends of poly(propylene oxide) glycols in polyurethane systems with TDI and 1,4-butanediol resulted in increased tensile strength\textsuperscript{(156)}. These blends were obtained by combining polyols of two and three different molecular weights, respectively.

3.6 The Effect of Crosslinking

The introduction of chemical crosslinks into a polyurethane elastomer can be achieved by a number of methods and has been found to have a significant effect on morphology and properties.
The introduction of crosslinking to the hard segments of elastomers by progressively replacing 1,4-butanediol with trimethylolpropane has been studied in both MDI/polyether and MDI/polyester-based polyurethanes. Increases in soft segment $T_g$ and reductions in strength and elongation at break indicated that the introduction of increasing levels of crosslinking reduced segmental mobility and impaired the crystallisation of the hard segments.

Crosslinking has also been introduced into hard segments by the use of diacetylene diols which are crosslinkable in the solid state by irradiation. This allowed the preservation of a phase separated domain morphology, and increasing levels of crosslinking resulted in ultimate tensile strength increasing and going through a maximum.

The introduction of crosslinking into the soft segment of a polyurethane elastomer by using co-poly(propylene oxide-tetramethylene oxide) triol was investigated and compared to a material using a similar, but difunctional polyol. Materials with various hard segment contents were prepared. The general observation from DSC analysis was that the crosslinking did not reduce the ability of the MDI/1,4-butanediol hard segments to undergo crystallisation, while ultimate tensile strength was found to increase due to the presence of the crosslinks. Similar results were obtained for a system in which the crosslinking was introduced by the use of co-poly(propylene oxide-ethylene oxide) triol in place of poly(propylene oxide) diol. The use of trifunctional castor oil blended with poly(propylene glycol) polyol has also been found to enhance mechanical properties in elastomers due to the introduction of soft segment crosslinking.

The use of excess isocyanate can result in the crosslinking of polyurethanes due to the formation of such structures as allophanates and biurets. Research performed by Petrovic and Fajnik on elastomers based on MDI and castor oil found that an increasing excess of isocyanate up to a value of 20% resulted in substantially increased mechanical properties, although only a slight increase in soft segment $T_g$ was observed. Ramesh et al. showed that for elastomers derived from TDI or 1,6-
hexamethylene diisocyanate and hydroxyl-terminated polybutadiene increasing levels of excess isocyanate up to 40% also caused increases in tensile properties.

3.7 The Effect of Thermal History and Synthesis Procedure

The morphology and physical properties of polyurethane elastomers may be significantly influenced by their thermal history.

Generally, three regions of endothermic activity which are associated with hard segment ordering have been observed in the DSC results of thermoplastic polyurethane elastomers. The behaviour of these endothermic features in response to variations in thermal history has been studied extensively, in particular for hard segments derived from MDI and 1,4-butanediol. The endotherms have been found to occur at temperatures of approximately 60-80°C, 120-190°C and above 200°C, and have been attributed to short-range, long-range and microcrystalline ordering of the hard segment domains, respectively\(^\text{165,166}\). Other researchers have assigned the terminology type I, type II and type III crystallinity\(^\text{167-172}\), although in some cases the appearance of the most ordered structures was only reported upon sample stretching. Endotherms occurring at the two lower temperatures have been attributed by Blackwell and Lee\(^\text{172}\) to hard segments which are crystallised in contracted and extended conformations. These are deemed to be due to structures containing some gauche and all-trans conformations, respectively. It has been found that annealing at temperatures up to approximately 200°C may cause increased ordering of the hard segment domains, evidenced by the fact that the lowest temperature endotherm becomes shifted to higher temperatures. If the annealing is performed for a sufficient period of time, or at a high enough temperature, this endotherm may then merge with that at intermediate temperatures. Severe annealing can then shift this endotherm to the higher temperature region.
In the case of hard segments derived from MDI and diacetylene chain extender compounds the increases in hard segment ordering brought about by annealing were found to result in substantially increased values of ultimate tensile strength.

The effect of the synthesis procedure i.e. one-shot versus two-shot reactions has been investigated in the case of thermoplastic polyurethanes with MDI/1,4-butanediol hard segments and either polyether or polyester soft segments. It was found that the perfection of the domain morphology and the tensile properties of the polyester-containing materials were reduced in the case of the one-shot reaction process. This was deemed to result from a broader molecular weight distribution of hard segments resulting from this procedure and, therefore, less effective inter-hard segment interactions and phase separation. This effect was not significant in the case of the polyether-containing materials. For these it appeared that the effect was compensated for by the greater incompatibility of the hard and soft segment structures.
Chapter 4

Experimental
4.1 Materials

4.1.1 Diisocyanate

4,4'-methylenebis(phenyl isocyanate) (MDI) of 98% purity was supplied by Aldrich Chemical Company Ltd.
The chemical structure of MDI is as follows.

\[
\text{OCN} - \text{CH}_2 - \textbf{NCO}
\]

4.1.2 Polyol

Poly(tetramethylene oxide) glycol (PTMG, Terathane ® 1000) with an average molecular weight of approximately 1000 was supplied by DuPont Chemicals.
The chemical structure of the PTMG polyol may be represented as follows.

\[
\text{HO-} \left[\left(\text{CH}_2\right)_4\text{O}\right]_n\text{H}
\]

Where \( n \) is approximately equal to 14.

4.1.3 Chain Extenders

With the exception of \textit{trans}-but-2-ene-1,4-diol, all dihydroxy, hydroxyamine and diamine chain extender compounds were supplied by Aldrich Chemical Company Ltd., and were used as received.
\textit{Trans}-but-2-ene-1,4-diol was synthesised according to the following reaction scheme\(^{(176)}\).
18g (0.474mol) of LiAlH₄ was added slowly to 125ml of tetrahydrofuran in a 500ml, three-necked, round-bottomed flask equipped with a tensile stirrer, a condenser and a dropping funnel. The mixture was brought to reflux and 10.2g (0.118mol) of 2-butyn-1,4-diol in 50ml of tetrahydrofuran was added dropwise over a period of 45 minutes. After refluxing for one hour the mixture was cooled to room temperature and 100ml of 0.1 N HCl was added dropwise over a period of one hour. The mixture was then refluxed for an additional 15 minutes. After cooling to room temperature, 100g of magnesium sulphate was added as a drying agent. This was removed by filtration and washed with two 200ml portions of dioxane. The combined filtrate and washings were treated with a second 100g addition of magnesium sulphate. After removal of the MgSO₄, the filtrate was rotary evaporated to give 8.7g (87% yield) of a viscous syrup.

The chemical structures of the chain extender compounds employed are shown below.

4.1.3.1 C₄ α,ω-Diol Chain Extender Compounds

1,4-butanediol

Trans-but-2-ene-1,4-diol

Cis-but-2-ene-1,4-diol
Chapter 4 Experimental

4.1.3.2 Hydroxyamine and Equivalent Dihydroxy Chain Extender Compounds

\[
\begin{align*}
\text{HOCH}_2\text{C} &= \text{C} = \text{C} = \text{CH}_2\text{OH} \\
\text{But-2-yne-1,4-diol} \\
\text{H} &\quad \text{C} = \text{C} \quad \text{Br} \\
\text{H} &\quad \text{C} = \text{C} \quad \text{Br} \\
\text{CH}_2\text{OH} &\quad \text{CH}_2\text{OH} \\
\text{(±)-2,3-Dibromobutane-1,4-diol} \\
\text{HOCH}_2\text{C} &= \text{C} = \text{Br} \\
\text{Br} &\quad \text{C} = \text{CH} \quad \text{CH}_2\text{OH} \\
\text{Trans-2,3-dibromobut-2-ene-1,4-diol}
\end{align*}
\]

3-Aminophenol 1,3-Dihydroxybenzene

2-Aminobenzyl alcohol 2-Hydroxybenzyl alcohol
4.1.3.3 Aromatic Diamine Chain Extender Compounds

- 4,4'-Methylenedianiline
- 4,4'-Oxydianiline
- 4,4'-Thiodianiline
- 4,4'-Sulphonyldianiline

4.1.3.4 2,4-Pentanediol Chain Extender Compounds

- (+)-2,4-Pentanediol
- (-)-2,4-Pentanediol
- meso-2,4-Pentanediol
4.1.3.5 Benzenedimethanol Chain Extender Compounds

\[ \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \]
\[ \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \]
1,2-Benzenedimethanol 1,4-Benzenedimethanol

4.2 Characterisation of the Starting Materials

4.2.1 Hydroxyl Number and Equivalent Weight Determination of the Polyol

The hydroxyl number of a polyol is defined as the number of milligrams of sodium or potassium hydroxide equivalent to the hydroxyl content of the polyol\(^{(1)}\). It is determined by acetylation of the polyol with an excess of acetic anhydride and titrating the excess reagent with a standard sodium hydroxide solution. The equivalent weight of a polyol is the mass of polyol which contains one mole of functional groups. The following experimental process was used for the hydroxyl number and equivalent weight determination of the poly(tetramethylene oxide) glycol (PTMG).

Approximately 3g of PTMG was accurately weighed into a 250 ml round-bottomed flask containing 200ml of acetylation mixture (acetic anhydride:pyridine in a 12.88% v/v ratio). The contents of the flask were refluxed for one hour and then cooled to room temperature. Several 25ml aliquots were then taken, diluted with 15ml of pyridine and titrated with a standard, approximately 0.2M, sodium hydroxide solution. A 10% w/v colourless solution of phenolphthalein in pyridine was used as the indicator, the end point being taken as the 15 second persistence of a faint pink colour. A blank titration was also performed in the absence of a PTMG sample.
The hydroxyl number of the PTMG was calculated from the following equation.

\[
\text{OH number} = 40.0 \times M (\text{NaOH soln.}) \times (\text{ml blank - ml sample}) / \text{sample weight}
\]

Where \( M \) is the molarity and 40.0 g mol\(^{-1}\) is the molar mass of NaOH.

The equivalent weight of the polyol (the mass of polyol containing one mole of functional groups) is related to the hydroxyl number by the following relationship.

\[
\text{Equivalent weight} = 40000 / \text{OH number}
\]

### 4.2.2 Nuclear Magnetic Resonance Spectroscopy

The starting materials were characterised by proton nuclear magnetic resonance (\(^1\)H NMR) spectroscopy. Thirty two scans per sample were collected using a Bruker Avance DPX 400 spectrometer operated at a frequency of 400.13MHz. Samples were dissolved in deuterated chloroform.

### 4.2.3 Fourier Transform Infrared Spectroscopy

The starting materials were characterised by Fourier transform infrared spectroscopy (FTIR). Compounds which were liquids at room temperature were analysed between NaCl discs, while solid samples were analysed in the diffuse reflectance (DRIFT) mode. Fifty scans per sample were performed over the wavenumber range 600-4000 cm\(^{-1}\). The equipment used was a Perkin Elmer System 2000 FTIR spectrometer.

### 4.2.4 Melting Point

The starting materials were characterised by melting point, as determined by differential scanning calorimetry (DSC). A ramp rate of 5°C min\(^{-1}\) was used with
approximately 10mg samples using a TA Instruments 2920 DSC. The sample chamber was purged with argon at a flow rate of approximately 20 ml min\(^{-1}\).

### 4.3 Synthesis Procedure for the Polyurethanes/urethaneureas

Prior to the preparation of all prepolymers and materials the PTMG polyol and the chain extender compounds with a melting point below 80°C were dried and degassed under a reduced pressure of <1kPa at a temperature of 80°C for a period of at least four hours. MDI was melted at 60°C and then filtered and degassed under a reduced pressure of <1kPa at a temperature of approximately 60°C for two hours prior to use.

The concept of equivalent weights was employed in order to determine the masses of reagents used in syntheses, one equivalent weight being the mass of reagent containing one mole of functional groups, i.e.

\[
\text{Equivalent weight} = \frac{\text{Molar mass of reagent}}{\text{Number of functional groups}}
\]

The equivalent weights of reagents were then reduced to molar equivalents by a scaling factor (usually six) in order to yield manageable quantities of materials. An example of the quantities of reagents used in a typical formulation are given in table 4.1.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Equivalent Weight (A) /g</th>
<th>Molar Ratio (B)</th>
<th>Mass Required / g ((A \times B / 6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI</td>
<td>125</td>
<td>2.1</td>
<td>43.8</td>
</tr>
<tr>
<td>PTMG</td>
<td>490.8</td>
<td>1</td>
<td>81.7</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>45.1</td>
<td>1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

*Table 4.1. Example quantities of reagents used in a typical formulation.*
4.3.1 **Prepolymer Synthesis**

2.1 molar equivalents (43.8g) of MDI (i.e. to give an overall excess of 5% isocyanate functionalities) were added with manual stirring to 1 molar equivalent (81.8g) of PTMG in a 1 litre capacity steel canister, and allowed to react under vacuum (<1kPa) in an oven at 80±2°C for approximately 1.5 hours. A 5% excess of MDI was employed in order to account for the possibility of additional reactions, such as with water, other isocyanate groups or urethane/urea groups.

The progress of the prepolymer synthesis reaction was followed titrimetrically. Samples of the prepolymer reaction mixture were taken at regular intervals, and the extent of the reaction was ascertained by isocyanate content determination as follows.

Approximately 2g of reaction mixture were accurately weighed and added to 25ml of a 10% v/v dibutylamine in toluene solution. The reaction mixture was allowed to dissolve and left for approximately fifteen minutes. The resulting solution was diluted with 100ml of isopropyl alcohol, a few drops of bromophenol blue indicator were added, and the excess dibutylamine was titrated with 1M hydrochloric acid. The end point was taken as the conversion of a blue colour to a yellow colour that persisted for at least fifteen seconds.

A plot of percentage free isocyanate vs time was constructed (Appendix I), and from it the approximate time taken for the prepolymer synthesis reaction to be completed was determined.

The percentage free isocyanate was calculated from the following equation (overleaf).

\[
\% \text{NCO} = 42 \times M \times \frac{(V_2-V_1)}{1000W} \times 100
\]

Where \(M\) is the molarity of HCl, \(V_1\) is the volume of HCl (in ml) required for titration of the blank dibutylamine solution, \(V_2\) is the volume of HCl (in ml) required for titration of the sample and \(W\) is the sample weight (in grams).
From the plot of percentage free isocyanate vs time the prepolymer synthesis reaction was deemed to be complete after a reaction time of approximately fifty minutes at a reaction temperature of 80°C.

4.3.2 \( C_4 \alpha_\omega\)-Diol Chain-Extended Polyurethanes

4.3.2.1 One-Shot Reaction Process

The compounds 1,4-butanediol (99% purity, as confirmed by \(^1\)H NMR spectroscopy), cis-but-2-ene-1,4-diol (95% purity), \( trans \)-but-2-ene-1,4-diol (>90% purity), but-2-yne-1,4-diol (99% purity), (\( \pm \))-2,3-dibromobutane-1,4-diol (99% purity) and \( trans \)-2,3-dibromobut-2-ene-1,4-diol (97% purity) were used as chain extenders to prepare polyurethanes by the one-shot method.

1 molar equivalent of chain extender compound was placed in a 1 litre capacity steel canister and dissolved in 1 molar equivalent of PTMG at 80±2°C with manual stirring. The mixture was de-gassed under a reduced pressure of <1kPa for about 1 hour. 2.1 molar equivalents of MDI were then added and mixing was performed mechanically under vacuum (<100Pa) using a 1 litre capacity planetary mixer, at a speed of approximately 100rpm for about 5 minutes. The reaction mixture was subsequently cast into an open mould of approximate dimensions 150mm x 150mm which had been treated with Ambersil Formula Ten/2 mould release agent. The resulting sheet was cured at 80±2°C for 48±1 hours.

Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.

4.3.2.2 Two-Shot Reaction Process

The compounds 1,4-butanediol, cis-but-2-ene-1,4-diol, \( trans \)-but-2-ene-1,4-diol and but-2-yne-1,4-diol were used as chain extenders to prepare polyurethanes by the two-shot method.
1 molar equivalent of chain extender was added to 1 molar equivalent of prepolymer (prepared as described in section 2.3.1) in a 1 litre capacity steel canister, and mixing was performed mechanically under vacuum (<100Pa) using a 1 litre capacity planetary mixer, at a speed of approximately 100rpm for about 5 minutes. The resulting mixture was cast into an open mould of approximate dimensions 150mm x 150mm, which had been treated with Ambersil Formula Ten/2 mould release agent. The resulting sheet was cured at either 60±2°C or 80±2°C for 48±1 hours. In the case of each chain extender composition, materials were cured at both of these temperatures. Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.

The two-shot reaction process can be represented as follows:

**Stage 1 Prepolymer Synthesis**

\[
2 \text{MDI} + \text{PTMG} \rightarrow \text{Prepolymer}
\]

This prepolymer structure may be represented schematically by the following.
Stage 2 Chain Extension:

\[ n \text{ OCN} \longrightarrow \text{NCO} \]

Prepolymer

\[ + \]

\[ n \text{ HO-R-OH} \]

Chain Extender

\[ \downarrow \]

\[ \begin{array}{c}
\text{N-C-O-R-O-C-N} \\
\text{H} \end{array} \]

Polyurethane elastomer

4.3.3 Hydroxyamine and Equivalent Dihydroxy Compound Chain-Extended Polyurethaneureas/urethanes

The hydroxyamine compounds used as chain extenders to prepare polyurethaneureas were 3-aminophenol (98% purity) and 2-aminobenzyl alcohol (97% purity). For comparative purposes polyurethanes were prepared with the equivalent dihydroxy chain extender compounds, 1,3-dihydroxybenzene (98% purity) and 2-hydroxybenzyl alcohol (99% purity), respectively.

Prepolymer synthesis was performed as described in section (2.3.1). 0.6 molar equivalents of chain extender were dissolved in 0.4 molar equivalents of PTMG at approximately 80°C on a magnetic hot plate. After degassing at <1kPa for approximately 1 hour, this was then added to one molar equivalent of prepolymer in a 1 litre capacity steel canister, and mixing was performed mechanically under vacuum.
(<100Pa) using a 1 litre capacity planetary mixer, at a speed of approximately 100rpm for about 5 minutes. The reaction mixture was subsequently cast into an open mould of approximate dimensions 150mm x 150mm which had been treated with Ambersil Formula Ten/2 mould release agent. The resulting sheet was cured at 80±2°C for 48±1 hours. Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.

4.3.4 Aromatic Diamine Chain-Extended Polyurethanes

The aromatic diamine compounds used as chain extenders to prepare polyurethanes were 4,4'-methylenedianiline (97% purity), 4,4'-oxydianiline (97% purity), 4,4'-thiodianiline (98% purity) and 4,4'-sulphonyldianiline (98% purity).

Prepolymer synthesis was performed as described in section (2.3.1). 0.3 molar equivalents of chain extender were dissolved in 0.7 molar equivalents of PTMG at approximately 80°C with manual stirring. After degassing at <1kPa for roughly 1 hour this was then added to one equivalent of the prepolymer in a 1 litre capacity steel canister, and mixing was performed by hand. The reaction mixture was subsequently cast into an open mould of approximate dimensions 150mm x 150mm which had been treated with Ambersil Formula Ten/2 mould release agent. A hot air gun was used to remove air voids and the resulting sheet was cured at 80±2°C for 48±1 hours. Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.

4.3.5 2,4-Pentanediol Chain-Extended Polyurethanes

The compounds used to prepare 2,4-pentanediol chain-extended polyurethanes were (+)-2,4-pentanediol (99% purity), (−)-2,4-pentanediol (99% purity), (±)-2,4-pentanediol (obtained by melting and mixing equal proportions by mass of the (+)- and (−)-pentanediol enantiomers) and 50% (±/-50% meso-2,4-pentanediol (98% purity).
Prepolymer synthesis was performed as described in section (2.3.1). One molar equivalent of chain extender was added to 1 molar equivalent of prepolymer in a 1 litre capacity steel canister, and mixing was performed mechanically under vacuum (<100Pa) using a 1 litre capacity planetary mixer, at a speed of approximately 100rpm for about 5 minutes. The reaction mixture was subsequently cast into an open mould of approximate dimensions 150mm x 150mm which had been treated with Ambersil Formula Ten/2 mould release agent. The resulting sheet was cured at 80±2°C for 48±1 hours. Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.

4.3.6 Benzenedimethanol Chain-Extended Polyurethanes

The compounds employed as chain extenders to prepare polyurethanes were 100% 1,4-benzenedimethanol (99% purity), 90%/10% 1,4/1,2-benzenedimethanol, 75%/25% 1,4/1,2-benzenedimethanol, 50%/50% 1,4/1,2-benzenedimethanol, 25%/75% 1,4/1,2-benzenedimethanol, 10%/90% 1,4/1,2-benzenedimethanol and 100% 1,2-benzenedimethanol (97% purity). The mixed composition chain extenders were prepared by melting and mixing the required proportions by mass of the 1,4- and 1,2-benzenedimethanol isomers.

Prepolymer synthesis was performed as described in section (2.3.1). 0.6 molar equivalents of chain extender was placed in a 1 litre capacity stainless steel cannister, and dissolved in 0.4 molar equivalents of PTMG at approximately 80°C with manual stirring. The mixture was degassed under a vacuum of <1kPa for about 1 hour. 1 molar equivalent of prepolymer was then added and mixing was performed mechanically under vacuum (<100Pa) using a 1 litre capacity planetary mixer, at a speed of approximately 100rpm for about 5 minutes. The reaction mixture was subsequently cast into an open mould of approximate dimensions 150mm x 150mm which had been treated with Ambersil Formula Ten/2 mould release agent. The resulting sheet was cured at 80±2°C for 48±1 hours. Materials were conditioned at room temperature for a period of one week prior to the execution of any characterisation.
4.4 Characterisation of Polyurethanes/urethaneureas

4.4.1 Fourier Transform Infrared Spectroscopy

Solid elastomer samples of approximate dimensions 30mm x 10mm x 2mm were analysed by Fourier transform infrared spectroscopy (FTIR) in the attenuated total internal reflectance mode (ATR). The wavenumber range 600-4000 cm\(^{-1}\) was investigated, with two hundred scans per sample being performed on a Unicam Mattson 3000 FTIR spectrometer.

The results of the FTIR spectroscopic analyses of polyurethanes display absorption peaks in the approximate wavenumber range 1700-1730 cm\(^{-1}\). These peaks are attributed to the absorbance of infrared radiation by the carbonyl functionalities present in urethane groups. Absorbance peaks with maxima in the range 1728-1730 cm\(^{-1}\) are generally attributed to urethane carbonyl groups not participating in inter-urethane hydrogen bonding interactions\(^{(177)}\). Conversely, peaks with maxima in the range 1699-1712 cm\(^{-1}\) are attributed to urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions i.e inter-hard segment interactions. The absolute value of the wavenumber within this range provides an indication of the relative strength of the hydrogen bonds. Thus, decreasing infrared absorption wavenumber values are associated with carbonyl bonds of reduced energy in accordance with the following relationships\(^{(178)}\), and are in turn the result of inter-urethane hydrogen bonds of increased strength.

\[
\text{wavenumber} = \frac{v}{c}
\]

\[
E = h\nu
\]

where \(v\) is the frequency of the radiation, \(c\) is the velocity of the radiation, \(E\) is the energy of the radiation and \(h\) is the Planck constant (6.626x10\(^{-34}\) Js).
The relative absorbances of the hydrogen bonded and non-hydrogen bonded peaks are proportional to the relative quantities of each type of urethane carbonyl group present and can, therefore, provide an indication of the degree of hard/soft segment phase separation present. Consequently, values of the parameter $X$, the fraction of hard segments participating in inter-urethane hydrogen bonding, were calculated from the following relationship (82).

$$X = \frac{A_{C=O,b}}{A_{C=O,b} + A_{C=O,f}}$$

where $A_{C=O,b}$ is the area of the hydrogen bonded urethane carbonyl group absorbance peak and $A_{C=O,f}$ is the area of the non-hydrogen bonded (free) urethane carbonyl group absorbance peak.

This calculation makes use of the Beer-Lambert law (178), which states that the absorbance of a species is directly proportional to the concentration of the species present, as follows.

$$A = \varepsilon bc$$

where $A$ is the absorbance, $\varepsilon$ is the absorption coefficient, $b$ is the path length or sample thickness and $c$ is the concentration of the absorbing species.

Values of absorbance were obtained by integration of the areas under the absorbance peaks. It was assumed that the ratio of the extinction coefficients for the non-hydrogen bonded and the hydrogen bonded urethane carbonyl groups equalled unity.

### 4.4.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on 10-15mg sample sizes over the temperature range -100 to 200°C using a ramp rate of 10°C/min⁻¹. Samples were crimped in aluminium sample pans and the sample chamber was purged with
argon at a flow rate of approximately 20ml min\(^{-1}\). Cooling was performed using liquid nitrogen. The equipment used was a TA Instruments 2920 Modulated DSC fitted with a dual sample cell.

A summary of the principles of DSC is given below.
Differential scanning calorimetry is a technique in which the difference in energy inputs into a substance and a thermally inert reference material is measured while the substance and reference material are subjected to a controlled temperature program\(^{(179)}\). The technique employed in this work is more specifically referred to as heat-flux DSC. This functions by using thermocouples to measure the difference in temperature between the sample and the reference as they are subjected to the temperature program.

Analyses of the kinetics of the reactions employed to prepare the \(C_4\ \alpha,\omega\)-diol chain-extended materials via the one-shot reaction process were performed by means of a TA Instruments Borchardt and Daniels kinetics analysis program. For this purpose the DSC instrument described above was used, and the reaction mixtures were prepared as described in section 4.3.2.1. In the case of each composition, immediately after the constituents had been mixed, a single drop of the reaction mixture was placed in an aluminium sample pan using a pipette. The pan was then crimped and analysed by DSC. The reaction mixtures were subjected to a temperature profile of 10°C min\(^{-1}\) from ambient until it was observed that the reaction exotherm was complete. The Borchardt and Daniels kinetics analysis program was then applied to the reaction exotherm.

The method used in the Borchardt and Daniels kinetics analysis program to determine the values of kinetic parameters such as reaction order, activation energy and pre-exponential factor is based on the general rate equation for \(n\)th order reactions.

\[
d\alpha/dt = k(1-\alpha)^n
\]
where $\alpha$ is the fraction converted, $k$ is the temperature dependent rate constant and $n$ is the reaction order.

The method also assumes an Arrhenius behaviour.

$$k = A \exp \left( -\frac{E_A}{RT} \right)$$

where $k$ is the temperature dependent rate constant, $A$ is the pre-exponential factor, $E_A$ is the activation energy, $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the reaction temperature.

4.4.3 Modulated-Temperature Differential Scanning Calorimetry

Modulated-temperature differential scanning calorimetry (M-TDSC) was performed on 8-10 mg sample sizes over the temperature range -100 to 200°C using a ramp rate of 3°C/min$^{-1}$. A modulation of ±1°C with a period of 60 seconds was applied to the 3°C/min$^{-1}$ ramp rate. The equipment used was a TA Instruments 2920 modulated DSC.

A summary of the principles of M-TDSC is presented below$^{(180)}$. The M-TDSC technique is a development of ‘conventional’ DSC. In M-TDSC the conventional linear temperature program is modulated by some form of perturbation. In the case of the M-TDSC method employed in this study the modulation was a sinusoidal oscillation. The temperature program in M-TDSC, therefore, consists of an underlying linear temperature profile (the overall heating rate) with a sinusoidal variation superimposed upon it.

The reason for the imposition of such a temperature program can be explained by considering the contributions to the total heat flow response of a differential scanning calorimeter. This may be considered to consist of two components, one of which is dependent on the rate of change of temperature and one which is dependent on the absolute value of temperature. The former depends on the heat capacity of the sample,
while the latter depends on the rate of a kinetically driven process. This can be expressed as follows.

\[ \frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T) \]

where \( \frac{dQ}{dt} \) is the heat flow into the sample, \( C_p \) is the thermodynamic heat capacity (due to molecular motions), \( T \) is the absolute temperature, \( t \) is time and \( f(t, T) \) is some function of time and temperature.

The modulated temperature programme can be expressed as follows.

\[ T = T_0 + bt + B \sin(\omega t) \]

where \( T_0 \) is the starting temperature, \( \omega \) is the frequency, \( b \) is the heating rate and \( B \) is the amplitude of the sinusoidal modulation.

If it is assumed that the temperature modulation is small, and that over this interval the response of the rate of the kinetic process to temperature can be approximated as linear the expression for the heat flow response can be written as follows.

\[ \frac{dQ}{dt} = C_p [b + B \cos(\omega t)] + f'(t, T) + C \sin(\omega t) \]

where \( f'(t, T) \) is the average underlying kinetic function (minus the effect of the sine wave modulation), \( C \) is the amplitude of the kinetic response to the sine wave modulation and \( [b + B \cos(\omega t)] \) is equal to \( \frac{dT}{dt} \) (the overall heating rate).

Therefore, in M-TDSC, the imposition of a sinusoidal modulation to the heating rate results in the heat flow signal containing a cyclic component. A Fourier transform treatment may then be used to deconvolute the cyclic component (the ‘reversing’ signal) from the underlying (or total) heat flow signal. The underlying heat flow signal is equivalent to a conventional DSC response. It is also useful to calculate an
additional signal, which is given by the difference between the underlying and the reversing signals. This is referred to as the ‘non-reversing’ signal. Thus, on the timescale of the temperature modulation during an M-TDSC experiment, the cyclic or reversing signal is indicative of events which are, at the time and temperature that the measurement is taken, reversible. Such events are, therefore, subject to thermodynamic control, for example glass transitions. These events are also apparent in the underlying signal. The non-reversing signal represents the contribution to the total heat flow signal of events which on the timescale of the modulation are irreversible, or in some way kinetically hindered. These events are, therefore, subject to kinetic control, for example crystallisation phenomena.

4.4.4 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) was performed on 3.0 ± 0.1mm thick samples in the single cantilever bending mode at a frequency of 10Hz and a strain level of x4. A ramp rate of 2°C min⁻¹ over the temperature range -70 to 180°C was applied to samples in order to obtain curves of log $E'$ and tan $\delta$ as a function of temperature. The equipment used was a Polymer Laboratories Dynamic Mechanical Thermal Analyser equipped with a Mark II head.

A summary of the principles of DMTA(18) and the origin of the parameters log $E'$ and tan $\delta$ is given below.

A sinusoidal oscillatory strain, $\varepsilon$ applied to a polymeric material at an angular frequency $\omega$, may be described by the following expression:

$$\varepsilon = \varepsilon_0 \sin \omega t$$

where $\varepsilon_0$ is the strain amplitude and $t$ is time.
materials chain-extended with the C₆ α,ω-diol compounds was butan-2-one (methylethylketone). Toluene was the solvent employed in the case of the other groups of materials, due to the fact that the majority of these materials were soluble in butan-2-one.

Samples were weighed prior to immersion in solvent and again immediately afterwards, subsequent to rapid surface drying. Values of volume fraction of solvent present in the swollen elastomer samples were calculated from the following relationship.

\[ \sigma_s = \frac{\nu_s}{\nu_s + \nu_e} = \frac{(m_s / \rho_s)}{(m_s / \rho_s) + (m_e / \rho_e)} \]

where \( \sigma_s \) is the volume fraction of solvent in the swollen elastomer, \( \nu_s \) is the volume of solvent in the swollen elastomer, \( \nu_e \) is the volume of elastomer in the swollen elastomer, \( m_s \) is the mass of solvent in the swollen elastomer, \( m_e \) is the mass of elastomer in the swollen elastomer, \( \rho_s \) is the density of the solvent, and \( \rho_e \) is the density of the elastomer.

Densities of material samples were calculated by means of the fluid displacement method. This method is based on the Archimedean principle, which states that a solid immersed in a liquid is subjected to the force of buoyancy, this force being equal to that of the weight of liquid displaced by the volume of the solid. The procedure used was as follows.

Material samples were initially weighed in air. A 100ml beaker, approximately half-filled with water was placed on a balance which was then tared to zero. A hypodermic needle, held using a clamp and stand, was used to impale the sample. The sample was then immersed to a depth of approximately 20mm in the water in order to avoid any surface tension effects. The sample weight in water was thereby obtained. The temperature of the water was noted in order to enable the water density to be obtained from tables of data. Material densities were then calculated from the following equation (overleaf).
Density = \frac{M_a}{M_w / \rho_w}

where $M_a$ is the mass of the sample in air, $M_w$ is the mass of the sample in water and $\rho_w$ is the density of water.
Chapter 5

$C_4 \alpha,\omega$-Diol Chain-Extended Polyurethanes
5.1 Results and Discussion

Polyurethane elastomers chain-extended with C₄ α,ω-diols were prepared and characterised in order to determine the effects of chain extender chemical structure and also reaction conditions on the physical and tensile properties of these materials. The compounds 1,4-butanediol, cis-but-2-ene-1,4-diol, trans-but-2-ene-1,4-diol, but-2-yne-1,4-diol, (±)-2,3-dibromobutane-1,4-diol and trans-2,3-dibromobut-2-ene-1,4-diol were employed as chain extenders, in order to ascertain the influence of unsaturation, configuration and halogen substituents on morphology and properties. The chemical structures of these compounds are shown in section 4.1.3.1. The effect on properties of employing different reaction processes (one-shot vs two-shot reactions) was also investigated for these C₄ diols. In addition, the effect of cure temperature (60°C vs 80°C) was studied for the two-shot processed materials incorporating the non-halogenated chain extender compounds.

5.1.1 Fourier Transform Infrared Spectroscopy

The results of the FTIR spectroscopic analyses of the C₄ α,ω-diol chain-extended polyurethanes are summarised in table 5.1. The urethane carbonyl absorption regions of these materials are shown in figures 5.1-5.3. Values of X, the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, were determined from the relative absorbances of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks (as described in section 4.4.1).

5.1.1.1 The Strength of the Inter-Urethane Hydrogen Bonds

In comparison to the equivalently processed 1,4-butanediol chain-extended polyurethanes, those chain extended with cis-but-2-ene-1,4-diol displayed increased values of wavenumber for their hydrogen bonded urethane carbonyl absorption
<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Processing Technique</th>
<th>Inter-Urethane Hydrogen-Bonded Carbonyl Absorption Maximum / (±1) cm(^{-1})</th>
<th>X ((±0.02))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>1701</td>
<td>0.74</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>1705</td>
<td>0.70</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>1703</td>
<td>0.66</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>1701</td>
<td>0.73</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>1699</td>
<td>0.75</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>1705</td>
<td>0.74</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>1699</td>
<td>0.72</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>1707</td>
<td>0.63</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1699</td>
<td>0.66</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1703</td>
<td>0.70</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1699</td>
<td>0.76</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1701</td>
<td>0.73</td>
</tr>
<tr>
<td>Trans-2,3-dibromobut-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1701</td>
<td>0.78</td>
</tr>
<tr>
<td>(+)-2,3-Dibromobutane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>1713</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 5.1. FTIR analysis results of the C\(_4\) α,ω-diol chain-extended polyurethanes.
maxima. This was the case for each of the three different processing techniques employed in the syntheses of the C₄ α,ω-diol chain-extended elastomers. This consistent observation indicated that the materials chain-extended with cis-but-2-ene-1,4-diol possessed inter-urethane hydrogen bonding interactions of a somewhat reduced strength in comparison to the equivalently processed 1,4-butanediol chain-extended materials." This can probably be explained as a consequence of the structural differences between the chain extender moieties involved. Under standard conditions, 1,4-butanediol exists in an all-trans planar zigzag conformation. This
highly symmetrical structure may permit the formation of effective, bi-directional inter-hard segment hydrogen bonding interactions, perpendicular to the main axes of the polyurethane chains. However, the configuration of cis-but-2-ene-1,4-diol, with its reduced symmetry about the C₄ axis, would probably not afford such regular and effective inter-hard segment hydrogen bonding interactions.

The polyurethanes prepared utilising trans-but-2-ene-1,4-diol as chain extender and processed via the one-shot, 80°C cure and two-shot, 80°C cure reaction methods displayed values of wavenumber for their inter-urethane hydrogen bonded carbonyl
Figure 5.3. FTIR analysis results of the one-shot, 80 °C cure processed $C_4 \alpha, \omega$-diol chain-extended polyurethanes: (a) 1,4-butanediol (b) cis-but-2-ene-1,4-diol (c) trans-but-2-ene-1,4-diol (d) but-2-yne-1,4-diol (e) trans-2,3-dibromobut-2-ene-1,4-diol (f) (±)-2,3-dibromobutane-1,4-diol.

absorption maxima which were comparable to those of the similarly processed 1,4-butanediol chain-extended materials. The value of this parameter for the trans-but-2-ene-1,4-diol chain-extended elastomer prepared via the two-shot, 60 °C cure scheme was intermediate between those of the equivalently processed elastomers incorporating 1,4-butanediol and cis-but-2-ene-1,4-diol. These results implied that the strength of the inter-urethane hydrogen bonds of the materials chain-extended with
trans-but-2-ene-1,4-diol were stronger than those of the similarly processed cis-but-2-ene-1,4-diol-containing elastomers, and generally of a similar strength to the equivalent 1,4-butanediol chain-extended materials. These observations could most likely be attributed to the configuration of trans-but-2-ene-1,4-diol. As is the case for 1,4-butanediol, the trans-configuration of this compound is symmetrical about the C₄ axis and may similarly allow the formation of effective inter-urethane hydrogen bonding interactions.

In the case of the elastomers prepared via the two-shot, 60°C cure and one-shot, 80°C cure processing techniques, the wavenumber values of the hydrogen bonded urethane carbonyl absorption maxima for the equivalently processed materials chain-extended with 1,4-butanediol and but-2-yne-1,4-diol were very similar. This could be explained to be the result of the linearity of the but-2-yne-1,4-diol moiety. Such a symmetrical structure may facilitate a similar type of bi-directional inter-hard segment hydrogen-bonding interaction to that which is possible with the all-trans, planar zigzag conformation of 1,4-butanediol, and also that which appears to result from the configuration of trans-but-2-ene-1,4-diol.

Despite this it was observed that the wavenumber value of the hydrogen bonded urethane carbonyl absorption maximum for the polyurethane incorporating but-2-yne-1,4-diol and prepared via the two-shot, 80°C cure processing technique, was significantly increased in comparison to the similarly processed 1,4-butanediol-containing material. This suggested that the inter-urethane hydrogen bonding interactions present in the but-2-yne-1,4-diol chain-extended material were of a reduced strength. This may be explained by further observation of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks of the but-2-yne-1,4-diol chain-extended elastomers. It was generally apparent that in comparison to the other C₄ α,ω-diol chain-extended polyurethanes the hydrogen bonded urethane carbonyl absorption peaks for all of the but-2-yne-1,4-diol chain-extended materials were noticeably broadened in the direction of greater wavenumbers. This had the effect of causing the non-hydrogen bonded urethane carbonyl absorption peaks to become shoulders on the hydrogen bonded urethane carbonyl absorption peaks, rather than distinct maxima. From this it may be inferred that while the but-2-yne-1,4-diol-
containing hard segments are quite capable of inter-hard segmental interactions of an equivalent strength to those present in the 1,4-butanediol chain-extended materials, there also existed substantial proportions of inter-urethane hydrogen bonds with a quite broad range of somewhat lower strengths. In order to account for this observation it may be considered that there is an alternative situation which is particularly viable for hard segments incorporating the but-2-yn-1,4-diol moiety. Therefore, it may be that the existence of a broad range of weaker inter-urethane hydrogen bonds within the but-2-yn-1,4-diol chain-extended elastomers is related to the presence of other, competing interactions between but-2-yn-1,4-diol-containing hard segments. Such interactions may arise, for example, between the carbon-carbon triple bonds present in adjacent but-2-yn-1,4-diol structures. These could exist in the form of interactions between the \( \pi \)-electrons which constitute such multiple bonds. Similar interactions are considered to exist between the aromatic structures of 4,4'-methylenebis(phenyl isocyanate) (MDI)\(^{83}\). Positive interactions between these structures may result in their alignment at the expense of the alignment of urethane groups and, consequently, at the expense of inter-urethane hydrogen bonds. In the case of the but-2-yn-1,4-diol chain-extended material prepared via the two-shot, 80°C cure reaction process, it may be possible that these interactions were responsible for the observation that the inter-urethane hydrogen bonding interactions of this elastomer appeared significantly weaker than those of the similarly processed 1,4-butanediol chain-extended elastomer, and also those of the alternatively processed but-2-yn-1,4-diol chain-extended materials. This could be explained in this case as being due to the combination of the two-shot reaction process and the 80°C cure temperature employed. The two-shot reaction scheme could have resulted in a regular build-up of segmental structure, while the 80°C cure temperature may have imparted sufficient kinetic energy and molecular mobility to enable the polyurethane molecules to become optimally organised, i.e. with interaction of the \( \pi \)-electrons of the carbon-carbon triple bonds taking precedence over inter-urethane hydrogen bonding interactions. Such a dependence of morphology on general interactions rather than on hydrogen bonds specifically has been previously reported by Seymour and Cooper\(^{80}\).
and also by Harrell\textsuperscript{(155)} for polyurethanes containing hard segments with no capability for hydrogen bonding.

In addition to this effect of processing technique it was observed that the increase in cure temperature from 60°C to 80°C for the \textit{trans}-but-2-ene-1,4-diol chain-extended polyurethanes prepared via the two-shot reaction processes, resulted in a decrease in value of wavenumber of the hydrogen bonded urethane carbonyl absorption maxima. This implied that the increased cure temperature caused an increase in the strength of the inter-urethane hydrogen bonding interactions of this elastomer. This was probably a result of the increase in kinetic energy and molecular mobility which was imparted to the polyurethane molecules with the increase in temperature, thus enabling improved inter-hard segment interactions. Such effects would be consistent with those that have been observed as a result of annealing at elevated temperatures\textsuperscript{(80,171,174)}. Such an increase may have been particularly significant in the case of the \textit{trans}-but-2-ene-1,4-diol chain-extended materials due to the relatively bulky nature of the \textit{trans}-but-2-ene-1,4-diol chain extender moiety. This could have imposed severe restrictions on the mobility of hard segments containing it at the 60°C cure temperature.

The polyurethane utilising \textit{trans}-2,3-dibromobut-2-ene-1,4-diol as chain extender possessed a value of wavenumber for its hydrogen bonded urethane carbonyl absorption maximum which was comparable to the lower values observed for the non-halogenated C\textsubscript{4} \textit{a,ω}-diol chain-extended elastomers. This comparability suggested that the former material possessed inter-urethane hydrogen bonding interactions of an equivalent strength to those of the strongest hydrogen bonds present in the non-halogenated C\textsubscript{4} diol chain-extended materials. This was most likely due to the highly symmetrical \textit{trans}-configuration of the \textit{trans}-2,3-dibromobut-2-ene-1,4-diol chain extender moiety. This should facilitate relatively high levels of structural regularity and, therefore, permit effective hydrogen bonding interactions of the type resulting from chain extension with 1,4-butanediol.

Of the C\textsubscript{4} \textit{a,ω}-diol chain-extended polyurethanes, that incorporating (±)-2,3-dibromobutane-1,4-diol as chain extender possessed the highest value of wavenumber for its hydrogen bonded urethane carbonyl absorption maximum. This implied that the strength of the inter-urethane hydrogen bonding interactions of this material were the
weakest of the C₄ α,ω-diol chain-extended materials. This was most likely the result of the racemic nature of the chain extender compound involved. The presence of equal proportions of the two enantiomers of 2,3-dibromobutane-1,4-diol would tend to reduce the levels of hard segment structural regularity present. This would have the effect of disrupting the ability of the hard segments within this material to interact regularly and effectively and would, therefore, reduce the tendency for strong inter-urethane hydrogen bonding interactions to form. Chain extender structural regularity has been previously found to be of importance in determining the ability of hard segment structures to interact and cause phase separation in elastomers chain-extended with mixtures of diols and diamines.

5.1.1.2 The Proportion of Urethane Carbonyl Groups Participating in Inter-Urethane Hydrogen Bonding Interactions

In the case of the polyurethanes synthesised via the two-shot, 60°C cure reaction process, values of X, the proportion of hard segments participating in inter-urethane hydrogen bonding interactions, were quite similar for the 1,4-butanediol, cis-but-2-ene-1,4-diol and but-2-yne-1,4-diol chain-extended materials. The value of this parameter was somewhat reduced for the material incorporating trans-but-2-ene-1,4-diol as chain extender. The reduced value of X observed for the latter elastomer provided evidence of the existence of a less extensive inter-urethane hydrogen bonding network in this material. This could probably be attributed to the relatively bulky nature of the trans-but-2-ene-1,4-diol moiety. Under certain circumstances, hard segments containing such a structure may have been unable to form particularly extensive interactions despite their ability to form quite strong interactions, as evidenced by the wavenumber value of the hydrogen bonded urethane carbonyl absorption peak. Therefore, the levels of molecular mobility afforded by the 60°C cure temperature could have been insufficient to enable the trans-but-2-ene-1,4-diol-containing hard segments to become involved in inter-hard segment hydrogen bonding interactions to the degree achieved by the other similarly processed polyurethanes.
Values of X of the two-shot, 80°C cure processed polyurethanes were such that the materials displayed quite similar values, with the exception of that incorporating but-2-yne-1,4-diol as chain extender. This was consistent with the observation that this elastomer possessed inter-urethane hydrogen bonds of relatively low strength and further indicated that the inter-urethane hydrogen bonding interactions were being negated, possibly in favour of other interactions such as between the π-electrons of the carbon-carbon triple bonds in the but-2-yne-1,4-diol moiety.

The two-shot, 80°C cure processed elastomer chain-extended with trans-but-2-ene-1,4-diol was observed to display an increased value of X in comparison to the equivalent two-shot, 60°C cure processed material. This could have arisen because of the increased levels of kinetic energy and molecular mobility which would have arisen from the higher cure temperature. Such an increase would probably enable the hard segments containing the relatively bulky trans-but-2-ene-1,4-diol structure to interact more effectively and facilitate more extensive inter-hard segment hydrogen bonds. This was consistent with the increased strength of the inter-urethane hydrogen bonds noted in the case of this material.

The value of X for the 1,4-butanediol chain-extended material prepared via the one-shot, 80°C cure process was significantly reduced in comparison to that prepared by the two-shot, 80°C cure process. This result may have been attributable to the fact that the one-shot scheme would involve simultaneous, competing reactions occurring between the three reagents. The result of this would probably be a less regular build-up of segmental structure than that which should arise as a result of a two-stage reaction scheme. This would in turn tend to lead to reduced levels of structural coincidence and less regular interactions between hard segments. The ability of inter-urethane hydrogen bonds to form extensive networks would, consequently, be inhibited. Such an effect of processing technique on properties has been observed in the case of polyurethanes containing polyester polyols(81).

The values of X displayed by the cis-but-2-ene-1,4-diol, trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol chain-extended polyurethanes prepared via the one-shot reaction process were not significantly reduced in comparison to the equivalent two-shot processed elastomers. It may have been the case that the inductive effect of the
carbon-carbon double and triple bonds present in these chain extender compounds caused reductions in the nucleophilic character of their hydroxyl functional groups. This could then have had the effect of retarding the rates of reaction of these functional groups with the isocyanate functionalities of MDI, thereby creating reaction processes with some degree of two-shot character. The result would be a relatively systematic build-up of segmental structure which should facilitate more extensive inter-hard segment interactions such as inter-urethane hydrogen bonds.

The greatest value of X displayed by the C₄ α,ω-diol chain-extended elastomers was observed when trans-2,3-dibromo-but-2-ene-1,4-diol was the chain extender compound employed. This indicated that this polyurethane possessed a particularly extensive inter-hard segmental hydrogen bonding network. This may have been due to a combination of effects. Firstly, the trans-configuration of this compound should permit the possibility of extensive inter-urethane hydrogen bonding networks. Also, the reactivity of this compound's hydroxyl groups towards MDI's isocyanate groups could have been significantly reduced due to the inductive effects of both the carbon-carbon double bond and the substituent bromine atoms. This may have resulted in a reaction with significant two-shot character. It would, therefore, have been possible for relatively regular segmental build-up to occur, resulting in high levels of structural coincidence and enabling effective inter-hard segment interactions.

By far the lowest value of X of the C₄ diol chain-extended polyurethanes was observed when the chain extender compound used was (±)-2,3-dibromobutane-1,4-diol. This was concurrent with the particularly low strength of inter-urethane hydrogen bonds observed for this elastomer and would again most likely have been the result of the racemic nature of the chain extender compound. The presence of mixed enantiomers would probably preclude the effective interaction of the hard segment structures and severely disrupt the tendency for phase separation to occur. Therefore, the formation of a hard/soft segment domain morphology with significant quantities of inter-urethane hydrogen bonding interactions would not be well advanced.
5.1.2 Differential Scanning Calorimetry

The results of the DSC analyses of the \( C_4 \alpha,\omega \)-diol chain-extended polyurethanes displayed step transitions in their heat flow curves at sub-ambient temperatures. These indicated changes in the heat capacity of the materials at the glass transition temperature \( (T_g) \) of the PTMG polyol/soft segment component of the materials.\(^{166}\) Values of \( T_g \) at the midpoint of the transitions were obtained from the points of inflection of the heat flow curves. The majority of the \( C_4 \) diol chain-extended elastomers also exhibited endothermic features in their DSC results. These were indicative of changes in heat capacity of the materials due to the dissociation/melting of phase-separated hard segment domain structures.\(^{80}\) The peak temperatures at which the endotherms were observed were designated \( T_m \).

The results of the DSC analyses of the \( C_4 \alpha,\omega \)-diol chain-extended materials are summarised in table 5.2 and are shown in figures 5.4-5.6.

In the case of each of the three processing techniques employed, the lowest value of soft segment \( T_g \) was observed for the polyurethane chain-extended with \( 1,4 \)-butanediol. This may have been a consequence of the fact that the elastomers chain-extended with this compound possessed the most phase-separated hard/soft segment domain morphologies.\(^{166}\) The result would be fewer hard segment structures being dissolved within the soft segment domains and, consequently, soft segment mobility would be less restricted by the presence of such rigid and bulky structures. Alternatively, the relatively high levels of rigidity of the other \( C_4 \) diol chain extender moieties, due to their unsaturated structures, may have imparted greater restrictions on soft segment mobility when dissolved among soft segments. Thus, the values of soft segment \( T_g \) could conceivably have been greater despite similar levels of phase separation being present.

Generally, the soft segment glass transition temperatures of the polyurethanes chain-extended with the unsaturated \( C_4 \) diols were similar within each of the groups of differently processed elastomers. This suggested either the presence of similar degrees of phase separation or that differing degrees of phase separation were compensated for.
<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Processing Technique</th>
<th>$T_g$ / (±1.0)°C</th>
<th>$T_m$ / (±2.0)°C</th>
<th>Main Endotherm Melting Enthalpy ($\Delta H_m$) / (±1.0) Jg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-48</td>
<td>118</td>
<td>11</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-45</td>
<td>75/136</td>
<td>6</td>
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<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-41</td>
<td>131</td>
<td>7</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-43</td>
<td>151</td>
<td>8</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-45</td>
<td>148</td>
<td>11</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-40</td>
<td>50/142</td>
<td>5</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-39</td>
<td>141</td>
<td>7</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-40</td>
<td>157</td>
<td>8</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-45</td>
<td>155</td>
<td>4</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-40</td>
<td>60/150</td>
<td>5</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-40</td>
<td>155</td>
<td>5</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-42</td>
<td>142</td>
<td>4</td>
</tr>
<tr>
<td>Trans-2,3-dibromobut-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-41</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>(+)-2,3-Dibromobutane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-16</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.2. DSC results of the $C_4 \alpha,\omega$-diol chain-extended polyurethanes.
by varying chain extender rigidities, i.e. varying degrees of soft segment mobility restriction occurred due to hard/soft segment mixing.

The value of soft segment $T_g$ of the polyurethane chain-extended with $(\pm)$-2,3-dibromobutane-1,4-diol was by a significant margin the highest of the $C_4 \alpha, \omega$-diol chain-extended elastomers. This was most likely the result of the racemic nature of this chain extender compound. The presence of equal proportions of two different enantiomers could have caused disruption of the regularity and effectiveness of inter-hard segmental interactions, thereby reducing the thermodynamic drive for phase separation and the formation of a well ordered hard/soft segment domain morphology.

This would in turn lead to relatively large quantities of hard segments remaining dissolved amongst the soft segments, thus restricting soft segment mobility and increasing the value of soft segment $T_g$. Such inhibited inter-hard segment interactions were evidenced by the results of the FTIR spectroscopic analysis.

Figure 5.4. DSC results of the two-shot, 60°C cure processed $C_4 \alpha, \omega$-diol chain-extended polyurethanes.
Values of soft segment $T_g$ were generally observed to increase for each of the different C$_4$ α-ω-diol chain extender compositions as the cure temperature of the two-shot reactions was increased from 60°C to 80°C. This indicated that the two-shot 80°C cure reaction process resulted in an increased level of phase mixing. This could have arisen due to the fact that the increase in cure temperature would have resulted in the enhanced mobility of polymer chains.

All of the polyurethanes incorporating 1,4-butandiol, cis-but-2-ene-1,4-diol, trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol as chain extender compounds exhibited marked endothermic features at temperatures in excess of 100°C. These were attributed to the melting of phase-separated hard segment domain structures. The driving force for the formation of such hard segment aggregates was the thermodynamic incompatibility of the hard and soft segment structures$^{(20)}$. 

Figure 5.5. DSC results of the two-shot, 80°C cure processed C$_4$ α,ω-diol chain-extended polyurethanes.
Figure 5.6. DSC results of the one-shot, 80°C cure processed \(C_4\,\alpha,\omega\)-diol chain-extended polyurethanes.

The elastomers incorporating \(\text{cis}\)-but-2-ene-1,4-diol as the chain extender compound displayed a similar but somewhat less significant secondary endothermic event at temperatures of approximately 50-80°C. Similar events have been attributed to the dissociation of hard segment domain structures with reduced levels of phase separation/perfection\(^{165}\) in elastomers derived from MDI, PTMG and 1,4-butanediol. Such domains would, therefore, be disrupted by reduced levels of thermal energy. The presence of such morphologies was consistent with the less effective inter-hard segment hydrogen bonding interactions suggested by the results of the FTIR analyses. These were most likely the result of the \(\text{cis}\)-configuration of the chain extender compound which would tend to result in relatively non-linear polymer sequences with reduced abilities to interact effectively.

In the case of elastomers prepared via the two-shot reaction procedures the values of enthalpy per unit mass of the main endothermic events (\(\Delta H_m\)) were found to be
greatest when the chain extender employed was 1,4-butanediol. The corresponding values for the equivalently processed trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol chain-extended materials were somewhat reduced and similar to each other, while those for the elastomers incorporating cis-but-2-ene-1,4-diol were further reduced. It was also noted that the endotherms of the polyurethanes incorporating cis-but-2-ene-1,4-diol displayed markedly broadened peak bases and were thus less distinct. These results indicated that the 1,4-butanediol chain-extended polyurethanes synthesised via the two-shot reaction processes possessed the most phase-separated/cohesive domain morphologies. This was probably a consequence of the ability of the hard segment structures containing this moiety to participate most favourably in cohesive hard segment interactions, itself most likely attributable to the all-trans planar zigzag conformation of 1,4-butanediol. Consequently, the energy required to disrupt such cohesive structures would be relatively large. The results also suggested that the materials chain-extended with cis-but-2-ene-1,4-diol possessed the least perfectly phase-separated domain morphologies, i.e. with domains which were composed of hard segment domains with a broader distribution of melting temperatures. This was again probably due to the cis-configuration of the chain extender compound which would tend to result in hard segments with reduced linearity and which would not permit such regular and cohesive interactions between hard segments. These results were in general agreement with those present in the literature. Ramesh et al. (98) and Lin et al. (100) reported similar findings for chain extension with 1,4-butanediol and cis-but-2-ene-1,4-diol in the case of polyurethanes derived from TDI/hydroxyl-terminated polybutadienes and from MDI/polyether commercial prepolymers, respectively. DMTA and mechanical testing were the characterisation methods used in these studies.

In the case of the two-shot, 60°C cured elastomers the absolute temperatures at which the main hard segment domain melting endotherms were observed increased with increasing unsaturation in the chain extender moiety. This indicated that the resistance to thermal dissociation of the hard segment domains was increased by the presence of relatively rigid carbon-carbon double and triple bonds. It may be the case that at a given temperature such bonds have the effect of reducing the mobility of the hard
segments containing them. This has been previously observed in the case of 1,4-
butanediol and cis-but-2-ene-1,4-diol chain-extended polyurethanes\(^{85}\) prepared from
hydroxyl-terminated polybutadiene and various diisocyanates. The possible existence
of interactions between the \(\pi\)-electrons of the triple bonds in but-2-yne-1,4-diol, as
suggested by the results of the FTIR analyses, may also have contributed to the
particularly high level of thermal stability displayed by the hard segment domains of
the elastomer containing this compound.

For the two-shot, 80\(^{\circ}\)C cured polyurethanes the temperatures at which the endotherms
occurred were generally increased in comparison to the equivalent 60\(^{\circ}\)C cured
compositions. This implied a general increase in the levels of perfection and cohesion
possessed by the hard segment domains and was probably due to the increased levels
of molecular mobility at the higher cure temperature. A particularly large shift in
temperature was evident for the endotherm of the 1,4-butanediol chain-extended
material. This indicated a particularly significant increase in the level of perfection of
the hard segment domain morphology of this elastomer and, therefore, an increase in
the thermal energy required to disrupt this morphology. This may have occurred due
to the all-\textit{trans} planar zigzag conformation of 1,4-butanediol which could have
allowed the hard segments to participate in particularly effective inter-hard segment
interactions. Thus, hard segment domain thermal stability was also observed to be a
function of the perfection of the domain morphology. Increases in the perfection of the
hard segment domain morphologies of these 80\(^{\circ}\)C cured elastomers were also
suggested by the fact that noticeable improvements in the definition of the endotherms
of the materials occurred, such that the width of the endothermic peak bases was
reduced from approximately 50\(^{\circ}\)C to roughly 30\(^{\circ}\)C. Such improvements in the
perfection of domain morphology are analogous to those that have been observed by
Seymour and Cooper\(^{79}\) as a result of annealing processes. Significant increases in
definition of the major endotherms of the two-shot prepared cis-but-2-ene-1,4-diol
chain-extended materials with increasing cure temperature were not evident. This was
probably because the reduced linearity of the configuration of this chain extender
moiety imposed restrictions on the degree to which the perfection of the hard segment
domain morphology could be improved.

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Chapter 5  C₄ α,ω-Diol Chain-Extended Polyurethanes

The values of enthalpy per unit mass of the main endothermic features displayed by the polyurethanes prepared via the one-shot reaction process were reduced in comparison to those observed for the equivalently chain-extended, two-shot processed materials. This was indicative of reductions in the levels of phase separation and in the cohesive nature of the hard segment domain structures present. Such reductions were most likely a consequence of the fact that the one-shot reaction process should result in less regular segmental build-up, due to the occurrence of simultaneous, competing reactions of the two diols with MDI. This will tend to lead to less effective inter-hard segment interactions (as evidenced by the results of the FTIR analyses) and a reduced thermodynamic driving force for phase separation.

It was observed that the main hard segment domain melting endotherms of the one-shot prepared 1,4-butanediol and cis-but-2-ene-1,4-diol chain-extended polyurethanes were particularly broad and ill-defined. In the case of the cis-but-2-ene-1,4-diol-containing composition this was most likely due to a combination of the fact that the one-shot process caused the formation of less regular segmental structures, and that the non-linear nature of the cis-but-2-ene-1,4-diol-containing hard segments disrupted the effectiveness of inter-hard segment interactions. For the 1,4-butanediol-containing composition the poorly defined nature of the endothermic activity may have been a consequence of the reactivity of 1,4-butanediol’s hydroxyl functional groups. Due to the lack of inductive effects from unsaturated bonds or other electron withdrawing substituents, the hydroxyl groups of 1,4-butanediol will be the most nucleophilic of those of the C₄ diol chain extenders used. This is in agreement with the literature and was evidenced by the results of the kinetic studies performed on the one-shot reaction compositions (section 5.1.2.1). Thus, a composition containing 1,4-butanediol would tend to involve the most simultaneous competing reactions with MDI, since the reactivity of 1,4-butanediol would be most similar to that of the PTMG polyol. It should be noted that despite possessing a relatively irregular hard
segment domain morphology the soft segment $T_g$ of the one-shot processed 1,4-butanediol chain-extended polyurethane was relatively low. This implied that the low values of soft segment $T_g$ generally observed for the elastomers containing this chain extender compound were probably a result of the flexibility of this moiety, and the reduced restrictions on soft segment mobility that this should afford.

Although reduced in size in comparison to those of the equivalently chain-extended two-shot processed polyurethanes, the endothermic features exhibited by the one-shot processed elastomers chain-extended with trans-but-2-ene-1,4-diol, but-2-yne-1,4-diol and trans-2,3-dibromo-but-2-ene-1,4-diol were relatively well defined. This was probably a consequence of the fact that in addition to resulting in linear polymer molecules with the ability to become involved in effective inter-hard segment interactions, these compounds would have reduced reactivity towards MDI. This was again evidenced by the results of the kinetic analyses performed on the one-shot reaction compositions and was most likely due to the inductive effects of the unsaturated bonds and halogen substituents present in these chain extenders. The reduced reactivities would lead to less competition with the PTMG polyol for reaction with the isocyanate functional groups of MDI, effectively resulting in processes with some two-shot character. Thus, more regular segmental structures would arise and the ability of hard segments to interact effectively would be increased.

The (±)-2,3-dibromobutane-1,4-diol chain-extended polyurethane did not display a discernible endotherm of any description. This was consistent with the elevated value of soft segment $T_g$ displayed by this elastomer and was again probably due to the racemic nature of the chain extender compound. The effective interaction of hard segments and, consequently, phase separation and domain formation were inhibited.

5.1.2.1 Kinetic Analysis of the One-Shot Reaction Compositions

The results of the analyses of the reaction kinetics of the $C_4\alpha,\omega$-diol chain-extended polyurethanes prepared via the one-shot reaction process are summarised in table 5.3. Values of the reported parameters are averages of two experiments. An example of the raw data analysed is shown in Appendix III.
Table 5.3. Kinetic analysis results of the C₄ α,ω-diol chain-extended polyurethane compositions prepared via the one-shot reaction process.

The results displayed in table 5.3 demonstrate that at a given temperature, the rates of reaction of the one-shot processed C₄ α,ω-diol chain-extended compositions will tend to decrease with increasing unsaturation in the chain extender moiety. This can probably be attributed to the progressively increasing electron withdrawing character of increasingly unsaturated carbon-carbon bonds. The results also show that at a given temperature the rate of reaction of the trans-2,3-dibromo-but-2-ene-1,4-diol chain-extended composition would be the least of the C₄ α,ω-diol chain-extended compositions. This can be similarly ascribed to the inductive characteristics of the unsaturated bond and also the bromine substituents present in this chain extender compound.

5.1.3 Modulated-Temperature Differential Scanning Calorimetry

The results of the M-TDSC analyses performed on the C₄ α,ω-diol chain-extended polyurethanes did not display any significantly different features to those observed in the results of the conventional DSC analyses of these materials.

It was generally observed that the endothermic activity displayed in the results of the conventional DSC analyses was concomitant with similar features in the non-reversing heat flow signals of the M-TDSC results (figure 5.7). This indicated that the processes
responsible for these events were subject to kinetic control and was, therefore, consistent with their description as melting phenomena\(^{(180)}\).

Figure 5.7. *M-TDSC result of the two-shot, 80° C cure processed polyurethane chain-extended with 1,4-butandiol.*

5.1.4 Dynamic Mechanical Thermal Analysis

The DMTA results of the C\(_4\) \(\alpha,\omega\)-diol chain-extended polyurethanes displayed tan \(\delta\) peaks at sub-ambient temperatures. These peaks were coincident with significant decreases in values of log \(E'\) and were indicative of the glass transition temperature (\(T_g\)) of the PTMG polyol/soft segment component of the materials\(^{(78)}\). The majority of the C\(_4\) \(\alpha,\omega\)-diol chain-extended materials also displayed noticeable increases and decreases in values of tan \(\delta\) and log \(E'\), respectively, which were coincident with the endothermic events observed in the DSC analyses. Consequently, these features were similarly indicative of the disruption/melting of hard segment domain structures\(^{(85)}\), and the temperatures at which they occurred were designated \(T_m\).
The results of the DMTA analyses of the C₄ α,ω-diol chain extended polyurethanes are shown in figures 5.8-5.13 and are summarised in table 5.4.

**Figure 5.8.** DMTA results of the two-shot, 60°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) cis-but-2-ene-1,4-diol (b) trans-but-2-ene-1,4-diol (c) 1,4-butanediol (d) but-2-yn-1,4-diol.

Within each group of similarly processed polyurethanes, values of soft segment $T_g$ were generally observed to be similar for the elastomers incorporating the various unsaturated chain extender compounds. The values of soft segment $T_g$ of the 1,4-butanediol chain-extended materials were consistently observed to be somewhat reduced in comparison. These observations were in agreement with the results of the DSC analyses and further suggested that the elastomers incorporating unsaturated chain extender compounds probably possessed similar levels of phase separation. Alternatively, differing degrees of phase separation may have been masked by differences in the extent to which soft segment mobility was restricted by the presence of hard segments dissolved amongst soft segments. The results also provided further evidence that hard segments containing the 1,4-butanediol chain extender moiety
Table 5.4. DMTA results of the C₄ α,ω-diol chain-extended polyurethanes.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Processing Technique</th>
<th>$T_g$ / (±1.0)°C</th>
<th>$T_m$ / (±2.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-25</td>
<td>110</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-22</td>
<td>80/130</td>
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<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-20</td>
<td>125</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>-21</td>
<td>140</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-22</td>
<td>140</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-19</td>
<td>50/130</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-20</td>
<td>130</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>-18</td>
<td>145</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-25</td>
<td>60/130</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-21</td>
<td>65/130</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-20</td>
<td>145</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-20</td>
<td>60/135</td>
</tr>
<tr>
<td>Trans-2,3-dibromobut-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>-21</td>
<td>60/130</td>
</tr>
<tr>
<td>(±)-2,3-Dibromobutene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>
imposed reduced restrictions on soft segment mobility when dissolved amongst such segments, probably mainly due to the relatively flexibility of the saturated 1,4-butanediol structure.

As was the case for the results of the DSC analyses, the value of soft segment $T_g$ of the elastomer chain-extended with (±)-2,3-dibromobutane-1,4-diol was significantly greater than those of the other $C_4$ α,ω-diol chain-extended materials. This again implied that the mixed enantiomeric composition of this compound caused the existence of relatively ineffective inter-hard segment interactions and a low level of phase separation. Therefore, the resulting relatively homogeneous composition with hard segments remaining dissolved amongst soft segments would result in the significant restriction of soft segment mobility.

The majority of the $C_4$ α,ω-diol chain-extended polyurethanes displayed noticeable increases in values of tan δ and corresponding decreases in values of log $E'$ at
temperatures in excess of 100°C. The absolute temperatures at which these features occurred were coincident with those of the endothermic events observed in the DSC analyses and were similarly attributed to the melting of phase-separated hard segment domains and their reinforcing characteristics. In addition, the elastomers chain-extended with cis-but-2-ene-1,4-diol and also the majority of the one-shot processed polyurethanes displayed similar, but less significant events at temperatures of approximately 50-80°C. These were consistent with the observation of additional endothermic activity in the DSC results of these materials and could be similarly ascribed to the dissociation of less well ordered hard segment domain morphologies. Such features have been previously described in the case of polyurethaneureas prepared from MDI, PTMG and ethylenediamine. Their occurrence provided further evidence that less effective inter-hard segment interactions arose due to the non-linear configuration of cis-but-2-ene-1,4-diol and also due to the irregular build-up of segmental structure from competing reactions in the one-shot processes.
In the case of the two-shot, 60°C cure processed elastomers, the temperature at which hard segment domain disruption was observed increased with increasing unsaturation in the chain extender moiety. This was concurrent with the observations of the DSC analyses and further indicated that the thermal stability of the hard segment domains was to some degree dependent on the presence of relatively rigid carbon-carbon double and triple bonds in the chain extender moiety.

In the case of the two-shot, 80°C cured polyurethanes the temperatures at which the hard segment domain disruptions occurred were increased in comparison to the equivalent 60°C processed materials. These results also agreed with those of the DSC experiments and indicated that the increase in cure temperature caused increases in the level of perfection of the hard segment domain morphologies and, therefore, in their cohesivity and resistance to melting. The magnitude of the temperature increase was again found to be particularly significant for the 1,4-butanediol chain-extended material, once more implying that this moiety facilitated the formation of effective
inter-hard segment interactions and a well phase-separated morphology. The thermal stability of the hard segment domains was, therefore, again found to be a function of the perfection of the phase-separated domain morphology.

Figure 5.12. DMTA results of the one-shot, 80°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) (±)-2,3-dibromobutane-1,4-diol (b) cis-but-2-ene-1,4-diol (c) 1,4-butanediol (d) trans-but-2-ene-1,4-diol (e) trans-2,3-dibromo-but-2-ene-1,4-diol (f) but-2-yne-1,4-diol.

The increases and decreases in values of tan δ and log $E'$, respectively, at temperatures in excess of 100°C, which indicated hard segment domain melting for the polyurethanes prepared via the one-shot, 80°C cure process, were generally less well defined than those synthesised via the equivalent two-shot technique. This was due to the fact that the rate of change of these parameters was significantly greater for the one-shot processed elastomers at temperatures of approximately 60°C and above. This was concurrent with the broader endotherms observed in the DSC results of these materials and provided further evidence that due to the build-up of less regular
Figure 5.13. DMTA results of the one-shot, 80°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) (±)-2,3-dibromobutane-1,4-diol (b) cis-but-2-ene-1,4-diol (c) 1,4-butanediol (d) trans-but-2-ene-1,4-diol (e) trans-2,3-dibromo-but-2-ene-1,4-diol (f) but-2-yne-1,4-diol.

Segmental structures the one-shot processed elastomers generally possessed less effectively phase-separated, less hard segment domain reinforced morphologies. Consequently, the melting of these morphologies was initiated at lower temperatures. The material incorporating (±)-2,3-dibromobutane-1,4-diol as chain extender displayed no discrete changes in the tan δ and log $E'$ curves to indicate the disruption of some form of hard segment domain morphology. In addition, the values of tan δ and log $E'$ for this material increased and decreased, respectively, significantly more rapidly than those of the other C₄ α,ω-diol chain extended materials, at temperatures above the soft segment $T_g$. These observations were evidence of a lack of a reinforcing, phase-separated hard segment domain morphology in this material. This was probably due to the racemic nature of the chain extender compound; the presence of two enantiomers precluding regular and effective inter-hard segment interactions.
With the exception of the (±)-2,3-dibromobutane-1,4-diol chain-extended polyurethane it was observed that values of tan δ and reductions in log $E'$ at the soft segment glass transition temperature were qualitatively greatest for each of the three processing techniques employed when the chain extender used was cis-but-2-ene-1,4-diol. This further indicated that these elastomers possessed relatively poorly phase-separated and less hard segment domain reinforced morphologies. Thus, the restriction of soft segment mobility by such hard segment domains was less significant.

By a significant margin the greatest value of peak tan δ and the corresponding decrease in log $E'$ values at the soft segment $T_g$ were observed for the (±)-2,3-dibromobutane-1,4-diol chain-extended elastomer. These were indicative of the lowest level of phase-separated, reinforcing hard segment domain morphology amongst the C$_4$α,ω-diol chain-extended materials. These qualitative observations of the values of peak tan δ and the associated decreases in log $E'$ values were entirely consistent with the other observations from the DMTA experiments and also with those of the FTIR and DSC analyses.

5.1.5 Wide Angle X-Ray Scattering

The results of the WAXS analyses of the C$_4$α,ω-diol chain-extended polyurethanes were generally similar. The main feature observed was a diffuse scattering peak with a maximum intensity at an approximate value of 2θ of 20°. Such a feature is generally attributed to scattering from an amorphous arrangement of chain segments. However, some differences between the WAXS results of these materials were evident (figures 5.14-5.16.).

All of the elastomers chain-extended with 1,4-butanediol and but-2-yne-1,4-diol displayed a relatively low intensity shoulder on the main scattering peak at an approximate 2θ value of 10-12°. This corresponded to a repeat distance of approximately 0.74-0.88nm. These observations indicated the presence of some form of ordered domain morphology. In the case of the cis-but-2-ene-1,4-diol chain-
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C₄α,ω-Diol Chain-Extended Polyurethanes

Figure 5.14. WAXS results of the two-shot, 60°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) 1,4-butanediol (b) cis-but-2-ene-1,4-diol (c) trans-but-2-ene-1,4-diol (d) but-2-yne-1,4-diol.

extended polyurethanes similar features were observed, although these were of notably increased intensity and were evident as distinct subsidiary peaks. This suggested that the structures causing them were more prevalent in these materials. Similar features have been reported(89) in the case of polyurethanes synthesised from TDI/poly(ethylene-co-propylene) adipate and chain extended with α,ω-aliphatic diols. These features may, therefore, have been due to the type of less well ordered hard segment domain morphology that was suggested by the lower temperature features (50-80°C) in the results of the DSC and DMTA experiments. Consequently, the results of the WAXS analyses provided further evidence to support the suggestion that chain extension with cis-but-2-ene-1,4-diol resulted in less well ordered domain morphologies than with 1,4-butanediol, trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol.

In comparison to the other C₄ diol chain-extended elastomers, that incorporating trans-
Figure 5.15. WAXS results of the two-shot, 80°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) 1,4-butanediol (b) cis-but-2-ene-1,4-diol (c) trans-but-2-ene-1,4-diol (d) but-2-ynediol.

2,3-dibromobut-2-ene-1,4-diol exhibited somewhat different additional features in its WAXS behaviour. The intensity of the scattering peak at a value of 2θ of approximately 20° was relatively low and displayed a scattering peak superimposed upon it at an approximate 2θ value of 24° (repeat distance = 0.37nm). An additional lower intensity peak with a maximum at an approximate value of 2θ of 5° (repeat distance = 1.76nm) was also evident. These features indicated the presence of phase-separated domain structures which were probably the result of effective inter-hard segment interactions. These would be facilitated by the symmetrical trans-configuration of the chain extender compound.

The material chain-extended with (±)-2,3-dibromobutane-1,4-diol exhibited a particularly low intensity and broad scattering peak at an approximate 2θ value of 20°. No additional scattering features were observed. These results implied a relative
lack of a phase-separated domain morphology and were, therefore, in agreement with the findings of the other characterisation techniques.

![Graph](image)

**Figure 5.16.** WAXS results of the one-shot, 80°C cure processed C₄ α,ω-diol chain-extended polyurethanes: (a) 1,4-butanediol, (b) cis-but-2-ene-1,4-diol, (c) trans-but-2-ene-1,4-diol, (d) but-2-yne-1,4-diol, (e) trans-2,3-dibromobut-2-ene-1,4-diol, (f) (±)-2,3-dibromobutane-1,4-diol.

5.1.6 Small Angle X-Ray Scattering

SAXS analysis was carried out on the C₄ α,ω-diol chain-extended polyurethanes prepared via the two-shot, 80°C cure process, on the two-shot, 60°C and one-shot, 80°C processed polyurethanes incorporating 1,4-butanediol as chain extender and on the elastomer chain extended with (±)-2,3-dibromobutane-1,4-diol. The results of the SAXS analyses are shown in figure 5.17.
With the exception of the (±)-2,3-dibromobutane-1,4-diol chain-extended polyurethane the results of the SAXS experiments performed on the C₄ diol chain-extended elastomers were generally similar. A common feature observed was a scattering peak corresponding to a repeat distance of approximately 100-120nm. This was indicative of the presence of a phase-separated hard/soft segment domain morphology (72). The scattering intensities of these peaks was generally similar, which indicated that the phase-separated domain morphologies of the majority of the C₄ α,ω-diol chain-extended materials were quite similar (174), and that the C₄ diol compounds generally facilitated effective inter-hard segment interactions and phase separation.

The SAXS result for the (±)-2,3-dibromobutane-1,4-diol chain-extended elastomer, however, did not display a scattering peak. This was in agreement with the results of the other characterisation techniques and implied that the racemic nature of this chain extender compound inhibited effective inter-hard segment interactions and phase separation.
5.1.7 Tensile Testing

The results of the tensile testing experiments performed on the C₄ α,ω-diol chain-extended polyurethanes are summarised in table 5.5. The plots of stress vs strain are shown in figures 5.18-5.20.

Within the series' of C₄ diol chain-extended polyurethanes prepared via the two-shot reaction processes it was observed that those incorporating 1,4-butanediol displayed the greatest values of ultimate tensile strength. The values of ultimate tensile strength were observed to be somewhat reduced for the equivalently processed but-2-yne-1,4-diol chain-extended materials, and still further reduced for those containing cis-and trans-but-2-ene-1,4-diol. In addition, the values of 100%, 200% and 300% modulus were found to be greatest in the cases of the 1,4-butanediol and the but-2-yne-1,4-diol chain-extended materials.

These results indicated that the 1,4-butanediol chain-extended polyurethanes possessed the most phase-separated, hard segment domain reinforced morphologies of the C₄ diol chain-extended elastomers. This was consistent with the results of the DSC and DMTA analyses and could probably be ascribed to the all-trans planar zigzag conformation of the 1,4-butanediol moiety, and the effective inter-hard segment interactions facilitated by it.

The relatively high values of tensile properties displayed by the but-2-yne-1,4-diol chain-extended elastomers were probably also largely due to effective inter-hard segment interactions and high levels of phase separation. These interactions and the resulting highly hard segment domain reinforced morphologies were again implied by the results of the other characterisation techniques. Such effective interactions would probably be facilitated by the linear nature of the but-2-yne-1,4-diol moiety. The inherent strength and stiffness of the carbon-carbon triple bonds in this compound may also have contributed to the tensile properties of the but-2-yne-1,4-diol chain-extended materials.

The inferior values of tensile properties of the cis-but-2-ene-1,4-diol chain-extended polyurethanes were most likely attributable to the cis-configuration of this compound.
<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Processing Technique</th>
<th>Ultimate Tensile Strength / MPa</th>
<th>Elongation at Break / %</th>
<th>100% Modulus / MPa</th>
<th>200% Modulus / MPa</th>
<th>300% Modulus / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 60°C</td>
<td>39.0 ±2.5</td>
<td>580±10</td>
<td>7.4±0.2</td>
<td>4.6±0.1</td>
<td>3.8±0.1</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C</td>
<td>29.4 ±1.1</td>
<td>515±10</td>
<td>5.8±0.1</td>
<td>4.0±0.2</td>
<td>3.8±0.2</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C</td>
<td>27.9±1.5</td>
<td>545±10</td>
<td>5.8±0.1</td>
<td>3.9±0.1</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 60°C</td>
<td>31.9±1.3</td>
<td>470±5</td>
<td>7.2±0.1</td>
<td>4.8±0.1</td>
<td>4.2±0.2</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 80°C</td>
<td>48.9±1.9</td>
<td>490±5</td>
<td>7.5±0.5</td>
<td>5.3±0.3</td>
<td>5.0±0.2</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C</td>
<td>28.8±1.0</td>
<td>470±15</td>
<td>6.4±0.1</td>
<td>4.5±0.1</td>
<td>4.2±0.1</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C</td>
<td>30.0±3.2</td>
<td>515±25</td>
<td>5.8±0.2</td>
<td>4.2±0.2</td>
<td>3.9±0.1</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 80°C</td>
<td>39.6±3.0</td>
<td>410±10</td>
<td>6.6±0.2</td>
<td>4.9±0.2</td>
<td>5.2±0.2</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>31.9±1.8</td>
<td>550±5</td>
<td>7.6±0.3</td>
<td>5.0±0.2</td>
<td>4.4±0.1</td>
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<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>31.4±1.9</td>
<td>500±10</td>
<td>6.4±0.2</td>
<td>4.4±0.1</td>
<td>4.1±0.1</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>32.5±1.5</td>
<td>450±10</td>
<td>5.4±0.1</td>
<td>4.2±0.2</td>
<td>4.2±0.1</td>
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<tr>
<td>But-2-yne-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>31.3±2.0</td>
<td>510±15</td>
<td>7.1±0.2</td>
<td>4.8±0.1</td>
<td>4.2±0.1</td>
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<tr>
<td>Trans-2,3-dibromobut-2-ene-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>16.2±1.0</td>
<td>555±15</td>
<td>7.3±0.1</td>
<td>4.8±0.1</td>
<td>4.0±0.1</td>
</tr>
<tr>
<td>(±)-2,3-Dibromobutane-1,4-diol</td>
<td>1-Shot, 80°C</td>
<td>3.4±1.0</td>
<td>690±60</td>
<td>1.9±0.2</td>
<td>1.0±0.1</td>
<td>0.7±0.1</td>
</tr>
</tbody>
</table>

Table 5.5. Tensile testing results of the C₄ α-ω-diol chain-extended polyurethanes.
This structure would have resulted in non-linear polymer molecules which may not have allowed such regular interactions between hard segments and would, therefore, have caused less effective phase separation/domain formation. The results of the FTIR, DSC and DMTA experiments provided evidence to support this.

The tensile properties of the cis- and trans-but-2-ene-1,4-diol chain-extended elastomers were found to be very similar. This was observed in spite of the fact that the latter materials were shown by the other characterisation techniques to possess more effective inter-hard segment interactions and better defined domain morphologies. It appeared, therefore, that these differences in morphology were insufficient to cause significant differences in tensile properties.

While the effect of chain extender structure on the values of 100%, 200% and 300% modulus of the one-shot processed polyurethanes was very similar to that found for the two-shot prepared materials, the values of ultimate tensile strength of the former
elastomers were observed to be very similar. This indicated that in comparison to the two-shot reaction processes, the one-shot method did not enable the formation of such enhanced levels of phase separation in the case of the 1,4-butanediol chain extended polyurethane. This was consistent with the findings of the DSC and DMTA experiments and could again be explained as a consequence of the relatively high reactivity of 1,4-butanediol with MDI. Thus, simultaneous, competing reactions would have reduced the regularity of the segmental structure, compromised the ability of inter-hard segment interactions to occur and led to less advanced phase separation/domain formation.

The elastomer chain-extended with trans-2,3-dibromobut-2-ene-1,4-diol displayed values of 100%, 200% and 300% moduli which were comparable to those of the non-halogenated C₄ diol chain-extended polyurethanes with the most hard segment domain reinforced morphologies. This implied that the material incorporating trans-2,3-
dibromobut-2-ene-1,4-diol possessed a well phase-separated and a highly hard segment domain reinforced morphology. This was in agreement with the results of the other characterisation methods and was most likely a consequence of effective inter-hard segment interactions and phase separation due to the trans-configuration of the chain extender compound. However, despite these values of modulus this material possessed a somewhat reduced value of ultimate tensile strength. It may have been the case that the presence of hard segments dissolved within soft segment domains negated the ability of the soft segments to strain harden at higher elongations. This was evidenced by the linear nature of the stress-strain curve of the elastomer and may have been caused by the presence of bromine substituents with relatively large covalent radii in the chain extender compound.

The polyurethane chain-extended with (±)-2,3-dibromobutane-1,4-diol possessed the lowest values of ultimate tensile strength and 100%, 200% and 300% modulus, and
the greatest value of elongation at break of the C₄ α,ω-diol chain-extended materials. This was consistent with the results of the other characterisation techniques and provided further evidence that this material possessed the least phase-separated and least hard segment domain reinforced morphology of these materials. This could again most likely be attributed to the racemic nature of the chain extender compound and its inhibition of effective inter-hard segment interactions.

For each of the non-halogenated C₄ α,ω-diol chain-extended polyurethanes the change in processing conditions from a two-shot, 60°C cured process to a two-shot, 80°C cured process generally resulted in an increase in ultimate tensile strength, 100%, 200% and 300% moduli, and a decrease in elongation at break. These results were indicative of the fact that the higher cure temperature resulted in a more perfectly ordered and more reinforcing phase-separated domain morphologies. This was probably due to the increased levels of molecular mobility afforded and was also suggested by the results of the other characterisation techniques.

A general increase in ultimate tensile strength and values of moduli was also observed with the change in processing conditions from a one-shot, 80°C cure process to the equivalent two-shot technique. This was again consistent with the findings of the other characterisation methods used and was most likely due to a lack of simultaneous, competing reactions in the case of the two-shot prepared materials. Thus, more regular segmental structures and interactions could occur.

5.1.8 Swelling Studies

The results of the swelling studies performed on the C₄ α,ω-diol chain-extended polyurethanes are summarised in table 6.6.

In the case of each group of elastomers prepared by the different processing techniques, no significant differences between values of σₛ were observed between the various C₄ diol chain-extended compositions. However, a general decrease in values of σₛ was observed for each chain-extended composition with the change in processing method from a two-shot, 60°C to a two-shot, 80°C cure process. This
<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Processing Technique</th>
<th>Volume Fraction of Butan-2-one in the Swollen Elastomer, $\alpha_5 (\pm 0.04)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>0.79</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>0.82</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>0.82</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 60°C cure</td>
<td>0.77</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>0.60</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>0.72</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>0.65</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>2-Shot, 80°C cure</td>
<td>0.65</td>
</tr>
<tr>
<td>Butane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>Soluble</td>
</tr>
<tr>
<td>Cis-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>Soluble</td>
</tr>
<tr>
<td>Trans-but-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>0.80</td>
</tr>
<tr>
<td>But-2-yne-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>0.79</td>
</tr>
<tr>
<td>Trans-2,3-dibromobut-2-ene-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>Soluble</td>
</tr>
<tr>
<td>(±)-2,3-Dibromobutane-1,4-diol</td>
<td>1-Shot, 80°C cure</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Table 5.6. Results of the swelling studies performed on the $C_4 \alpha,\omega$-diol chain-extended polyurethanes.
confirmed the results of the other characterisation techniques and implied that the increase in cure temperature caused the formation of more phase-separated, more hard segment domain reinforced domain morphologies. Consequently, these would be more able to impart resistance to swelling caused by solvent ingress.

Of the one-shot processed polyurethanes, it was only possible to obtain values of $\sigma_S$ for those incorporating trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol due to the fact that the other materials were soluble. This suggested that the trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol chain-extended elastomers possessed the most phase-separated, hard segment domain reinforced morphologies of the one-shot processed polyurethanes. This was again consistent with the results of the other characterisation methods.

It was observed that in comparison to the $\sigma_S$ values of the equivalently chain-extended two-shot processed elastomers, those of the one-shot processed polyurethanes incorporating trans-but-2-ene-1,4-diol and but-2-yne-1,4-diol were increased. This was indicative of the presence of less effectively phase-separated domain morphologies in the one-shot prepared materials, which once more supported the results of the other characterisation techniques.

5.1.9 General Observations

With the exception of the elastomer incorporating ($\pm$)-2,3-dibromobutane-1,4-diol which appeared transparent, all polyurethanes chain-extended with the C₄ α,ω-diol compounds appeared opaque to the naked eye. This optical opacity was indicative of the presence of well phase-separated hard/soft segment domain morphologies in these materials. Such a heterogeneous structure would result in regions of unequal density and refractive index and, therefore, cause the scattering of incident radiation with visible wavelengths.

The transparent nature of the ($\pm$)-2,3-dibromobutane-1,4-diol chain-extended material indicated a lack of a significantly phase-separated domain morphology with regions of discretely differing refractive index. This reduced heterogeneity was supported by the results of the other characterisation methods employed and was most likely caused by
the impairment of inter-hard segment interactions by the presence of two enantiomers as chain extenders.

5.2 Conclusions

Variations in the chemical structure of $C_4 \alpha,\omega$-diol chain extender compounds and changes in reaction conditions were observed to significantly influence the morphologies and properties of polyurethanes prepared from them. It was found that of the $C_4$ diol chain-extended polyurethanes prepared via the two-shot reaction procedures, those incorporating 1,4-butanediol possessed the most phase-separated and perfectly formed domain morphologies. This was probably attributable to the all-trans planar zigzag conformation of 1,4-butanediol. Such a structure should allow the occurrence of particularly regular and effective interactions between hard segments.

Of the two-shot processed elastomers chain-extended with the unsaturated $C_4$ diols, those containing but-2-yne-1,4-diol displayed the most effectively phase-separated domain morphologies. This was most likely a consequence of the linear nature of the but-2-yne-1,4-diol moiety and the resulting ability of hard segments containing it to interact effectively.

The least phase-separated, least perfectly formed domain morphologies of the two-shot processed materials were observed for the cis-but-2-ene-1,4-diol chain-extended polyurethanes. This was probably due to the cis-configuration of this compound which would tend to result in hard segment structures with reduced linearity/symmetry, and a reduced ability to become involved in effective inter-hard segment interactions.

Amongst the $C_4 \alpha,\omega$-diol chain-extended polyurethanes prepared via the one-shot reaction process the elastomers incorporating trans-but-2-ene-1,4-diol, but-2-yne-1,4-diol and trans-2,3-dibromobut-2-ene-1,4-diol were found to possess the most perfectly formed domain morphologies. The reduced level of perfection in the case of the cis-but-2-ene-1,4-diol chain-extended material was probably once more a result of the cis-configuration of this compound. That of the polyurethane incorporating 1,4-butanediol
was most likely due to the relatively high reactivity of this compound's hydroxyl groups with the isocyanate functionalities of MDI, thereby resulting in competing reactions with the PTMG polyol. This would tend to cause the build-up of less regular segmental structures and lead to less effective inter-hard segment interactions and phase separation. The more perfect morphologies of the polyurethanes chain-extended with diols containing unsaturation and/or halogen substituents was probably a consequence of the inductive effects of these groups. This should reduce the levels of competing reactions, resulting in the build-up of more regular segmental structures and lead to enhanced degrees of phase separation.

Amongst the one-shot reaction processed elastomers, that incorporating (±)-2,3-dibromobutane-1,4-diol possessed the morphology with the least phase-separated character. This could probably be explained as a result of the racemic nature of the compound. The presence of two enantiomers would tend to disrupt structural regularity amongst the hard segments and, therefore, impair their ability to interact and lead to hard/soft segment phase separation.

It was generally observed that the materials synthesised via the two-shot, 80°C cure reaction process possessed more perfectly formed domain structures than the equivalently chain-extended elastomers prepared by the two-shot, 60°C and the one-shot, 80°C cure methods. This was probably attributable to the fact that the two-shot technique should result in the most regular segmental structures, while the increased molecular mobility afforded by the higher cure temperature should facilitate enhanced levels of phase separation.

The results of the characterisations performed on the C₄ α,ω-diol chain-extended polyurethanes indicated that while the ability of inter-urethane hydrogen bonds to form appeared to strongly influence the morphology and properties of these materials, other inter-hard segment interactions were also of influence.

The results of the WAXS indicated that the morphology responsible for the endothermic features observed at a temperature of approximately 60-80°C in the results of the DSC analyses possessed periodicity on the scale of approximately 0.7-0.9nm.
Chapter 6

Hydroxyamine Chain-Extended Polyurethaneureas
6.1 Results and Discussion

The morphologies and properties of polyurethaneureas synthesised by chain extension with hydroxyamine compounds were characterised and compared to those of polyurethanes chain-extended with the equivalent dihydroxy compounds (diols). The hydroxyamine compounds employed as chain extenders were 3-aminophenol and 2-aminobenzyl alcohol, and the equivalent dihydroxy compounds used were 1,3-dihydroxybenzene and 2-hydroxybenzyl alcohol, respectively. The chemical structures of these compounds are shown in section 4.1.3.2.

6.1.1 Fourier Transform Infrared Spectroscopy

The results of the FTIR spectroscopic analyses of the hydroxyamine and the equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes are summarised in table 6.1. The urethane carbonyl absorption regions of these materials are shown in figures 6.1 and 6.2. Values of $X$, the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, were determined from the relative absorbances of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks (as described in section 4.4.1).

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Inter-Urethane Hydrogen Bonded Carbonyl Absorption Maximum / (±1cm$^{-1}$)</th>
<th>$X$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Aminophenol</td>
<td>1713</td>
<td>0.48</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>1709</td>
<td>0.50</td>
</tr>
<tr>
<td>2-Aminobenzyl alcohol</td>
<td>1713</td>
<td>0.38</td>
</tr>
<tr>
<td>2-Hydroxybenzyl alcohol</td>
<td>1711</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 6.1. FTIR analysis results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes.

The polyurethaneurea synthesised with the hydroxyamine chain extender compound, 3-aminophenol, possessed an increased value of wavenumber for the maximum of its
hydrogen bonded urethane carbonyl absorption peak, in comparison to that of the polyurethane chain-extended with the equivalent dihydroxy compound, 1,3-dihydroxybenzene.

The elastomer prepared with 2-aminobenzyl alcohol as the chain extender did not display a distinct hydrogen bonded urethane carbonyl absorption peak. Instead, this feature appeared as a shoulder on the non-hydrogen bonded urethane carbonyl absorption peak. An approximate value of wavenumber for the absorption maximum of this feature was obtained from the point of inflection of the shoulder. In contrast,
Figure 6.2. FTIR analysis results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes: (a) 2-hydroxybenzyl alcohol (b) 2-aminobenzyl alcohol.

the material incorporating the equivalent diol, 2-hydroxybenzyl alcohol, did possess a distinct hydrogen bonded urethane carbonyl absorption peak. In addition, the wavenumber value of the maximum of this peak was reduced in comparison to that of the 2-aminobenzyl alcohol chain-extended elastomer. These results together indicated that the polyurethaneureas prepared with hydroxyamine compounds as chain extenders possessed inter-urethane hydrogen bonding interactions of a reduced strength in comparison to those present in the equivalent diol chain-extended polyurethanes\(^{(86)}\).
Inter-urea hydrogen bonding interactions and those between urea and urethane groups have been shown\(^{(124,183)}\) to result in carbonyl infra-red absorption peaks with maxima at wavenumber values of approximately 1643 cm\(^{-1}\) and 1698 cm\(^{-1}\), respectively. It might be expected that such features would have been evident in the FTIR analysis results of the hydroxyamine chain-extended materials, since these materials contained substantial quantities of urea linkages. These urea groups resulted from the reaction of the amine functional groups of the hydroxyamine chain extender compounds with the isocyanate functionalities of MDI. However, no such features were evident. This was in contradiction to the results of Sung et al.\(^{(124)}\) for polyurethaneureas derived from TDI/PTMG and chain-extended with ethylenediamine, and to those of Ning and co-workers\(^{(183)}\) for model compounds containing polyoxpropylene diol/polyoxpropylene diamine and phenyl isocyanate.

A possible reason for the reduction in strength of the inter-urethane hydrogen bonding interactions observed for the hydroxyamine chain-extended elastomers was the mixed functionality of the chain extender compounds involved. Chain extension with such compounds would have resulted in the formation of polymer chains with a less symmetrical nature than those resulting from chain extension with dihydroxy compounds. These polymers, therefore, may not have facilitated such effective inter-hard segment hydrogen bonds as those which may have occurred in the diol chain-extended materials.

The polyurethaneurea chain-extended with 3-aminophenol displayed a very similar value of X, the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, to the polyurethane chain-extended with the equivalent dihydroxy-functional compound, 1,3-dihydroxybenzene. The elastomer chain-extended with 2-aminobenzyl alcohol also possessed a similar value of X to that chain-extended with the equivalent diol, 2-hydroxybenzyl alcohol. In view of the fact that chain extension with hydroxyamine compounds introduced urea linkages into the polymer chains in place of urethane groups, and that no evidence of distinct inter-urea or urethane-urea hydrogen bonds was observed, it may be inferred from these results that the inter-hard segment hydrogen bonding interactions in the hydroxyamine chain-
extended polyurethaneureas were somewhat homogenised. Therefore, the strengths of the inter-urethane, urethane-urea and inter-urea hydrogen bonding interactions in these materials were not individually distinguishable.

6.1.2 Differential Scanning Calorimetry

The results of the DSC analyses of the hydroxyamine and equivalent dihydroxy compound chain-extended materials displayed step transitions in their heat flow curves at sub-ambient temperatures. These indicated changes in the heat capacity of the materials at the glass transition temperature \( T_g \) of the PTMG polyol/soft segment component of the materials\(^{166}\). Values of \( T_g \) at the midpoint of the transitions were obtained from the points of inflection of the heat flow curves. Some of the DSC results of the hydroxyamine and equivalent diol chain-extended elastomers also exhibited endothermic features. These were indicative of changes in heat capacity of the materials due to the dissociation/melting of phase-separated hard segment domain structures\(^{80}\). The peak temperatures at which the endotherms were observed were designated \( T_m \).

The results of the DSC analyses of the hydroxyamine and equivalent dihydroxy chain-extended polyurethaneureas/urethanes are summarised in table 6.2 and are shown in figure 6.3.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>( T_g ) / (±1.0)°C</th>
<th>( T_m ) / (±2.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Aminophenol</td>
<td>-46</td>
<td>75</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>-42</td>
<td>75</td>
</tr>
<tr>
<td>2-Aminobenzyl alcohol</td>
<td>-53</td>
<td>175</td>
</tr>
<tr>
<td>2-Hydroxybenzyl alcohol</td>
<td>-43</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 6.2. DSC results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes.

The values of soft segment \( T_g \) of both of the hydroxyamine chain-extended...
polyurethaneureas were reduced in comparison to those of the equivalent diol chain-extended polyurethanes. These reduced values for the materials incorporating 3-aminophenol and 2-aminobenzyl alcohol indicated that in comparison to those synthesised with the equivalent diols, increased levels of phase separation were present\(^{(166)}\). Thus, the mobility of soft segments within soft segment domains was less inhibited by the presence of ‘dissolved’ hard segment structures. This may have occurred as a result of the fact that the hard segment structures of the hydroxyamine chain-extended elastomers contained significant proportions of urea groups. This was in contrast to the hard segments of the dihydroxy compound chain-extended materials which contained urethane groups exclusively. Consequently, as a result of the particularly high values of cohesive energy density of the urea groups\(^{(5)}\), the levels of
cohesive interaction between the hard segments of the hydroxyamine chain-extended polyurethaneureas may have been greater than between those of the equivalent diol chain-extended polyurethanes. Therefore, the degree of thermodynamic incompatibility between the hard and soft segment structures would have been greater for the former materials, which would in turn lead to an increased thermodynamic drive for phase separation. This would be consistent with the observation\(^{124-133}\) that diamine chain-extended materials tend to exhibit more phase-separated domain morphologies than similar diol containing materials.

It should be noted that increased levels of phase separation were apparent in the case of the hydroxyamine chain-extended elastomers, despite the fact that these materials appeared to possess inter-hard segment hydrogen bonding interactions of a reduced strength in comparison to the equivalent dihydroxy compound chain-extended materials. This is in contrast to some observations in the literature where increased phase separation for diamine chain-extended materials has been associated with more extensive and stronger inter-hard segment hydrogen bonds\(^{124}\). However, other observations have indicated that hydrogen bonding interactions are not the sole driving force for phase separation to occur. This has been found to be the case\(^{80,155}\) for polyurethanes synthesised from chloroformates and piperazine, and in which phase separation/domain formation is observed despite no capability for hydrogen bonding to occur. In addition, inconsistencies between the thermal behaviour of domain structures and that of inter-urethane hydrogen bonds upon annealing of polyurethanes derived from MDI, PTMG and 1,4-butanediol have provided further evidence to support this.

The materials chain extended with the hydroxyamine, 3-aminophenol and the equivalent diol, 1,3-dihydroxybenzene, both displayed a rather small endothermic event with a peak at a temperature of approximately 75°C. These features indicated the dissociation or melting of some form of phase-separated hard segment domain structures. The formation of such morphologies could be attributed to the thermodynamic incompatibility of the hard and soft segments\(^{20}\). The similarities in
the characteristics of the endothermic events of these two materials indicated that the domain morphologies causing them were probably quite similar.

The polyurethane chain-extended with 2-hydroxybenzyl alcohol displayed some evidence of rather broad, ill-defined endothermicity at a temperature of approximately 140°C. However, the polyurethaneurea chain extended with the equivalent hydroxyamine, 2-aminobenzyl alcohol displayed somewhat better defined evidence of such a feature at the higher temperature of approximately 175°C. These results indicated that the material chain-extended with 2-aminobenzyl alcohol possessed a hard segment domain morphology with a more phase-separated, more cohesive structure. This would, therefore, tend to be dissociated by higher thermal energies. This was consistent with the reduced value of soft segment $T_g$ observed for this elastomer and could once more be explained as being due to the presence of highly cohesive urea groups in the hard segments of the hydroxyamine chain-extended elastomer. These could have increased the level of thermodynamic incompatibility between the hard and soft segment structures, thereby creating a greater driving force for phase separation.

6.1.3 Modulated-Temperature Differential Scanning Calorimetry

The M-TDSC results of the majority of the hydroxyamine and equivalent diol chain-extended elastomers did not display any significantly different features to those observed in the results of the conventional DSC analyses.

However, the total and non-reversing heat flow signals of the polyurethaneurea chain-extended with 2-aminobenzyl alcohol displayed a well-defined endotherm with a peak at a temperature of approximately 170°C (figure 6.4). The existence of such an endotherm implied that the hard segment domain morphology of this polyurethaneurea was significantly more phase-separated and more perfectly formed than that of the equivalent dihydroxy chain-extended polyurethane. This provided further evidence that chain extension with the hydroxyamine compound resulted in more cohesive inter-hard segment interactions and a greater degree of thermodynamic incompatibility.
It was generally observed that the endothermic events displayed in the conventional DSC analyses were accompanied by similar features in the non-reversing heat flow signals of the M-TDSC results. This indicated that the processes responsible for these events were subject to kinetic control and was, therefore, consistent with their description as melting phenomena\(^\text{(179)}\).

![Graph](image_url)

**Figure 6.4. M-TDSC results of the 2-aminobenzyl alcohol chain-extended polyurethaneurea.**

### 6.1.4 Dynamic Mechanical Thermal Analysis

The results of the DMTA experiments performed on the hydroxyamine and equivalent dihydroxy chain-extended elastomers displayed tan δ peaks at sub-ambient temperatures. These peaks were coincident with significant decreases in values of log $E'$ and were indicative of the glass transition temperature ($T_g$) of the PTMG polyol/soft segment component of the materials\(^\text{(78)}\). Some of the elastomers also displayed noticeable increases and decreases in values of tan δ and log $E'$, respectively, which were coincident with the endothermic events observed in the results of the DSC
analyses. Therefore, these features were similarly indicative of the melting of phase-separated hard segment domain structures, and the temperatures at which they occurred were designated $T_m$.

The DMTA results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes are summarised in table 6.3 and are shown in figures 6.5-6.8.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>$T_g$ / (±1.0)°C</th>
<th>$T_m$ / (±2.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Aminophenol</td>
<td>-22</td>
<td>70</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>-19</td>
<td>70</td>
</tr>
<tr>
<td>2-Aminobenzyl alcohol</td>
<td>-24</td>
<td>-</td>
</tr>
<tr>
<td>2-Hydroxybenzyl alcohol</td>
<td>-22</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3. DMTA results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes.

The values of soft segment $T_g$ of both of the polyurethaneureas chain-extended with the hydroxyamine compounds were reduced in comparison to the polyurethanes chain-extended with the equivalent diols. These results were in agreement with those of the DSC analyses. The reduced values of $T_g$ in the case of the hydroxyamine compound chain-extended elastomers could be similarly explained to be a result of the urea linkages that are present within their hard segments. These linkages may be more thermodynamically incompatible with soft segment structures than are urethane groups due to their high values of cohesive energy density. They may, therefore, give rise to greater levels of phase separation than that which occurs in the corresponding diol chain-extended materials.

The elastomers chain-extended with 1,3-dihydroxybenzene and 3-aminophenol displayed marked increases and decreases in values of tan δ and log $E'$, respectively, at approximately 70°C. These features were indicative of the disruption of phase-separated hard segment domain morphologies. Such disruption would cause the
observed changes in values of $\tan \delta$ and $\log E'$ due to the increased levels of molecular mobility thus afforded. It was observed that the magnitude of the changes were qualitatively greater in the case of the 1,3-dihydroxybenzene chain-extended polyurethane than for the 3-aminophenol chain-extended polyurethaneurea. It was also found that the rates of change of these values with increasing temperature above the $T_m$ were greater for the 1,3-dihydroxybenzene-containing material. In addition it was generally noticed that the rates of reduction and increase of $\log E'$ and $\tan \delta$ values, respectively, with increasing temperature above the soft segment $T_g$, were greater for both of the dihydroxy compound chain-extended materials than for the equivalent hydroxyamine chain-extended elastomers. Also, the temperatures at which the values of $\tan \delta$ and $\log E'$ increased and decreased, respectively, and indicated dissociation of the elastomers, i.e. at temperatures in excess of 100°C, were greater for both of the hydroxyamine-containing polyurethaneureas than for the equivalent dihydroxy compound-containing polyurethanes.

Figure 6.5. DMTA results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes: (a) 1,3-dihydroxybenzene (b) 3-aminophenol.
Figure 6.6. DMTA results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes: (a) 1,3-dihydroxybenzene (b) 3-aminophenol.

These results generally indicated that at temperatures above the soft segment $T_g$ the thermal stability (retention of storage modulus) of the hydroxyamine chain-extended elastomers was greater than that of the equivalent diol chain-extended materials\(^{(78)}\). This in turn suggested that the presence of urea groups in the former imparted enhanced levels of cohesion in comparison to urethane linkages alone. This was in agreement with the behaviour of the soft segment glass transition temperatures and the results of the DSC and M-TDSC analyses.

The peak values of tan $\delta$ and the corresponding reductions in log $E'$ values at the soft segment $T_g$ were, qualitatively, observed to be significantly greater for the 2-hydroxybenzyl alcohol chain-extended elastomer than for the material incorporating 2-aminobenzyl alcohol. This was most likely due to significantly increased levels of phase separation being present in the latter. This would have resulted in much more highly reinforcing hard segment domain morphologies with the ability to restrict
severely the mobility of the soft segment structures at their glass transition temperature. Such an effect has been reported by Minoura et al.\(^{85}\) in the case of polyurethanes prepared from hydroxyl-terminated polybutadiene, various diisocyanates and low molecular weight aliphatic diols. The corresponding values of these parameters for the materials chain-extended with the hydroxyamine compound, 3-aminophenol and the equivalent diol, 1,3-dihydroxybenzene, were considerably more similar. This implied that the differences in phase-separated domain morphology between these elastomers were not as distinct as between those synthesised with 2-hydroxybenzyl alcohol and 2-aminobenzyl alcohol. These observations were consistent with those of the DSC and M-TDSC results and suggested that the particularly significant differences between the latter pair of materials may have been a result of the ortho-substitution of their functional groups. Such substitution would have resulted in highly non-linear, asymmetrical hard segment structures and could, therefore, have severely impaired the ability of hard segments to interact effectively in
Chapter 6  Hydroxyamine Chain-Extended Polyurethaneureas

Figure 6.8.  DMTA results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes: (a) 2-hydroxybenzyl alcohol (b) 2-aminobenzyl alcohol.

the case of the 2-hydroxymethyl benzene chain-extended material. However, in the case of the 2-aminobenzyl alcohol chain extended elastomer, the presence of highly cohesive interactions between the urea groups in its hard segments could have compensated for this.

6.1.5 Wide Angle X-Ray Scattering

The results of the WAXS analyses of the hydroxyamine and the equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes were generally similar. The main feature observed for each elastomer was a diffuse scattering peak with a maximum scattering intensity at a value of 2Θ of approximately 20°. Such a feature is generally attributed to scattering from an amorphous arrangement of chain segments(84). However, some differences between the results obtained for these two groups of materials were evident (figures 6.9 and 6.10).
For the elastomers chain-extended with the hydroxyamine compound, 3-aminophenol, and the equivalent diol, 1,3-dihydroxybenzene, it was observed that in addition to the broad scattering peak at a 2θ value of approximately 20° the hydroxyamine chain-extended elastomer also displayed two sharp, relatively low intensity scattering peaks, at 2θ values of approximately 9.5° and 28.5°. These corresponded to repeat distances of approximately 0.93nm and 0.31nm, respectively.

In the case of the 2-aminobenzyl alcohol and 2-hydroxybenzyl alcohol chain-extended materials that containing 2-aminobenzyl alcohol possessed a quite sharp, low intensity peak at a 2θ value of approximately 9.5° (repeat distance = 0.93nm), and a rather broad shoulder across the range of 2θ values from approximately 24° to 27° (repeat distances = 0.33-0.37nm).

These additional scattering features in the cases of the elastomers incorporating the hydroxyamine compounds were indicative of the presence of phase-separated domain
structures\textsuperscript{[171]}. Their appearance in the WAXS analysis results of the hydroxyamine chain-extended polyurethaneureas indicated that these materials possessed better defined and more regularly ordered hard and soft segment domain morphologies than the equivalent diol chain-extended polyurethanes. These results were in agreement with those of the DSC, M-TDSC and DMTA experiments and implied that the presence of urea groups within the hard segment structures led to particularly high levels of thermodynamic incompatibility with the relatively non-polar soft segments. The consequence was enhanced degrees of phase separation.

6.1.6 Small Angle X-Ray Scattering

SAXS analysis was carried out on the polyurethaneurea chain-extended with 2-aminobenzyl alcohol, and on the polyurethane chain-extended with the equivalent...
diol, 2-hydroxybenzyl alcohol. The results of the SAXS analyses are shown in figure 6.11.

![Figure 6.11. SAXS results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes.]

The SAXS analyses performed on the hydroxyamine and equivalent diol chain-extended materials both displayed scattering shoulders. These features implied the existence of phase separated hard/soft segment domain structures\(^{72}\). However, the intensity of that observed for the hydroxyamine chain-extended polyurethaneurea was significantly greater than for the equivalent polyurethane. This indicated the presence of a more perfectly phase-separated domain morphology in the case of the former material\(^{174}\) and was, therefore, consistent with the results of the other characterisation techniques.
6.1.7 Tensile Testing

The results of the tensile testing experiments performed on the hydroxyamine and the equivalent dihydroxy compound chain-extended elastomers are summarised in table 6.4. The plots of stress vs strain are shown in figure 6.12.

![Stress-strain plots of hydroxyamine and dihydroxy compound chain-extended polyurethaneureas/urethanes](image)

Figure 6.12. Stress-strain plots of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneureas/urethanes.

The polyurethaneureas chain-extended with the hydroxyamine compounds, 3-aminophenol and 2-aminobenzyl alcohol, possessed greater values of ultimate tensile strength, and 100%, 200% and 300% moduli than those of the polyurethanes chain-extended with the equivalent dihydroxy-functionalised compounds, 1,3-dihydroxybenzene and 2-hydroxybenzyl alcohol, respectively. Both of the hydroxyamine chain-extended elastomers were also observed to possess values of elongation at break which were significantly reduced in comparison to the materials chain-
Table 6.4. Tensile testing results of the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethanes/urethaneureas.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Ultimate Tensile Strength / MPa</th>
<th>Elongation at Break / %</th>
<th>100% Modulus / MPa</th>
<th>200% Modulus / MPa</th>
<th>300% Modulus / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>11.8±2.0</td>
<td>690±30</td>
<td>2.2±0.1</td>
<td>1.4±0.1</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>3-Aminophenol</td>
<td>13.3±1.5</td>
<td>530±15</td>
<td>2.5±0.1</td>
<td>1.7±0.1</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>2-Hydroxybenzyl alcohol</td>
<td>3.1±0.2</td>
<td>690±15</td>
<td>1.3±0.1</td>
<td>0.7±0.1</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>2-Aminobenzyl alcohol</td>
<td>13.7±1.0</td>
<td>350±10</td>
<td>5.6±0.2</td>
<td>3.9±0.3</td>
<td>3.9±0.3</td>
</tr>
</tbody>
</table>
extended with the equivalent dihydroxy compounds. These observations indicated that the elastomers chain-extended with the hydroxyamine compounds possessed more physically crosslinked and hard segment domain reinforced morphologies than the equivalent diol chain-extended materials. This was consistent with the results of the DSC, M-TDSC, DMTA, WAXS and SAXS analyses and provided further evidence that the presence of urea linkages in the hard segment structures produced more phase separation.

It was observed that the differences in tensile properties between the hydroxyamine and equivalent dihydroxy compound chain-extended materials were particularly significant in the case of the 2-aminobenzyl alcohol and 2-hydroxybenzyl alcohol chain-extended elastomers. These differences were consistent with those observed in the DSC and the DMTA results and supported the suggestion that the ortho-substitution of the functional groups largely negated phase separation in the case of the diol chain-extended polyurethane, but did not adversely affect the morphology of the polyurethaneurea containing the hydroxyamine compound.

6.1.8 Swelling Studies

The results of the swelling studies performed on the hydroxyamine and equivalent dihydroxy compound chain-extended materials are shown in table 6.5.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Volume Fraction of Toluene in the Swollen Elastomer, $\sigma_5 (\pm 0.04)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Aminophenol</td>
<td>0.57</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>0.62</td>
</tr>
<tr>
<td>2-Aminobenzyl alcohol</td>
<td>0.46</td>
</tr>
<tr>
<td>2-Hydroxybenzyl alcohol</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 6.5. Results of the swelling studies performed on the hydroxyamine and equivalent dihydroxy compound chain-extended polyurethaneurea/urethanes.
The values of $\sigma_5$, the volume fraction of solvent present in the swollen elastomer, were observed to be consistently greater for the dihydroxy compound chain-extended polyurethanes than for the equivalent hydroxyamine chain-extended polyurethaneureas. These results were in agreement with those of the other characterisation techniques used, in suggesting that the hydroxyamine chain-extended elastomers possessed more highly phase-separated domain morphologies than the equivalent diol chain-extended materials. Thus, the phase-separated morphologies in the polyurethaneureas imparted increased degrees of physical crosslinking and a greater reinforcing effect to resist the swelling caused by solvent ingress.

The difference between values of $\sigma_5$ for the materials chain extended with 2-aminobenzyl alcohol and 2-hydroxybenzyl alcohol was particularly great, and reflected similarly significant differences observed in the results of the DSC, DMTA and tensile testing experiments. This provided further evidence that the ortho-substitution of functional groups in the diol chain extender may have severely inhibited the ability of hard segment structures to interact, whereas this inhibition could have been largely circumvented in the case of the hydroxyamine compound.

6.1.9 General Observations

The polyurethaneureas incorporating the hydroxyamine chain extender compounds 3-aminophenol and 2-aminobenzyl alcohol appeared white and opaque to the naked eye. This was probably a result of the relatively advanced formation of an inhomogeneous structure, with quite discrete hard and soft segment domains being present in these elastomers. The opacity was observed due to the fact that such dual-phase morphologies are composed of regions with differing refractive indices. This leads to the scattering of incident visible radiation when the domain size is of the order of the wavelength of such radiation\(^{(182)}\). The optical appearance of these elastomers was, therefore, consistent with the results of the other characterisation techniques employed.

In contrast, the polyurethanes synthesised with the dihydroxy-functional chain extender compounds 1,3-dihydroxybenzene and 2-hydroxybenzyl alcohol appeared
colourless and transparent to the naked eye. This transparency suggested a relative lack of a phase-separated domain morphology and an absence of regions with discretely differing refractive indices. As a consequence, the appearance of the diol chain-extended polyurethanes further indicated that these materials were composed of a less phase-separated morphology than the equivalent hydroxyamine chain-extended polyurethaneureas.

6.2 Conclusions

The morphologies and properties of the polyurethaneureas chain-extended with the hydroxyamine chain extender compounds were found to be significantly different to those of the polyurethanes chain-extended with the equivalent dihydroxy-compounds. The elastomers chain-extended with the hydroxyamine compounds were observed to display considerably greater degrees of phase separation and hard/soft segment domain formation than the equivalent dihydroxy compound chain extended materials. This was probably a consequence of the presence of urea linkages in the polyurethaneurea materials due to the reaction between the chain extender’s amine functional groups and the isocyanate functionalities of MDI. Such linkages possess particularly high values of cohesive energy density and may therefore lead to particularly significant levels of thermodynamic incompatibility between the hard and soft segment structures.

These results were observed despite the fact that the dihydroxy compound chain-extended polyurethanes apparently possessed stronger inter-hard segment hydrogen bonding interactions than the equivalent hydroxyamine chain-extended polyurethaneureas. The general thermodynamic incompatibility of the hard and soft segment structures therefore appeared to be the dominating influence in determining the morphology of the materials, rather than the specific ability of the hard segments to participate in inter-hard segment hydrogen bonding interactions. This was further supported by the fact that the hydroxyamine chain-extended polyurethaneurea which exhibited the most phase-separated domain morphology, i.e that incorporating 2-
aminobenzyl alcohol, possessed a less extensive inter-hard segment hydrogen bonding network than the 3-aminophenol chain-extended polyurethaneurea.
Chapter 7

Aromatic Diamine Chain-Extended Polyurethaneureas
7.1 Results and Discussion

Polyurethaneureas chain-extended with aromatic diamine compounds were prepared and characterised in order to elucidate the effect on morphology and properties of the chemical structure of the link group between the aromatic rings in these compounds. The diamine compounds 4,4'-methylenedianiline, 4,4'-oxydianiline, 4,4'-thiodianiline and 4,4'-sulphonyldianiline were used in order to investigate the influence of methylene (CH₂), ether (O), thioether (S) and sulphonyl (SO₂) link groups. The chemical structures of these compounds are shown in section 4.1.3.3.

7.1.1 Fourier Transform Infrared Spectroscopy

The results of the FTIR spectroscopic analyses of the aromatic diamine chain-extended materials are summarised in table 7.1. The urethane carbonyl absorption regions of these materials are shown in figure 7.1. Values of X, the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, were determined from the relative absorbances of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks (as described in section 4.4.1).

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Inter-Urethane Hydrogen Bonded Carbonyl Absorption Maximum / (±1)cm⁻¹</th>
<th>X (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Methylenedianiline</td>
<td>1713</td>
<td>0.39</td>
</tr>
<tr>
<td>4,4'-Oxydianiline</td>
<td>1711</td>
<td>0.42</td>
</tr>
<tr>
<td>4,4'-Thiodianiline</td>
<td>1713</td>
<td>0.36</td>
</tr>
<tr>
<td>4,4'-Sulphonyldianiline</td>
<td>1713</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 7.1. FTIR analysis results of the aromatic diamine chain-extended polyurethaneureas.

It should be noted that despite containing quantities of urea groups from reactions between amine and isocyanate functionalities, distinct carbonyl absorption peaks due
FTIR analysis results of the aromatic diamine chain-extended polyurethaneureas: (a) 4,4'-methylenedianiline (b) 4,4'-oxydianiline (c) 4,4'-thiodianiline (d) 4,4'-sulphonyldianiline.

Figure 7.1. FTIR analysis results of the aromatic diamine chain-extended polyurethaneureas: (a) 4,4'-methylenedianiline (b) 4,4'-oxydianiline (c) 4,4'-thiodianiline (d) 4,4'-sulphonyldianiline.

to inter-urea and urethane-urea hydrogen bonding interactions (at wavenumber values of 1643cm⁻¹ and 1698cm⁻¹, respectively\(^{[124,183]}\)) were not observed in the results of these polyurethaneureas. This suggested that the inter-hard segment hydrogen bonding interactions were somewhat homogenised and resulted in carbonyl absorptions at wavenumber values characteristic of inter-urethane interactions.

The materials chain-extended with 4,4'-methylenedianiline and 4,4'-oxydianiline
displayed distinct hydrogen bonded urethane carbonyl absorption peaks. However, in the case of the elastomers incorporating 4,4'-thiodianiline and 4,4'-sulphonyldianiline as chain extenders, the corresponding peaks formed shoulders on the non-hydrogen bonded urethane carbonyl absorption peaks. For these materials, an approximate value of wavenumber for the absorption maximum of this feature was obtained from the point of inflection of the shoulder. The values of wavenumber for the hydrogen bonded urethane carbonyl absorption maxima of the aromatic diamine chain-extended polyurethaneureas were similar, which indicated that the strengths of the inter-urethane hydrogen bonding interactions of these elastomers were also similar. However, the broadening to greater wavenumber values of the hydrogen bonded urethane carbonyl absorption peaks of the 4,4'-thiodianiline and 4,4'-sulphonyldianiline chain-extended materials indicated that these elastomers possessed substantial quantities of inter-urethane hydrogen bonding interactions with somewhat reduced strengths.

Values of X, the proportion of hard segments participating in inter-urethane hydrogen bonding interactions, observed for the polyurethaneureas chain-extended with 4,4'-methylenedianiline and 4,4'-oxydianiline were similar to each other and greater than those exhibited by the 4,4'-thiodianiline and 4,4'-sulphonyldianiline chain-extended elastomers. The values of X for the latter two materials were in turn similar. These results implied that the two former elastomers possessed greater proportions of hard segments participating in inter-hard segment hydrogen bonding interactions than the latter.

7.1.2 Differential Scanning Calorimetry

The results of the DSC analyses of the aromatic diamine chain-extended polyurethaneureas displayed step transitions in their heat flow curves at sub-ambient temperatures. These indicated changes in the heat capacity of the materials at the glass transition temperature \( T_g \) of the PTMG polyol/soft segment component of the
materials\(^{(166)}\). Values of \(T_g\) at the midpoint of the transitions were obtained from the points of inflection of the heat flow curves.

The results of the DSC analyses of the aromatic diamine chain-extended materials are summarised in table 7.2 and are shown in figure 7.2.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>(T_g) / (±1.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Methyleneedianiline</td>
<td>-53</td>
</tr>
<tr>
<td>4,4'-Oxydianiline</td>
<td>-54</td>
</tr>
<tr>
<td>4,4'-Thiodianiline</td>
<td>-54</td>
</tr>
<tr>
<td>4,4'-Sulphonyldianiline</td>
<td>-47</td>
</tr>
</tbody>
</table>

Table 7.2. DSC results of the aromatic diamine chain-extended polyurethaneureas.

Figure 7.2. DSC results of the aromatic diamine chain-extended polyurethaneureas.

The values of soft segment \(T_g\) of all the aromatic diamine chain-extended elastomers
were very similar, except for that incorporating 4,4'-sulphonyldianiline as chain extender, which was somewhat greater. The similarity in values of soft segment $T_g$ between the 4,4'-methylenedianiline, 4,4'-oxydianiline and 4,4'-thiodianiline chain-extended materials was probably a result of the fact that they contained relatively small proportions of the aromatic diamine chain extender compounds. This was a consequence of the fact that these compounds possessed relatively high melting points, which necessitated their dissolution in quite large proportions of PTMG. Any differences in aromatic diamine chain extender structure or phase separation between these elastomers were, therefore, over-shadowed by the ‘diluting’ effect of the high PTMG content.

The increased value of soft segment $T_g$ of the 4,4'-sulphonyldianiline chain-extended polyurethaneurea may have been a result of the presence of hard segment structures being dispersed within soft segment domains. These could have the effect of reducing the mobility of the soft segment structures. Such a reduction in mobility would be particularly significant in the case of the 4,4'-sulphonyldianiline chain-extended material, as a result of the relative bulkiness and rigidity of the sulphonyl group present in this chain extender moiety. The increased value of soft segment $T_g$ of this material may also have been due to a relatively low level of phase separation being present\(^{(166)}\). This may have arisen as a result of impaired inter-hard segment interactions, and therefore a relatively low level of thermodynamic incompatibility between the hard and soft segment structures. This again, could have been caused by the bulky nature of the sulphonyl group within the chain extender compound.

Small changes in the baseline slope of all of the aromatic diamine chain-extended materials were observed at a temperature of approximately 50-60°C. These may have been due to the dissociation of hard segment aggregates. However, these features were not of sufficient significance for any definitive inferences to be made about their origin. The general similarity of the DSC results of these materials at temperatures above the soft segment $T_g$, may again have been attributable to the relatively high proportion of PTMG contained in these materials, and the ‘diluting’ effect that this would have had on any hard segment domain structures present.
7.1.3 Modulated-Temperature Differential Scanning Calorimetry

The results of the M-TDSC analyses performed on the aromatic diamine chain-extended polyurethaneureas did not display any significantly different features to those observed in the results of the conventional DSC analyses of these materials. However, it was observed that the small changes in baseline slope present in the conventional DSC results at a temperature of approximately 50-60°C were accompanied by small endothermic features in the non-reversing heat flow signals of the M-TDSC results (figure 7.3). This indicated that these events were subject to kinetic control and could be attributed to the melting/dissociation of phase-separated hard segment domain structures (180).

Figure 7.3. M-TDSC results of the 4,4'-sulphonyldianiline chain-extended polyurethaneureas.
7.1.4 Dynamic Mechanical Thermal Analysis

The results of the DMTA analyses of the aromatic diamine chain-extended polyurethaneureas displayed a peak in the values of tan $\delta$ at sub-ambient temperatures. These peaks were coincident with significant decreases in values of $\log E'$ and were indicative of the glass transition temperature ($T_g$) of the PTMG polyol/soft segment component of the materials\(^{(78)}\).

The DMTA results of the aromatic diamine chain-extended materials are summarised in Table 7.3 and shown in Figures 7.4 and 7.5.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>$T_g$ / (±1.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Methylenedianiline</td>
<td>-32</td>
</tr>
<tr>
<td>4,4'-Oxydianiline</td>
<td>-32</td>
</tr>
<tr>
<td>4,4'-Thiodianiline</td>
<td>-32</td>
</tr>
<tr>
<td>4,4'-Sulphonyldianiline</td>
<td>-22</td>
</tr>
</tbody>
</table>

Table 7.3. DMTA results of the aromatic diamine chain-extended polyurethaneureas.

Values of soft segment $T_g$ were very similar for all of the aromatic diamine chain-extended elastomers with the exception of that containing 4,4'-sulphonyldianiline, which was somewhat greater. These results were in agreement with those of the DSC analyses. This once again suggested that the similarity in values of $T_g$ between the 4,4'-methylenedianiline, 4,4'-oxydianiline and 4,4'-thiodianiline chain-extended materials was probably a result of the fact that they contained a relatively small proportion of aromatic diamine chain extender compound, and a rather large proportion of PTMG. Consequently, the high PTMG content had a diluting effect on any soft segment $T_g$ variations between these elastomers. These results also further indicated that the 4,4'-sulphonyldianiline chain extender moiety, either resulted in reduced levels of phase separation or caused particularly significant restrictions on soft segment mobility. Both of these effects could probably be attributed to the inherent bulkiness of the sulphonyl group in the chain extender structure.

Increasing and decreasing values of tan $\delta$ and $\log E'$, respectively, were observed with
Figure 7.4. DMTA results of the aromatic diamine chain-extended polyurethanes: (a) 4,4'-sulphonyldianiline (b) 4,4'-oxydianiline (c) 4,4'-thiodianiline (d) 4,4'-methyleneedianiline.

increasing temperature for the aromatic diamine chain-extended polyurethanes, at temperatures above their soft segment glass transition temperature. These were due to increasing levels of kinetic energy and molecular mobility as a result of the increasing temperature and, therefore, reductions in storage modulus. The magnitudes of these changes were qualitatively observed to be least in the case of the elastomer chain-extended with 4,4'-thiodianiline, somewhat greater in the case of the 4,4'-sulphonyldianiline chain-extended material, greater still for the 4,4'-oxydianiline chain-extended elastomer, and greatest for that incorporating 4,4'-methyleneedianiline. The 4,4'-thiodianiline chain-extended polyurethaneurea probably displayed the least variations in these parameters as a consequence of the fact that this material possessed the most phase-separated hard/soft segment domain morphology of the aromatic diamine chain-extended elastomers. This would impart a relatively high degree of thermal stability to the material i.e. retention of storage modulus at elevated
Figure 7.5. DMTA results of the aromatic diamine chain-extended polyurethaneureas: (a) 4,4'-sulphonyldianiline (b) 4,4'-oxydianiline (c) 4,4'-thiodianiline (d) 4,4'-methylenedianiline.

Such a morphology may have been attributable to the presence of the sulphur atom in the chain extender moiety, which could have enhanced the thermodynamic incompatibility between the hard and soft segment structures in this material. This morphology was suggested despite the fact that the FTIR spectroscopic results indicated that the inter-hard segment hydrogen bonding interactions for this composition were relatively weak and inextensive. Such a dependence of morphology on the general ability of inter-hard segment interactions to occur, rather than hydrogen bonding interactions specifically has been previously reported\(^{80,155}\) for polyurethanes with no capability for inter-hard segment hydrogen bonding.

The relatively small changes in the values of tan δ and log $E'$, respectively, in the case of the 4,4'-sulphonyldianiline chain-extended material may have been due to the presence of a quite highly phase-separated and well formed hard and soft segment domain morphology. Alternatively, the inherently bulky and rigid nature of the
compound's sulphonyl group may have imparted an increased degree of thermal
stability to the material. Such a structure would have required increased levels of
kinetic energy in order to cause a certain level of molecular mobility. The former
explanation seemed to be the least likely in view of the fact that the value of peak tan
\( \delta \) and the corresponding decrease in \( \log E' \) values for this elastomer were the greatest
of the aromatic diamine chain-extended materials. Such a loss of storage modulus
implied a relative lack of a reinforcing, phase separated domain morphology (85). This
was in contradiction to work published in the literature (88) which reported the results of
tensile testing performed on a similarly chain-extended polyurethaneurea, but
synthesised with TDI and hydroxyl-terminated polybutadiene.

The particularly significant changes in values of tan \( \delta \) and \( \log E' \) observed above the
soft segment \( T_g \) for the 4,4'-methylenedianiline chain-extended polyurethaneurea,
implied that this material possessed a poorly hard segment domain reinforced
morphology. This was probably a result of relatively low levels of polar interactions
between hard segment structures, due to the presence of the methylene group in the
chain extender moiety. The consequence would be a reduced thermodynamic driving
force for phase separation to occur. This was consistent with work reported by
Ramesh and co-workers (98) and was observed in spite of the fact that the FTIR
spectroscopic results of this elastomer suggested the presence of a relatively extensive
network of inter-urethane hydrogen bonding interactions.

The comparatively small changes in the measured DMTA parameters for the
elastomer chain-extended with 4,4'-oxydianiline could probably be explained as a
result of increased levels of phase separation and, therefore, greater hard segment
domain reinforcement. This was probably a consequence of more significant polar
interactions occurring between the hard segments of the former material, possibly due
to the presence of the ether link in the chain extender moiety. Effective inter-hard
segment interactions were consistent with the results of the FTIR spectroscopic
analyses of this polyurethaneurea.
7.1.5 Wide Angle X-Ray Scattering

The results of the WAXS analyses of the aromatic diamine chain-extended polyurethaneureas were generally very similar. A common feature observed was a diffuse scattering peak with a maximum in scattering intensity at a 2θ value of approximately 20°. Such a feature is generally attributed to scattering from an amorphous arrangement of chain segments\(^{(84)}\).

As a consequence of the general similarity of the WAXS results obtained for this group of materials it was not possible to deduce any significant morphological differences between them (figure 7.6). This may have been due to the relatively high proportion of PTMG contained in these materials and the diluting effect that this would have had on any hard segment domain structures present.

Figure 7.6. WAXS results of the aromatic diamine chain-extended polyurethaneureas: (a) 4,4'-methylenedianiline (b) 4,4'-oxydianiline (c) 4,4'-thiodianiline (d) 4,4'-sulphonyldianiline.

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7.1.6 Tensile Testing

The results of the tensile testing experiments performed on the aromatic diamine chain-extended polyurethaneureas are summarised in table 7.4. The plots of stress vs strain are shown in figure 7.7.

The elastomer chain-extended with 4,4'-methylenedianiline possessed the lowest values of ultimate tensile strength, 100% modulus and elongation at break of all the aromatic diamine chain-extended materials. This was probably a consequence of the fact that this material possessed the least phase-separated, least hard segment domain reinforced morphology. This was consistent with the results of the DMTA experiments and further indicated that the presence of the methylene group in the chain extender moiety did not promote the formation of particularly cohesive interactions between hard segments.

The elastomers incorporating 4,4'-thiodianiline and 4,4'-sulphonyldianiline possessed the greatest values of ultimate tensile strength of the aromatic diamine chain-extended materials. The 4,4'-sulphonyldianiline chain-extended material also displayed the greatest value of elongation at break, although its values of 100%, 200% and 300% moduli were significantly reduced in comparison to those of the elastomers incorporating 4,4'-thiodianiline and 4,4'-oxydianiline. These results imply that the 4,4'-sulphonyldianiline chain-extended polyurethaneurea possessed a less well phase-separated domain morphology than the latter two materials with, consequently, reduced levels of hard segment domain reinforcement. This could probably be attributed to the bulky sulphonyl group present in this chain extender moiety, which would have the effect of impairing the ability of the hard segment structures to interact effectively and cohesively. This confirmed the DMTA results. The high value of ultimate tensile strength possessed by this elastomer can most likely be explained as a result of the occurrence of strain crystallisation at higher values of elongation. This was evident from the plots of stress vs strain for the aromatic diamine chain-extended materials.

The high value of ultimate tensile strength in the case of the 4,4'-thiodianiline chain-
<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Ultimate Tensile Strength / MPa</th>
<th>Elongation at Break / %</th>
<th>100% Modulus / MPa</th>
<th>200% Modulus / MPa</th>
<th>300% Modulus / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Methylenedianiline</td>
<td>1.5±0.2</td>
<td>130±5</td>
<td>1.5±0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4,4'-Oxydianiline</td>
<td>5.1±0.6</td>
<td>340±25</td>
<td>2.5±0.3</td>
<td>1.8±0.2</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>4,4'-Thiodianiline</td>
<td>8.2±0.2</td>
<td>390±15</td>
<td>3.3±0.3</td>
<td>2.2±0.1</td>
<td>1.9±0.1</td>
</tr>
<tr>
<td>4,4'-Sulphonyldianiline</td>
<td>8.9±1.2</td>
<td>585±20</td>
<td>1.8±0.2</td>
<td>1.0±0.1</td>
<td>0.7±0.1</td>
</tr>
</tbody>
</table>

*Table 7.4.* Tensile testing results of the aromatic diamine chain-extended polyurethanes.
extended elastomer was accompanied by the greatest values of 100%, 200% and 300% moduli of the aromatic diamine chain-extended materials. This could probably be attributed to the fact that this material possessed the most phase-separated and most hard segment domain reinforced morphology of this group of polyurethaneureas. This was consistent with the retention of storage modulus at increasing temperatures displayed by the results of the DMTA experiments, and can probably be explained as being due to the presence of the sulphur atom in the chain extender moiety. This may have created the driving force for enhanced phase separation to occur, as a consequence of the thermodynamic incompatibility between this structure and the PTMG soft segment structures.

![Stress-strain plots of the aromatic diamine chain-extended polyurethaneureas.](image)

Figure 7.7. Stress-strain plots of the aromatic diamine chain-extended polyurethaneureas.

The elastomer chain-extended with 4,4'-oxydianiline possessed values of ultimate tensile strength, elongation at break and 100%, 200% and 300% moduli which were
intermediate between those of the materials chain-extended with 4,4'-
methylenedianiline and 4,4'-thiodianiline. These results implied that the levels of
phase separation and hard segment domain reinforcement possessed by this
polyurethaneurea were also intermediate. It may be inferred, therefore, that the
polarity induced by the ether link in the 4,4'-oxydianiline moiety facilitated inter-hard
segment interactions of a more cohesive character than those allowed by the 4,4'-
methylenedianiline structure. Consequently, increased hard/soft segment
thermodynamic incompatibility and phase separation could result. However, the ether
link of 4,4'-oxydianiline would be more thermodynamically compatible with the
PTMG soft segment structures than the sulphur atom present in 4,4'-thiodianiline.
Therefore, the level of phase separation evident for the former elastomer would tend to
be somewhat reduced in comparison to that of the latter.

7.1.7 Swelling Studies

The results of the swelling studies performed on the aromatic diamine chain-extended
polyurethaneureas are shown in table 7.5.

<table>
<thead>
<tr>
<th>Chain Extender Compound</th>
<th>Volume Fraction of Toluene in the Swollen Elastomer, $\sigma_5$ (±0.04)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-Methylenedianiline</td>
<td>Soluble</td>
</tr>
<tr>
<td>4,4'-Oxydianiline</td>
<td>0.74</td>
</tr>
<tr>
<td>4,4'-Thiodianiline</td>
<td>0.65</td>
</tr>
<tr>
<td>4,4'-Sulphonyldianiline</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

*Table 7.5. Results of the swelling studies performed on the aromatic diamine chain-
extended polyurethaneureas.*

Values of $\sigma_5$ were not obtained for the polyurethaneureas chain-extended with 4,4'-
methylenedianiline and 4,4'-sulphonyldianiline due to the fact that these elastomers
were soluble in the solvent used. This could probably be ascribed to the relative lack
of a reinforcing, physically crosslinked hard segment domain morphology in these
materials. The fact that the polyurethaneureas incorporating 4,4'-oxydianiline and 4,4'-thiodianiline were insoluble in the solvent used suggested that these elastomers possessed more phase-separated and hard segment domain reinforced morphologies than the two former materials. Consequently, these results were consistent with those of the DMTA and tensile testing experiments performed.

Of the two insoluble polyurethaneureas, that chain-extended with 4,4'-thiodianiline displayed the lowest value of $\sigma_s$. This was again consistent with the results of the DMTA and tensile testing experiments and was most likely a consequence of increased thermodynamic incompatibility between the hard and soft segment structures, due to the presence of the sulphur atom in the chain extender compound. Increased phase separation has been previously suggested\cite{184} in the case of elastomers chain-extended with sulphur-containing compounds in comparison to those with the equivalent oxygen-containing structures. This was the case for materials synthesised from MDI and poly(ethylene-co-butylene) adipate, and chain extended with either $N,N'$-ethylene thiourea or $N,N'$-ethylene urea.

### 7.1.8 General Observations

The polyurethaneureas incorporating 4,4'-methylenedianiline and 4,4'-sulphonyldianiline appeared similarly translucent to the naked eye, while those chain-extended with 4,4'-oxydianiline and 4,4'-thiodianiline were opaque. The translucent appearance of the former materials indicated that they possessed relatively low levels of phase separation and poorly defined hard and soft segment domain morphologies. Therefore, their reduced heterogeneity and possession of morphologies with less discretely differing refractive indices would be relatively unable to cause the scattering of incident radiation with visible wavelengths. This general observation was concurrent with the results of the DMTA, tensile testing and swelling experiments performed on these elastomers.

The opacity displayed by the 4,4'-oxydianiline and 4,4'-thiodianiline chain-extended materials indicated that the levels of phase separation possessed by these materials was somewhat greater than those of the other aromatic diamine chain-extended
polyurethaneureas. Consequently, increased heterogeneity with more discrete hard and soft segment domain structures would be more able to induce the scattering of incident visible radiation\(^{(182)}\). The opacity of these elastomers was again consistent with the results of the DMTA, tensile testing and swelling experiments performed on them.

### 7.2 Conclusions

It was found that variations in the structure of the link group between the aromatic ring structures of the aromatic diamine chain extender compounds had a noticeable effect on the morphologies and properties of the polyurethaneureas prepared from them.

The polyurethaneurea chain-extended with 4,4'-thiodianiline was found to possess the greatest degree of phase separation amongst the aromatic diamine chain-extended elastomers. This material, therefore, displayed the most advanced level of formation of a hard and soft segment domain morphology. These observations were probably a consequence of the reduced thermodynamic compatibility of the hard and soft segment structures, which was most likely a consequence of the presence of sulphur atoms within the 4,4'-thiodianiline moieties. Such a well developed domain morphology was observed for this elastomer despite the fact that the inter-hard segment hydrogen bonding interactions present were among the least extensive of those of the aromatic diamine chain-extended materials. Therefore, it appeared that the thermodynamic incompatibility of the hard and soft segment structures was the dominating influence in determining the morphology of this polyurethaneurea, rather than the ability of the hard segments to participate in inter-hard segment hydrogen bonding interactions.

Chain extension utilising 4,4'-oxydianiline resulted in an elastomer with a quite high degree of phase separation and hard/soft segment domain formation. This was most likely attributable to the existence of cohesive polar interactions between hard segment structures, as a result of the presence of the ether link in the chain extender structure.
The material synthesised using 4,4'-sulphonyldianiline as chain extender was found not to possess a particularly well phase-separated, well defined hard/soft segment domain morphology. This observation was explained as a result of the inherently bulky nature of the sulphonyl group present in the chain extender compound. Such a structure could have inhibited the ability of cohesive inter-hard segment interactions to occur.

The polyurethaneurea prepared with 4,4'-methylenedianiline as chain extender displayed the least phase-separated and least perfectly formed hard/soft segment domain morphology of the aromatic diamine chain-extended elastomers. This was probably a consequence of the relative lack of cohesive interactions between the hard segment structures of these materials due to the presence of the relatively non-polar methylene link group within the chain extender moiety.
Chapter 8

2,4-Pentanediol Chain-Extended Polyurethanes
8.1 Results and Discussion

Polyurethane elastomers chain-extended with the single (+)- and (-)- enantiomers of 2,4-pentanediol, a racemic mixture of (±)-2,4-pentanediol and a combination of three 2,4-pentanediol stereoisomers (50% (±)-/50% meso-2,4-pentanediol) were prepared. The chemical structures of these compounds are shown in section 4.1.3.4. These materials were then characterised in order to investigate the influence of such chain extender structural variations on morphology and properties.

8.1.1 Fourier Transform Infrared Spectroscopy

The results of the FTIR spectroscopic analyses of the 2,4-pentanediol chain-extended polyurethanes are summarised in table 8.1. The urethane carbonyl absorption regions of these materials are shown in figure 8.1. Values of $X$, the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, were determined from the relative absorbances of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks (as described in section 4.4.1).

<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>Inter-Urethane Hydrogen Bonded Carbonyl Absorption Maximum / (±1)cm$^{-1}$</th>
<th>$X$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-2,4-Pentanediol</td>
<td>1707</td>
<td>0.61</td>
</tr>
<tr>
<td>(-)-2,4-Pentanediol</td>
<td>1707</td>
<td>0.62</td>
</tr>
<tr>
<td>(±)-2,4-Pentanediol</td>
<td>1709</td>
<td>0.55</td>
</tr>
<tr>
<td>50% (±)-/50% meso-2,4-Pentanediol</td>
<td>1711</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 8.1. FTIR analysis results of the 2,4-pentanediol chain-extended polyurethanes.

The polyurethanes chain-extended with the single (+)- and (-)-2,4-pentanediol enantiomers possessed identical values of wavenumber for their inter-urethane hydrogen bonded carbonyl absorption maxima. These materials also displayed very
similar values of $X$, the proportion of hard segments participating in hydrogen bonding interactions. These results indicated that both the strength and the extent of the inter-urethane hydrogen bonding interactions occurring between the hard segments of these elastomers were very similar. It would be expected that these two materials should contain similar hard segment interactions, since the two enantiomeric chain extender compounds were simply mirror images of each other. Therefore, the hard segments resulting from chain extension with these enantiomers ought to be
effectively identical.
The absolute values of wavenumber for the inter-urethane hydrogen bonded carbonyl absorption maxima of these single enantiomer chain-extended polyurethanes, and their values of $X$, were the least and greatest, respectively, amongst the 2,4-pentanediol chain-extended elastomers. These together implied that the inter-urethane hydrogen bonds of these materials were the strongest of those present within the 2,4-pentanediol chain-extended materials, and that the extent of formation of inter-hard segmental hydrogen bonding networks within them was the greatest. Such strong and effective interactions were probably observed in these elastomers as a result of the fact that they were chain-extended with single enantiomeric compounds. This could have caused the resulting hard segments to possess relatively high levels of regularity and structural coincidence, thereby enabling effective inter-hard segment interactions. Such an effect of chain extender structural regularity on morphology and properties has been previously reported\(^{137}\) in the case of elastomers containing MDI and PTMG, and chain extended with mixed compositions of diol and diamine compounds. Characterisation of these materials was performed using FTIR analysis, DSC and tensile testing.
The polyurethane prepared with the racemic mixture of 2,4-pentanediol enantiomers exhibited a greater value of wavenumber for its inter-urethane hydrogen bonded carbonyl absorption maxima than the materials chain-extended with the single enantiomers. This material also possessed a comparatively reduced value of $X$. These results suggested that the inter-hard segment hydrogen bonding interactions of this elastomer were somewhat reduced in both strength and number. These observations may be explained by the fact that chain extension with a combination of two different enantiomers of 2,4-pentanediol would reduce the levels of structural coincidence amongst the resulting hard segments. Consequently, the ability of interactions such as hydrogen bonds to occur effectively between hard segments would be reduced, both in strength and in number.
Of the 2,4-pentanediol chain-extended polyurethanes, that incorporating the mixed isomers of 2,4-pentanediol (50% (±)/50% meso-2,4-pentanediol) displayed the greatest value of wavenumber for its inter-urethane hydrogen bonded carbonyl
absorption maxima, and also the least value of X of this group of materials. These


together imply that this elastomer possessed the weakest and least extensive inter­
urethane hydrogen bonding interactions. This level of inter-hard segment interaction

can probably be explained as a result of the fact that chain extension was, effectively,


occurring with three different chain extender structures i.e. the (+)- and (-)-2,4-
pentanediol enantiomers and also the meso-stereoisomer. Consequently, the presence


of these different stereo isomers would probably result in hard segment structures with


very low levels of structural coincidence. Accordingly, inter-hard segment hydrogen


bonding interactions would be severely impaired, and reduced in both strength and


number.


8.1.2 Differential Scanning Calorimetry


The results of the DSC analyses of the 2,4-pentanediol chain-extended polyurethanes
displayed step transitions in their heat flow curves at sub-ambient temperatures. These


indicated changes in the heat capacity of the materials due to the glass transition
temperature \( T_g \) of the PTMG polyol/soft segment component of the materials\(^{166} \). Values of \( T_g \) at the midpoint of the transitions were obtained from the points of


inflection of the heat flow curves. Some of the DSC results for the 2,4-pentanediol
chain-extended elastomers also exhibited endothermic features. These were indicative


of changes in heat capacity of the materials due to the dissociation/melting of phase­


separated hard segment domain structures\(^{80} \). The peak temperatures at which the


endotherms were observed were designated \( T_m \).


The results of the DSC analyses of the 2,4-pentanediol chain-extended polyurethanes
are summarised in table 8.2 and are shown in figure 8.2.


The values of soft segment glass transition temperature of the polyurethanes chain­
extended with the single (+)- and (-)-2,4-pentanediol enantiomers were very similar,


and were the least of the 2,4-pentanediol chain-extended elastomers. The similarity of


the soft segment glass transition temperatures of these two materials was consistent


with the similarity of their FTIR results, and was probably due to the fact that chain
extension using either of these two single enantiomers should result in materials with identical hard segment structures, and identical degrees of inter-hard segment interaction. The result should be very similar degrees of hard/soft segment incompatibility and phase separation. The fact that the values of the soft segment glass transition temperatures of these single enantiomer chain-extended elastomers were the lowest of the 2,4-pentanediol chain-extended materials can probably be attributed to the fact that they possessed the most phase-separated hard/soft segment domain.
morphologies\textsuperscript{(166)}. This was most likely because chain extension with single enantiomeric compounds should result in relatively high levels of hard segment structural regularity and, therefore, facilitate effective inter-hard segment interactions. The value of soft segment $T_g$ of the elastomer chain-extended with the racemic mixture of (±)-2,4-pentanediol was somewhat greater than for those of the materials containing the single (+)- and (−)-2,4-pentanediol enantiomers. This increase was probably observed as a result of the fact that the presence of two different enantiomers reduced the levels of structural regularity amongst the hard segments. This would tend to have the effect of precluding to some degree the effective interaction of the hard segments containing them. As a consequence, the degree of hard/soft segment phase separation would be reduced in comparison to those chain-extended with the single enantiomers.

The value of soft segment $T_g$ of the elastomer chain-extended with the mixed 2,4-pentanediol isomers composition was the greatest of the 2,4-pentanediol chain-extended materials. This could most likely be attributed to the fact that chain extension was being performed with a combination of three different chain extender structures. As a result the structural regularity amongst the hard segments would be severely compromised, causing a significant reduction in the effectiveness of inter-hard segment interactions. Consequently, this would have led to the lowest levels of phase separation amongst the 2,4-pentanediol chain-extended materials.

The behaviour of the soft segment glass transition temperatures of the 2,4-pentanediol chain-extended polyurethanes were entirely consistent with the results of the FTIR analyses, in that decreasing strengths and quantities of inter-urethane hydrogen bonding interactions were concomitant with increasing values of soft segment $T_g$, i.e. reduced levels of phase separation.

Of the series of 2,4-pentanediol chain-extended elastomers synthesised, those utilising the single (+)- and (−)-2,4-pentanediol enantiomers displayed the most obvious endothermic activity in their DSC results. Both of these materials possessed endotherms in two temperature regions, the first occurring at approximately 65°C, and the second in the range 110-130°C. This endothermic activity is associated with the
melting of phase-separated hard segment domains. The driving force for the formation
of such structures is ascribed to the thermodynamic incompatibility of the hard and
soft segments\(^{(20)}\). The similarity of the endothermic features of these two materials
would be expected as a result of the fact that the (+)- and (−)-2,4-pentanediol
enantiomers are mirror images of each other and should result in similarly phase-
separated domain morphologies.

The materials incorporating the single pentanediol enantiomers as chain extenders,
probably displayed marked endothermic activity as a result of the fact that the hard
segments of these materials should possess relatively high levels of structural
regularity. Consequently, effective inter-hard segment interactions should be possible,
thereby facilitating the formation of relatively highly phase-separated hard and soft
segment domain morphologies.

The elastomer prepared with the racemic mixture of 2,4-pentanediol enantiomers
resulted in much less significant endothermic activity than those containing the single
enantiomers. The activity also occurred at a comparatively reduced temperature. This
indicated the presence of less well phase-separated hard/soft segment domain
structures with reduced levels of perfection and cohesion. Similar events have been
attributed\(^{(165)}\) to the dissociation of hard segment domain structures with reduced
levels of phase separation/perfection in elastomers derived from MDI/PTMG/1,4-
butanediol. These would be disrupted by reduced levels of thermal energy and their
formation could probably be attributed to the fact that reduced levels of hard segment
structural regularity should arise from the presence of mixed enantiomers. This in turn
should result in less effective inter-hard segmental interactions and reduced
thermodynamic incompatibility between the hard and soft segment structures.

The polyurethane incorporating the mixed 2,4-pentanediol isomers chain extender
composition displayed a lack of endothermic activity. This was most likely a
consequence of the fact that this elastomer contained three different chain extender
structures and the fact that the corresponding low levels of structural regularity
amongst the hard segments would severely disrupt inter-hard segment interactions.
This disruption obviously occurred to such an extent that phase separation and
hard/soft segment domain formation was largely negated.
The decreasing levels of phase separation suggested by these diminishing levels of endothermic activity were consistent with the increasing values of soft segment $T_g$ observed, and also with the reduced levels of inter-hard segment interactions suggested by the results of the FTIR analyses.

### 8.1.3 Modulated-Temperature Differential Scanning Calorimetry

The results of the M-TDSC analyses performed on the 2,4-pentanediol chain-extended polyurethanes did not display any significantly different features to those observed in the results of the conventional DSC analyses of these materials.

It was generally observed that the endothermic activity displayed in the results of the conventional DSC analyses was accompanied by similar features in the non-reversing heat flow signals of the M-TDSC results (figure 8.3). This indicated that the processes responsible for these events were subject to kinetic control and was, therefore, consistent with their description as melting phenomena\(^{180}\).

![Figure 8.3. M-TDSC results of the (−)-2,4-pentanediol chain-extended polyurethane.](image-url)
8.1.4 Dynamic Mechanical Thermal Analysis

The results of the DMTA analyses of the 2,4-pentanediol chain-extended polyurethanes displayed peaks in the values of tan δ at sub-ambient temperatures. These peaks were coincident with significant decreases in values of log $E'$ and were indicative of the glass transition temperature ($T_g$) of the PTMG polyol/soft segment component of the materials (78). Some of the 2,4-pentanediol chain-extended elastomers also displayed noticeable increases and decreases in values of tan δ and log $E'$, respectively, which were coincident with the endothermic events observed in the results of the DSC analyses. Therefore, these features were similarly indicative of the melting of phase-separated hard segment domain structures (85), and the temperatures at which they occurred were designated $T_m$.

The DMTA results of the 2,4-pentanediol chain-extended elastomers are summarised in Table 8.3 and are shown in figures 8.4 and 8.5.

<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>$T_g$ / ($\pm 1.0^\circ$C)</th>
<th>$T_m$ / ($\pm 2.0^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-2,4-Pentanediol</td>
<td>-10</td>
<td>60/130</td>
</tr>
<tr>
<td>(-)-2,4-Pentanediol</td>
<td>-12</td>
<td>60/120</td>
</tr>
<tr>
<td>(±)-2,4-Pentanediol</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>50% (±)- / 50% meso-2,4-Pentanediol</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 8.3. DMTA results of the 2,4-pentanediol chain-extended polyurethanes.

In response to the changes in 2,4-pentanediol chain extender structure, the behaviour of the soft segment glass transition temperatures observed in the DMTA results of the 2,4-pentanediol chain-extended polyurethanes was consistent with that displayed by the results of the DSC analyses. Values of soft segment $T_g$ were observed to be very similar in the case of the two single enantiomer chain-extended elastomers, and were then observed to increase progressively as chain extension was performed with the racemic mixture of enantiomers and then with the mixed isomers composition. This provided further evidence to support the suggestion that these changes caused increasingly irregular hard segment structures, increasingly less effective inter-hard
Figure 8.4. DMTA results of the 2,4-pentanediol chain-extended polyurethanes: (a) 50% (±)-/50% meso-2,4-pentanediol (b) (±)-2,4-pentanediol (c) (+)-2,4-pentanediol (d) (−)-2,4-pentanediol.

segment interactions and decreasing levels of phase separation.

The polyurethanes synthesised with the single (+)- and (−)-2,4-pentanediol enantiomers possessed marked increases and decreases in values of tan δ and log $E'$, respectively, at a temperature of approximately 70°C. These materials also displayed similar features in the approximate temperature range of 120-130°C. These features coincided with endothermic events observed in the DSC results and were, therefore, attributable to the dissociation of phase-separated hard segment domain morphologies and the disruption of their reinforcing properties. The result was an increase in molecular mobility and, therefore, reduced values of storage modulus. The fact that such events occurred at different temperatures was probably a result of the presence of differing levels of morphological order, the greater dissociation temperature being associated with a greater level of order(78). Relatively well ordered hard segment domain morphologies were probably evident in the materials chain-extended with the single 2,4-pentanediol enantiomers since these materials contained hard segment.
structures with relatively high levels of structural regularity. These would have possessed the capability to interact with sufficient effectiveness to cause significant levels of hard/soft segment incompatibility, phase separation and domain formation.

![Figure 8.5. DMTA results of the 2,4-pentanediol chain-extended polyurethanes: (a) 50% (±)/50% meso-2,4-pentanediol (b) (±)-2,4-pentanediol (c) (+)-2,4-pentanediol (d) (–)-2,4-pentanediol.](image)

The elastomer chain-extended with the racemic mixture of 2,4-pentanediol isomers displayed only a small decrease in values of log $E'$ at a temperature of approximately 60°C. This suggested that in comparison to the materials chain extended with the pure 2,4-pentanediol enantiomers, the formation of reinforcing hard segment domain morphology was relatively poorly advanced. This was in accordance with the observation of limited endothermic activity in the DSC results of this elastomer, and was probably due to the restricted ability of hard segment structures to interact effectively. This may have been due to the presence of two chain extender structures and the resulting reduction in levels of structural coincidence.
The polyurethane incorporating the mixed 2,4-pentanediol isomers did not exhibit any features in the DMTA results which indicated the disruption of a hard segment domain morphology. This was probably a consequence of the presence of three chain extender structures in this material and was consistent with the lack of endothermic features in the elastomer’s DSC results. These structures would tend to reduce the levels of hard segment structural coincidence to such a degree that insufficient cohesive hard segment interactions would be present to cause significant phase separation, and the formation of a hard/soft segment domain morphology.

As for the DSC results, the decreasing evidence for hard segment domain structures with increasing numbers of 2,4-pentanediol chain extender enantiomers/stereoisomers present, was concurrent with the progressively increasing values of soft segment \( T_g \) observed.

Generally, with increasing temperature above the soft segment glass transition temperature, the 2,4-pentanediol chain-extended polyurethanes displayed increasing and decreasing values of \( \tan \delta \) and \( \log E' \), respectively. This was again due to increasing levels of kinetic energy causing enhanced molecular motion in the materials, and therefore reduced values of storage moduli. The rate of change of these values was, qualitatively, significantly greater for the elastomer chain-extended with the racemic mixture of (±)-2,4-pentanediol than for those chain extended with the single (+)- and (−)-2,4-pentanediol enantiomers. These rates of change were greater still for the material incorporating the mixed 2,4-pentanediol isomers composition. This sequence can probably be attributed to the progressive reductions in hard segment structural regularity as the number of 2,4-pentanediol chain extender structures present increased. The consequence would be increasingly less effective and cohesive hard segment interactions and, therefore, reduced hard segment domain reinforcement.

The value of peak \( \tan \delta \) and the corresponding decrease in \( \log E' \) values for the elastomers prepared with the single (+)- and (−)-2,4-pentanediol enantiomers were, qualitatively, very similar. This similarity was akin to others observed in the FTIR,
DSC and DMTA results. This could again be explained by the fact that the
reinforcement imparted to these materials by their hard segment domain structures
should be identical, due to the mirror image relationship of their enantiomeric chain
extender compounds.

Values of peak tan δ and the corresponding decreases in log $E'$ values were observed
to increase for the polyurethane chain-extended with the racemic mixture of (±)-2,4-
pentanediol. They were found to increase still further in the case of that containing the
mixed 2,4-pentanediol isomer composition. These results can most likely be ascribed
to the decreasing levels of hard segment structural regularity, phase separation and
reinforcing domain formation\(^{(85)}\) due to the number of chain extender structures
increasing.

8.1.5 Wide Angle X-Ray Scattering

The results of the WAXS analyses of the 2,4-pentanediol chain-extended
polyurethanes were generally very similar. The main feature observed for each
material was a diffuse scattering peak with a maximum scattering intensity at a value
of 2$\Theta$ of approximately 20°. Such a feature is generally attributed to scattering from
an amorphous arrangement of chain segments\(^{(84)}\).

In addition to the main scattering peak the elastomers chain-extended with the single
(+)- and (−)-2,4-pentanediol enantiomers, and also that containing the racemic mixture
of enantiomers, displayed a marked shoulder superimposed on this peak (figure 8.6).
This shoulder occurred at a value of 2$\Theta$ of approximately 10°, which corresponds to a
repeat distance of approximately 0.88nm). This feature was probably due to scattering
from some form of phase-separated domain morphology\(^{(171)}\). Such a shoulder was
discernible in the case of the material chain-extended with the mixed 2,4-pentanediol
isomers composition, but was significantly less prominent. These results indicated that
the elastomer chain-extended with the mixed isomers did not possess such a well
ordered, highly phase-separated hard/soft segment domain morphology as the other
2,4-pentanediol chain extended materials\(^{(89)}\). This was consistent with the results of
the FTIR, DSC and DMTA experiments and could probably be attributed to the
presence of three different chain extender structures in this polyurethane. This would result in relatively low levels of hard segment structural coincidence and, therefore, less effective inter-hard segment interactions. These results also suggested that the scattering feature observed at a value of $2\Theta$ of approximately $10^\circ$ was due to the type of domain morphology which was indicated by the presence of features at a temperature of approximately $50-70^\circ\text{C}$ in the results of the DSC and DMTA experiments.

![WAXS results of the 2,4-pentanediol chain-extended polyurethanes](image)

**Figure 8.6.** WAXS results of the 2,4-pentanediol chain-extended polyurethanes: (a) (+)-2,4-pentanediol (b) (−)-2,4-pentanediol (c) (±)-2,4-pentanediol (d) 50% (±)-/50% meso-2,4-pentanediol.

Any differences in the degree of perfection of the domain morphologies of the three more highly phase-separated 2,4-pentanediol chain-extended polyurethanes were not sufficient to cause noticeable differences between the WAXS results of these elastomers. This was probably a consequence of the fact that very highly ordered hard/soft segment domain morphologies would not be facilitated by the pendant
methyl groups present in the 2,4-pentanediol chain extender moiety. These groups would tend to impair the ability of hard segment structures containing them to interact, and would effectively act as internal plasticisers. This has been reported\(^{[85]}\) in polyurethanes derived from hydroxyl-terminated polybutadiene, various diisocyanates and other aliphatic diols with side groups.

8.1.6 Small Angle X-Ray Scattering

SAXS analysis was carried out on the 2,4-pentanediol chain-extended elastomers incorporating the (+)-2,4-pentanediol enantiomer, the racemic mixture of (±)-2,4-pentanediol and the mixed 2,4-pentanediol isomers composition. The results of the SAXS analyses are shown in figure 8.7.

![Graph showing SAXS results for 2,4-pentanediol chain-extended polyurethanes](image)

Figure 8.7. SAXS results of the 2,4-pentanediol chain-extended polyurethanes.
The results of the SAXS analyses performed on the polyurethanes chain-extended with the single enantiomer and the racemic mixture of 2,4-pentanediol displayed scattering shoulders, that of the single enantiomer-containing material having the greater intensity. The SAXS result of the elastomer incorporating the mixed isomers composition did not exhibit a significant scattering feature. These reductions in scattering intensity were consistent with the results of the other characterisation techniques employed and further indicated that the presence of increasing numbers of enantiomers/stereoisomers caused reductions in the ability of hard segments to form a phase-separated domain morphology\(^{(174)}\).

**8.1.7 Tensile Testing**

The results of the tensile testing experiments performed on the 2,4-pentanediol chain-extended polyurethanes are summarised in table 8.4. The plots of stress vs strain are shown in figure 8.8.

The polyurethanes chain-extended with the single (+)- and (-)-2,4-pentanediol enantiomers possessed very similar values of ultimate tensile strength, elongation at break and 100%, 200% and 300% modulus values. The values of elongation at break were the least of the 2,4-pentanediol chain-extended elastomers, while the modulus values were the greatest. The values of ultimate tensile strength of these materials were significantly greater than that of the mixed 2,4-pentanediol isomers chain-extended material.

It would be expected that the tensile properties of both of the single enantiomer chain-extended elastomers ought to be similar, since the two enantiomers are simply mirror images of each other and ought to result in hard segment structures with identical abilities to interact. Thus, the resulting phase-separated domain morphologies of these polyurethanes should be similar, with equivalent levels of hard segment domain reinforcement being provided by them.

The values of modulus and elongation at break of the materials incorporating the single enantiomer chain-extenders were the greatest and least of the 2,4-pentanediol...
<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>Ultimate Tensile Strength / MPa</th>
<th>Elongation at Break / %</th>
<th>100% Modulus / MPa</th>
<th>200% Modulus / MPa</th>
<th>300% Modulus / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-2,4-Pentanediol</td>
<td>14.7±3.9</td>
<td>470±25</td>
<td>3.5±0.1</td>
<td>2.4±0.1</td>
<td>1.8±0.2</td>
</tr>
<tr>
<td>(-)-2,4-Pentanediol</td>
<td>9.5±1.9</td>
<td>500±55</td>
<td>4.0±0.1</td>
<td>2.5±0.1</td>
<td>1.9±0.2</td>
</tr>
<tr>
<td>(±)-2,4-Pentanediol</td>
<td>32.7±10.7</td>
<td>605±40</td>
<td>2.2±0.2</td>
<td>1.5±0.2</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>50% (±)-/50% meso-2,4-</td>
<td>1.6±0.2</td>
<td>785±100</td>
<td>1.3±0.1</td>
<td>0.6±0.05</td>
<td>0.3±0.05</td>
</tr>
</tbody>
</table>

Table 8.4. Tensile testing results of the 2,4-pentanediol chain-extended polyurethanes.
chain extended elastomers, respectively. This implied that these materials possessed the most phase-separated and most reinforcing hard/soft segment domain morphologies of this series of materials. This confirmed the results of the other characterisation techniques and further indicated that these properties were most likely the result of the fact that chain extension utilising a single enantiomeric compound would tend to produce hard segment structures which could interact effectively and, therefore, cause significant hard/soft segment thermodynamic incompatibility. The relatively high values of ultimate tensile strength of the single enantiomer chain-extended materials could also be explained as being the result of these effects.

Of the 2,4-pentanediol chain-extended elastomers, that synthesised with the mixed 2,4-pentanediol isomers composition possessed the greatest value of elongation at break and the lowest values of ultimate tensile strength and 100%, 200% and 300% moduli. This was again concurrent with the results of the other characterisation
techniques employed, and provided more evidence that the presence of three different 2,4-pentanediol structures caused an impaired ability of the hard segment structures to interact effectively undergo phase separation. Consequently, the formation of a hard/soft segment domain morphology was not allowed to progress to a level where substantial hard segment domain reinforcement was realised.

The polyurethane chain-extended with the racemic mixture of (±)-2,4-pentanediol possessed values of moduli and elongation at break intermediate between those of the pure enantiomer and the mixed isomer chain-extended materials. This suggested that this elastomer possessed a domain morphology which provided intermediate levels of phase separation and hard segment domain reinforcement. The reason for this was most likely that chain extension with a racemic mixture of enantiomers would result in the formation of a less phase-separated hard/soft segment domain morphology than those formed from a single enantiomer. However, the morphology should be more highly phase-separated than that arising from a mixture of three chain extender structures. The presence of such a morphology was also indicated by the results of the DSC, DMTA, WAXS and SAXS analyses. It was observed that the material incorporating the racemic mixture of 2,4-pentanediol enantiomers displayed the greatest value of ultimate tensile strength of the 2,4-pentanediol chain-extended elastomers. This was possibly a result of the fact that quite a low level of hard segment domain reinforcement enabled this material to become highly elongated, yet sufficient phase separation existed to allow the PTMG soft segments to strain harden at this level of elongation. The existence of strain hardening was evident from the plot of stress vs strain.

8.1.8 Swelling Studies

The results of the swelling studies performed on the 2,4-pentanediol chain-extended polyurethanes are shown in table 8.5.

The values of $\sigma_s$ obtained for the polyurethanes incorporating the single (±)- and (−)-2,4-pentanediol enantiomers were similar, and were significantly less than that
<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>Volume Fraction of Toluene in the Swollen Elastomer, $\sigma_s$ (±0.04)</th>
</tr>
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<tbody>
<tr>
<td>(+)-Pentanediol</td>
<td>0.32</td>
</tr>
<tr>
<td>(-)-Pentanediol</td>
<td>0.39</td>
</tr>
<tr>
<td>(±)-Pentanediol</td>
<td>0.67</td>
</tr>
<tr>
<td>50% (+)- / 50% meso-Pentanediol</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Table 8.5. Results of the swelling studies performed on the 2,4-pentanediol chain-extended polyurethanes.

observed for the elastomer chain-extended with the racemic mixture of enantiomers. The similarity of the values for the pure enantiomer chain-extended materials was again probably due to the fact that chain extension with compounds that are mirror images of each other should result in similarly phase-separated morphologies. These morphologies should then impart equivalent levels of hard segment domain reinforcement and physical crosslinking to resist swelling due to solvent ingress.

The increased value of $\sigma_s$ obtained for the material chain-extended with the racemic mixture of enantiomers was consistent with the reduced levels of phase separation implied by the results of the other characterisation techniques, and was most likely a consequence of the presence of two chain extender structures in the composition. This should lead to reduced levels of hard segment structural regularity and less cohesive inter-hard segment interactions. Thus, the thermodynamic driving force for phase separation and the formation of a physically crosslinked, reinforcing hard/soft segment domain morphology to occur would be reduced.

A value of $\sigma_s$ was not obtained for the elastomer chain-extended with the mixed 2,4-pentanediol isomers composition as a result of the fact that this material was soluble in the solvent used. This solubility once more implied the presence of low levels of phase separation and hard segment domain reinforcement was probably caused by the presence of three chain extender structures and, therefore, inhibited inter-hard segment interactions.
8.1.9 General Observations

The 2,4-pentanediol chain-extended polyurethanes incorporating the racemic mixture and the mixed isomer compositions appeared colourless and transparent to the naked eye. This was in agreement with the results of the other characterisation techniques in implying the presence of low levels of phase separation and hard/soft segment domain formation. The resulting relatively homogeneous structure would not possess regions with sufficiently distinct refractive indices to cause the scattering of incident visible radiation.

The materials chain-extended with the single 2,4-pentanediol enantiomers both appeared slightly translucent to the naked eye. This indicated that these elastomers possessed more phase-separated and more heterogeneous hard/soft segment domain structures than the materials incorporating the racemic mixture and mixed isomer 2,4-pentanediol compositions. Thus, these morphologies would be capable of causing the scattering of radiation with visible wavelengths due to the presence of regions with relatively discreet refractive indices\(^{182}\). Consequently, this general observation was also consistent with the findings of the other characterisation techniques.

8.2 Conclusions

It was found that increasing numbers of stereoisomers present in the 2,4-pentanediol chain-extender composition strongly influenced the properties of the resulting polyurethanes.

Of the 2,4-pentanediol chain-extended polyurethanes, those prepared with the single (+)- and (-)-2,4-pentanediol enantiomers appeared to possess the most phase-separated hard/soft segment domain morphologies. This was probably due to the high levels of regularity, structural coincidence and effective interactions afforded to the hard segment structures by the presence of a single chain extender structure. Therefore, the hard and soft segment structures would display a relatively high degree of thermodynamic incompatibility.
The elastomers incorporating the racemic mixture and the mixed isomers 2,4-pentanediol compositions possessed progressively less well phase-separated, less perfectly formed hard/soft segment domain morphologies than the pure enantiomer chain-extended materials. This was most likely the result of a progressive reduction in the ability of the hard segment structures of these materials to interact effectively. This in turn could occur due to the progressive reductions in hard segment regularity and structural coincidence which arose from the introduction of two and then three different chain extender structures to these materials. Thus, the levels of thermodynamic incompatibility between the hard and soft segment structures, and therefore the driving forces for phase separation were progressively reduced.

The results of the WAXS analyses performed on the the 2,4-pentanediol chain-extended elastomers indicated that the morphologies responsible for the endothermic features observed at a temperature of approximately 50-70°C in the results of the DSC analyses possessed periodicity on the scale of approximately 0.9nm.
Chapter 9

Benzenedimethanol Chain-Extended Polyurethanes
9.1 Results and Discussion

Polyurethane elastomers were synthesised by chain extension with two different benzenedimethanol isomers, and also with combinations of these isomers in varying ratios. The chemical structures of these compounds are shown in section 4.1.3.5. These materials were then characterised in order to elucidate the effects of these chain extender structural variations on morphology and properties. The benzenedimethanol isomers used for this purpose were 1,2-benzenedimethanol and 1,4-benzenedimethanol.

9.1.1 Fourier Transform Infrared Spectroscopy

The results of the FTIR spectroscopic analyses of the benzenedimethanol chain-extended materials are summarised in table 9.1. The urethane carbonyl absorption regions of these materials are shown in figure 9.1. Values of \( X \), the proportion of urethane carbonyl groups participating in inter-urethane hydrogen bonding interactions, were determined from the relative absorbances of the hydrogen bonded and non-hydrogen bonded urethane carbonyl absorption peaks (as described in section 4.4.1).

The values of wavenumber of the inter-urethane hydrogen bonded carbonyl absorption maxima remained constant for the benzenedimethanol chain-extended polyurethanes, as the proportion of 1,4-benzenedimethanol in the chain extender compositions was reduced from 100% through 90% to 75%. Similarly, values of \( X \), the proportion of hard segments participating in inter-urethane hydrogen bonding interactions, were very similar for the three polyurethanes represented by this composition range. These observations suggested that both the strength and the extent of formation of inter-hard segment hydrogen bonding interactions were very similar for these three materials.

In addition, the absolute values of wavenumber of the hydrogen bonded inter-urethane carbonyl absorption maxima of these elastomers were the lowest of those displayed by
Table 9.1. FTIR analysis results of the benzenedimethanol chain-extended polyurethanes.

the benzenedimethanol chain-extended materials, while their values of X were the greatest. This indicated that they possessed the strongest inter-urethane hydrogen bonds and the most extensive inter-hard segment hydrogen bonding networks amongst the benzenedimethanol chain-extended polyurethanes. These elastomers probably displayed such characteristics as a result of the predominant presence of the para-substituted 1,4-benzenedimethanol isomer. Such a linear and symmetrical structure should lead to high levels of structural coincidence between the hard segments, and should, therefore, facilitate the formation of effective and extensive inter-hard segment interactions such as hydrogen bonds. Similar structure-property effects have been reported\(^{102,138}\) in the case of elastomers chain extended with diamine- and dihydroxy-functionalised benzene.

The similarity of the characteristics of the hydrogen bonding interactions for these materials inferred that the maximum levels of inter-urethane hydrogen bonding strengths attainable and the maximum extent of formation of inter-hard segment hydrogen bonding networks, were both obtained when the proportion of 1,4-benzenedimethanol in the chain extender composition was no less than 75%. This
indicated that the ability of the para-substituted chain extender structures to become involved in such interactions was not significantly inhibited by the presence of up to 25% of the ortho-substituted 1,2-benzenedimethanol isomer.

Figure 9.1. FTIR analysis results of the benzenedimethanol chain-extended polyurethanes: (a) 100% 1,4 (b) 90%/10% 1,4/1,2 (c) 75%/25% 1,4/1,2 (d) 50%/50% 1,4/1,2 (e) 25%/75% 1,4/1,2 (f) 10%/90% 1,4/1,2 (g) 100% 1,2.

The value of wavenumber for the hydrogen bonded urethane carbonyl absorption maximum of the polyurethane chain-extended with the 50%/50% 1,4/-1,2-benzenedimethanol composition was increased in comparison to the materials containing greater proportions of 1,4-benzenedimethanol. The corresponding values
for the materials chain-extended with the 25%/75% and 10%/90% 1,4-/1,2-benzenedimethanol compositions were increased still further. Values of X for these three elastomers were progressively reduced in comparison to those of the materials containing greater proportions of 1,4-benzenedimethanol. Therefore, for the polyurethanes in this composition range, this combination of results indicated both a reduction in the strength of the inter-urethane hydrogen bonds and also a progressive reduction in the extent of the inter-hard segment hydrogen bonding networks. This was probably observed as a consequence of the decreasing proportion of 1,4-benzenedimethanol present in the chain extender compositions. Therefore, as the proportion of linear, para-substituted chain extender structures declined and the level of non linear, ortho-substituted chain extender structures increased, the ability of hard segment structures to participate in regular and effective inter-urethane hydrogen bonding interactions would become reduced.

In comparison to the materials chain-extended with the 25%/75% and 10%/90% 1,4-/1,2-benzenedimethanol chain extender compositions, the value of wavenumber for the hydrogen bonded urethane carbonyl absorption maximum of the elastomer chain-extended with the 100% 1,2-benzenedimethanol composition was slightly reduced. In addition the value of X for this material was greater than the former materials. It can be inferred from these results that the strength of inter-urethane hydrogen bonds, and the extent of formation of inter-hard segment hydrogen bonding networks were enhanced in the case of the 100% 1,2-benzenedimethanol chain-extended material. This can probably be explained as a result of the fact that chain extension was being performed utilising a single isomer. Structural regularity and inter-hard segment interactions would, consequently, be enhanced in comparison to the mixed chain extender compositions which contained only relatively low levels of the linear 1,4-benzenedimethanol isomer. Accordingly, such improved regularity could compensate to some degree for the fact that hard segments chain-extended solely with the ortho-substituted 1,2-benzenedimethanol moiety possessed reduced linearity and symmetry in comparison to those containing 1,4-benzenedimethanol. Structural regularity has been found\(^{(137)}\) to be an important consideration in determining the extent to which
hard segments in polyurethane/urethaneurea elastomers interact. This was reported in the case of chain extension with mixtures of diols and diamines.

9.1.2 Differential Scanning Calorimetry

The results of the DSC analyses of the benzenedimethanol chain-extended polyurethanes displayed step transitions in their heat flow curves at sub-ambient temperatures. These indicated changes in the heat capacity of the materials at the glass transition temperature ($T_g$) of the PTMG polyol/soft segment component of the materials\(^\text{[166]}\). Values of $T_g$ at the midpoint of the transitions were obtained from the points of inflection of the heat flow curves. Some of the DSC results of the benzenedimethanol chain-extended elastomers also exhibited endothermic features. These were indicative of changes in heat capacity of the materials due to the dissociation/melting of phase-separated hard segment domain structures\(^\text{[80]}\). The peak temperatures at which the endotherms were observed were designated $T_m$.

The results of the DSC analyses of the benzenedimethanol chain-extended materials are summarised in table 9.2 and are shown in figure 9.2.

<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>$T_g$ / (±1.0)°C</th>
<th>$T_m$ / (±2.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Benzenedimethanol (100%)</td>
<td>-47</td>
<td>145</td>
</tr>
<tr>
<td>1,4/-1,2-Benzenedimethanol (90%/10%)</td>
<td>-46</td>
<td>150</td>
</tr>
<tr>
<td>1,4/-1,2-Benzenedimethanol (75%/25%)</td>
<td>-42</td>
<td>-</td>
</tr>
<tr>
<td>1,4/-1,2-Benzenedimethanol (50%/50%)</td>
<td>-40</td>
<td>-</td>
</tr>
<tr>
<td>1,4/-1,2-Benzenedimethanol (75%/25%)</td>
<td>-37</td>
<td>-</td>
</tr>
<tr>
<td>1,4/-1,2-Benzenedimethanol (10%/90%)</td>
<td>-38</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Benzenedimethanol (100%)</td>
<td>-45</td>
<td>50/90</td>
</tr>
</tbody>
</table>

Table 9.2. DSC results of the benzenedimethanol chain-extended polyurethanes.
The lowest values of soft segment $T_g$ of the benzenedimethanol chain-extended polyurethanes were observed for the elastomers chain-extended with the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/1,2-benzenedimethanol compositions. The soft segment $T_g$ of the 100% 1,2-benzenedimethanol composition was slightly greater, while values of soft segment $T_g$ increased for the intermediate, mixed isomer chain extender compositions, such that maximum values were obtained for the materials incorporating the 50%/50%, 25%/75% and 10%/90% 1,4-/1,2-benzenedimethanol compositions. The materials chain-extended with the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/1,2-benzenedimethanol compositions probably displayed the lowest values of soft segment $T_g$, as a result of the fact that they possessed the most phase-separated domain morphologies of the benzenedimethanol chain-extended elastomers (166). These morphologies may have arisen as a result of the fact that these materials were chain-extended with the greatest proportions of the para-substituted
1,4-benzenedimethanol isomer. Consequently, the linear configuration of this compound may have resulted in the formation of relatively linear hard segments. These could have permitted particularly regular and cohesive inter-hard segment interactions and, therefore, resulted in a high degree of thermodynamic incompatibility between the hard and soft segment structures. The resulting high degree of phase separation and relatively low proportion of hard segments dispersed among soft segment domains would facilitate high levels of soft segment mobility.

The slightly greater value of soft segment $T_g$ exhibited by the 100% 1,2-benzenedimethanol chain-extended composition polyurethane was probably a result of the ortho-substitution of this chain extender compound. Chain extension utilising this single isomer should result in quite regular hard segment interactions and therefore effective phase separation, though at reduced levels in comparison to the para-substituted compound. This was most likely a consequence of the fact that the ortho-substitution of the functional groups of 1,2-benzenedimethanol would result in nonlinear hard segment structures. Therefore, the effectiveness of the hard segment interactions would be reduced, as would the degree of phase separation between the hard and soft segment structures. The consequent reduction in phase separation would then cause an increase in the levels of hard segments present within soft segment domains, and therefore a reduction in soft segment mobility.

The generally increased values of soft segment $T_g$ of elastomers chain-extended with the mixed isomer chain extender compositions were most likely a result of the fact that a combination of different isomers precluded the existence of such regular and effective inter-hard segment interactions. Thus hard/soft segment thermodynamic incompatibility would be reduced, as would the resulting level of phase separation. Consequently, soft segment mobility would be impaired.

It was apparent that a degree of correlation occurred between the results of the DSC and the FTIR analyses. This was evident in that the polyurethanes possessing the lowest values of soft segment $T_g$ also exhibited the strongest and most extensive hydrogen bonding interactions. However, inconsistencies were also apparent. For example, while the elastomer chain-extended with the 75%/25% 1,4-/1,2-benzenedimethanol composition displayed inter-urethane hydrogen bonding
interactions which were similar to those containing higher proportions of the 1,4-benzenedimethanol isomer, this material exhibited a significantly higher value of soft segment $T_g$, thereby indicating a less well phase-separated hard/soft segment domain morphology.

Similarly, despite possessing stronger and more extensive inter-urethane hydrogen bonds than the 100% 1,2-benzenedimethanol chain-extended polyurethane, that incorporating the 50%/50% 1,4-/1,2-benzenedimethanol composition displayed a significantly higher value of soft segment $T_g$.

These observations suggested that the ability of hard segment structures to participate in inter-urethane hydrogen bonding interactions was not the sole factor in determining the extent to which hard/soft segment phase separation could occur. This is in agreement with results existing in the literature. Elastomers synthesised from chloroformates and piperazine, for example, and characterised by DSC and tensile testing\(^{(80,155)}\) displayed significant phase separation/domain formation despite possessing no capability for inter-urethane hydrogen bonding.

The maximum values of soft segment $T_g$ attained in the case of the 25%/75% and the 10%/90% 1,4-/1,2-benzenedimethanol chain-extended compositions were possibly a result of the fact that they contained the least phase-separated hard/soft segment domain morphologies. The fact that these materials contained substantial proportions of polyurethane molecules incorporating the non-linear 1,2-benzenedimethanol isomer may also have contributed to these values. Such polymer chains could have had the effect of significantly reducing the mobility of soft segment structures when present amongst them.

Endothermic activity was observed in the DSC results of the polyurethanes chain-extended with the 100% 1,4-benzenedimethanol, the 90%/10% 1,4-/1,2-benzenedimethanol and the 100% 1,2-benzenedimethanol compositions. Those incorporating 100% and 90% of the 1,4-benzenedimethanol isomer possessed a single endotherm with a peak at approximately 145-150°C, while that containing 100% 1,2-benzenedimethanol displayed two endotherms, one at approximately 90°C and a less significant one at about 50°C. These features were indicative of the disruption of
Chapter 9  Benzenedimethanol Chain-Extended Polyurethanes

phase-separated hard segment domains. Such structures may arise as a result of the thermodynamic incompatibility of the hard and soft segment structures\(^{(20)}\). Their appearance was consistent with the reduced values of soft segment \(T_g\) observed for these elastomers.

The materials incorporating the single benzenedimethanol isomers probably displayed endothermic features since these elastomers possessed sufficiently regular and effective hard segment interactions to cause significant hard/soft segment thermodynamic incompatibility, phase separation and, consequently, ordered domain formation. The fact that the 100% 1,2-benzenedimethanol chain-extended polyurethane possessed two endotherms, both of which were at significantly lower temperatures than that of the 100% 1,4-benzenedimethanol-incorporating material, suggested that the phase-separated domain morphology of this material was less perfectly developed and cohesive\(^{(165)}\). Such features have been observed previously in polyurethanes prepared from MDI, PTMG and 1,4-butanediol. Therefore, the domains would be disrupted by reduced levels of thermal energy. This could probably be attributed to the non-linear, \textit{ortho}-substitution of the 1,2-benzenedimethanol moiety. This may tend not to allow such regular and effective inter-hard segment interactions to occur, in comparison to those facilitated by the linear and highly symmetrical 1,4-benzenedimethanol structure. Therefore, the driving force for phase separation would be reduced.

The materials containing the 100% 1,4-benzenedimethanol and the 90%/10% 1,4-/1,2-benzenedimethanol chain extender compositions possessed very similar endothermic activity. This was most likely a result of the fact that the presence of such a small proportion of 1,2-benzenedimethanol was insufficient to disrupt the ability of the 1,4-benzenedimethanol-containing hard segments to interact.

\subsection*{9.1.3 Modulated-Temperature Differential Scanning Calorimetry}

The majority of the results of the M-TDSC analyses performed on the benzenedimethanol chain-extended polyurethanes did not display any significantly different features to those observed in the results of the conventional DSC analyses of

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these materials. However, in the case of the elastomer incorporating the 25%/75% 1,4-/1,2-benzenedimethanol chain extender composition, endothermic features were observed in the total heat flow and non-reversing heat flow signals at temperatures of approximately 90°C and 160°C (figure 9.3).

Figure 9.3. M-TDSC results of the 25%/75% 1,4-/1,2-benzenedimethanol chain-extended polyurethane.

These features suggested the presence of two types of phase-separated hard segment domain morphology in this material. The observation of endothermic events in the DSC results of the 100% 1,4- and the 100% 1,2-benzenedimethanol chain-extended elastomers at temperatures of approximately 90°C and 150°C, respectively, indicated that the 25%/75% 1,4-/1,2-benzenedimethanol chain-extended material may have possessed hard segment domains incorporating hard segments containing each of the 1,4- and 1,2-benzenedimethanol isomers. The presence of such a morphology may have been possible if the proportion of 1,2-benzenedimethanol in the composition was sufficient to cause aggregation of the 1,2-benzenedimethanol-containing hard
segments, thereby leaving the residual 1,4-benzenedimethanol-containing hard segments to also aggregate.

It was generally observed that the endothermic activity displayed in the results of the conventional DSC analyses was accompanied by similar features in the non-reversing heat flow signals of the M-TDSC results. This indicated that the processes responsible for these events were subject to kinetic control and was, therefore, consistent with their description as melting phenomena\(^{180}\).

9.1.4 Dynamic Mechanical Thermal Analysis

The results of the DMTA analyses of the benzenedimethanol chain-extended polyurethanes displayed peaks in the values of tan \(\delta\) at sub-ambient temperatures. These peaks were coincident with significant decreases in values of log \(E'\) and were indicative of the glass transition temperature \(T_g\) of the PTMG polyol/soft segment component of the materials\(^{78}\). Some of the benzenedimethanol chain-extended elastomers also displayed noticeable increases and decreases in values of tan \(\delta\) and log \(E'\), respectively, which were coincident with the endothermic events observed in the results of the DSC analyses. Therefore, these features were similarly indicative of the melting of phase-separated hard segment domain structures\(^{85}\), and the temperatures at which they occurred were designated \(T_m\).

The DMTA results of the benzenedimethanol chain-extended materials are summarised in table 9.3 and are shown in figures 9.4 and 9.5.

The polyurethane chain-extended with the 100% 1,4-benzenedimethanol composition possessed the lowest value of soft segment \(T_g\), while that containing the 100% 1,2-benzenedimethanol composition was somewhat greater. The elastomers of intermediate composition possessed greater values of soft segment \(T_g\) than both of these materials. The actual value of the \(T_g\) for the materials of intermediate composition increased progressively with increasing 1,2-benzenedimethanol content, to reach a maximum in the cases of the 25%/75% and 10%/90% 1,4-/1,2-benzenedimethanol-containing compositions. These effects of composition on the
value of soft segment glass transition temperature were consistent with those observed in the DSC analyses. Therefore, these results further indicated that chain extension with the compositions containing the greatest proportions of 1,4-benzenedimethanol resulted in the most phase-separated domain morphologies, while chain extension with 1,2-benzenedimethanol alone led to a less phase-separated structure. It then appeared that the degree of phase separation decreased further in the cases of the elastomers chain-extended with the mixed isomer compositions. Again, these morphologies probably resulted from the fact that the linear structure of the 1,4-benzenedimethanol isomer facilitated more regular and effective inter-hard segment interactions than the non-linear 1,2-benzenedimethanol compound, which in turn allowed more effective interactions than the more highly mixed chain extender compositions.

The polyurethanes chain-extended with the 100% 1,4-benzenedimethanol and the 90%/10% 1,4-/1,2-benzenedimethanol compositions possessed marked increases and decreases in values of tan δ and log $E'$, respectively, at a temperature of approximately 140°C. The elastomer chain-extended with the 100% 1,2-benzenedimethanol composition displayed similar features, but at temperatures of 50°C and 90°C. All of

<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>$T_g$ / (±1.0)°C</th>
<th>$T_m$ / (±2.0)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Benzenedimethanol (100%)</td>
<td>-25</td>
<td>135</td>
</tr>
<tr>
<td>1,4-/1,2-Benzenedimethanol (90% / 10%)</td>
<td>-23</td>
<td>140</td>
</tr>
<tr>
<td>1,4-/1,2-Benzenedimethanol (75% / 25%)</td>
<td>-19</td>
<td>70</td>
</tr>
<tr>
<td>1,4-/1,2-Benzenedimethanol (50% / 50%)</td>
<td>-17</td>
<td>-</td>
</tr>
<tr>
<td>1,4-/1,2-Benzenedimethanol (25% / 75%)</td>
<td>-15</td>
<td>145</td>
</tr>
<tr>
<td>1,4-/1,2-Benzenedimethanol (10% / 90%)</td>
<td>-15</td>
<td>50</td>
</tr>
<tr>
<td>1,2-Benzenedimethanol (100%)</td>
<td>-21</td>
<td>50/90</td>
</tr>
</tbody>
</table>

Table 9.3. DMTA results of the benzenedimethanol chain-extended polyurethanes.
these features were coincident with endothermic features observed in the DSC results of these materials, and were similarly attributable to the melting of hard segment domain structures. The disruption of such a morphology would cause a reduction in their reinforcing effect and thus induce decreases in values of storage modulus.

Figure 9.4. DMTA results of the benzenedimethanol chain-extended polyurethanes: (a) 10%/90% 1,4/1,2 (b) 25%/75% 1,4/1,2 (c) 50%/50% 1,4/1,2 (d) 100% 1,2 (e) 75%/25% 1,4/1,2 (f) 100% 1,4 (g) 90%/10% 1,4/1,2.

The similarity of the DMTA results of the 100% 1,4- and the 90%/10% 1,4/-1,2-benzenedimethanol chain-extended elastomers was consistent with that exhibited by the DSC results and could also be explained to be due to the fact that the presence of 10% of the 1,2-benzenedimethanol isomer was insufficient to disrupt the ability of the linear 1,4-benzenedimethanol hard segments to interact. The increased temperatures at which the hard segment structures were observed to dissociate in the case of these polyurethanes could again be ascribed to the linear configuration of 1,4-benzenedimethanol’s functional groups. This probably resulted in more cohesive inter-hard segment interactions and, therefore, caused more advanced levels of phase
Figure 9.5. DMTA results of the benzenedimethanol chain-extended polyurethanes: (a) 10%/90% 1,4/1,2 (b) 25%/75% 1,4/1,2 (c) 50%/50% 1,4/1,2 (d) 100% 1,2 (e) 75%/25% 1,4/1,2 (f) 100% 1,4 (g) 90%/10% 1,4/1,2.

separation to occur. Such interactions were suggested by the results of the FTIR spectroscopic analyses. The existence of significant hard segment domain morphologies in the case of the 100% 1,2-benzenedimethanol chain-extended material was once more probably attributable to quite regular inter-hard segment interactions, which could have occurred due to the presence of a single chain extender isomer. The polyurethane chain-extended with the 75%/25% 1,4-/1,2-benzenedimethanol composition displayed small but noticeable increases and decreases in values of tan δ and log $E'$, respectively, at a temperature of approximately 70°C. This suggested the presence of a hard segment domain morphology, which most likely resulted from phase separation of hard segments containing the more regular and plentiful 1,4-benzenedimethanol moiety. The relatively small magnitude of the changes and the low temperature at which they occurred, suggested that they were due to relatively small quantities of imperfectly organised domain structures. This was probably the result of
the quite highly mixed nature of the chain extender composition involved. This would tend to reduce the level of interaction between the hard segment structures and, therefore, limit the extent to which hard/soft segment phase separation could occur. The elastomer containing the 50%/50% 1,4-/1,2-benzenedimethanol chain extender composition displayed an absence of distinct features in its DMTA results. This was consistent with the absence of endothermic features in the DSC results of this material and further indicated a general lack of a phase-separated domain morphology. This could again most likely be attributed to the presence of equal proportions of two chain extender moieties, which could have inhibited interactions between hard segments to such an extent that phase separation was largely negated.

The elastomer chain-extended with the 25%/75% 1,4-/1,2-benzenedimethanol composition displayed relatively small, but noticeable changes in values of tan δ and log $E'$ at a temperature of approximately 140°C. The similarity of this observation to the DMTA results of the elastomers chain-extended with the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/1,2-benzenedimethanol compositions, suggested that this may have been due to the presence of a hard segment domain morphology resulting from aggregation of the 1,4-benzenedimethanol-containing hard segments. The presence of such a morphology was also implied by the results of the M-TDSC analyses.

The polyurethane containing the 10%/90% 1,4-/1,2-benzenedimethanol chain extender composition also exhibited small, but noticeable, increases and decreases in values of tan δ and log $E'$, respectively, at a temperature of approximately 50°C. This indicated the existence of a small quantity of relatively poorly ordered hard segment domain aggregates, which probably arose from the aggregation of hard segments containing the 1,2-benzenedimethanol moiety. The relatively small quantity of hard segment domain structures present was probably a consequence of the fact that the small proportion of 1,4-benzenedimethanol present was sufficient to disrupt the ability of the 1,2-benzenedimethanol-containing hard segments to interact particularly effectively. Such a small quantity of an additional structure was able to do this probably as a result of the fact that the 1,2-benzenedimethanol moiety already possessed an inherently low level of linearity and structural regularity.
The values of peak tan $\delta$ and the corresponding decrease in log $E'$ values were qualitatively observed to be lowest in the case of the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/1,2-benzenedimethanol chain-extended materials. These values were somewhat greater for the polyurethanes chain-extended with the 100% 1,2-benzenedimethanol and the 75%/25% 1,4/-1,2-benzenedimethanol compositions. The values increased still further for the elastomers containing the 50%/50%, the 25%/75% and the 10%/90% 1,4/-1,2-benzenedimethanol chain extender compositions.

The fact that the values of peak tan $\delta$ and the corresponding decrease in log $E'$ values were least for the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/-1,2-benzenedimethanol chain-extended polyurethanes provided further evidence to support the suggestion that these materials possessed the most phase-separated and most hard segment domain reinforced morphologies of the benzenedimethanol chain-extended elastomers. These morphologies would, therefore, have had the effect of restricting soft segment molecular mobility to a relatively high degree. The increased values of peak tan $\delta$ observed for the 100% 1,2-benzenedimethanol and the 75%/25% 1,4/-1,2-benzenedimethanol chain-extended polyurethanes further indicated that these materials possessed less phase-separated and less hard segment domain reinforced morphologies. Thus, soft segment mobility would be less restricted. The further increased values of peak tan $\delta$ observed for materials containing the 50%/50%, the 25%/75% and the 10%/90% benzenedimethanol chain extender compositions, again indicated further reductions in the levels of phase separation and hard segment domain reinforcement.

9.1.5 Wide Angle X-Ray Scattering

WAXS analysis was performed on the polyurethanes chain-extended with the 100% 1,4-, 75%/25% 1,4/-1,2-, 50%/50% 1,4/-1,2-, 25%/75% 1,4/-1,2- and the 100% 1,2-benzenedimethanol compositions.

The main feature of the WAXS results of the benzenedimethanol chain-extended elastomers was a diffuse scattering peak with a maximum intensity at a value of $2\Theta$ of approximately 20°. Such a feature is generally attributed to scattering from an
amorphous arrangement of chain segments\(^{84}\). However, some variations between the WAXS results of these materials were observed as a result of the chain extender compositional changes imposed (figure 9.6).

![WAXS results of the benzenedimethanol chain-extended polyurethanes](image)

*Figure 9.6. WAXS results of the benzenedimethanol chain-extended polyurethanes: (a) 100% 1,4 (b) 75%/25% 1,4/1,2 (c) 50%/50% 1,4/1,2 (d) 25%/75% 1,4/1,2 (e) 100% 1,2).*

In the case of the polyurethane incorporating the 100% 1,4-benzenedimethanol chain extender composition, a relatively sharp scattering peak was superimposed on the main peak, close to the maximum of that peak. In addition, relatively low intensity subsidiary scattering peaks were observed in the cases of the 100% 1,4- and the 75%/25% 1,4/1,2-benzenedimethanol chain-extended polyurethanes at values of 2\(\Theta\) of approximately 10° and 26°, respectively. These corresponded to repeat distances of approximately 0.88nm and 0.34nm, respectively. These additional features indicated the existence of phase-separated domain morphologies\(^{171}\). The presence of an additional peak and more intense peaks in the
case of the 100% 1,4-benzenedimethanol chain-extended composition indicated that this elastomer possessed the most phase-separated, most perfectly formed domain morphology. Therefore, these results were consistent with those of the DSC and DMTA experiments.

It was observed that the polyurethanes chain-extended with the benzenedimethanol compositions containing 50-100% of the 1,2-benzenedimethanol isomer displayed relatively low intensity but quite sharp scattering peaks, with maxima at values of 2θ of approximately 9.5° and 12.5°. These corresponded to repeat distances of 0.93nm and 0.71nm, respectively, and indicated the existence of phase-separated morphologies. These features exhibited the greatest scattering intensities for the elastomer chain-extended with the 100% 1,2-benzenedimethanol composition. This indicated that of these materials, the levels of phase separation and domain formation were greatest in the case of that containing the 100% 1,2-benzenedimethanol chain extender composition. This again indicated that the presence of a single chain extender structure resulted in increased levels of regular inter-hard segment interactions and, consequently, relatively advanced phase separation. This was again concurrent with the results of the FTIR, DSC and DMTA experiments.

### 9.1.6 Tensile Testing

The results of the tensile testing experiments performed on the benzenedimethanol chain-extended polyurethanes are summarised in table 9.4. The plots of stress vs strain are shown in figures 9.7.

The greatest values of ultimate tensile strength and 100%, 200% and 300% modulus of the benzenedimethanol chain-extended polyurethanes were observed for the materials incorporating the 100% 1,4-benzenedimethanol and the 90%/10% 1,4-/1,2-benzenedimethanol chain extender compositions. These tensile properties indicated that these elastomers possessed the most phase-separated and hard segment domain reinforced morphologies of the benzenedimethanol chain-extended materials. As suggested by the results of the FTIR, DSC, DMTA and WAXS analyses this
<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>Ultimate Tensile Strength / MPa</th>
<th>Elongation at Break / %</th>
<th>100% Modulus / MPa</th>
<th>200% Modulus / MPa</th>
<th>300% Modulus / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Benzenedimethanol (100%)</td>
<td>26.6±1.9</td>
<td>860±20</td>
<td>4.2±0.1</td>
<td>2.4±0.1</td>
<td>1.9±0.1</td>
</tr>
<tr>
<td>1,4/1,2- Benzenedimethanol (90% / 10%)</td>
<td>24.3±4.6</td>
<td>550±15</td>
<td>4.2±0.2</td>
<td>2.7±0.2</td>
<td>2.4±0.2</td>
</tr>
<tr>
<td>1,4/1,2- Benzenedimethanol (75% / 25%)</td>
<td>15.3±0.5</td>
<td>735±40</td>
<td>1.3±0.1</td>
<td>0.8±0.1</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td>1,4/1,2- Benzenedimethanol (50% / 50%)</td>
<td>8.7±1.3</td>
<td>935±25</td>
<td>1.0±0.2</td>
<td>0.5±0.1</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>1,4/1,2- Benzenedimethanol (25% / 75%)</td>
<td>11.0±2.9</td>
<td>470±35</td>
<td>1.6±0.1</td>
<td>1.0±0.1</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>1,4/1,2- Benzenedimethanol (10% / 90%)</td>
<td>10.7±2.4</td>
<td>545±20</td>
<td>1.1±0.1</td>
<td>0.7±0.1</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td>1,2-Benzenedimethanol (100%)</td>
<td>1.9±0.2</td>
<td>740±45</td>
<td>1.7±0.1</td>
<td>1.5±0.1</td>
<td>0.7±0.1</td>
</tr>
</tbody>
</table>

Table 9.4. Tensile testing results of the benzenedimethanol chain-extended polyurethanes.
suggested that the para-substitution of the hydroxyl functional groups in the 1,4-benzenedimethanol isomer resulted in the formation of linear hard segment structures, with the ability to interact regularly and with high levels of cohesion. The value of elongation at break of the 100% 1,4-benzenedimethanol chain-extended elastomer was observed to be significantly greater than that containing the 90%/10% 1,4/-1,2-benzenedimethanol composition. The reduced value for that containing the 90%/10% 1,4/-1,2-benzenedimethanol composition was probably attributable to the quantity of 1,2-benzenedimethanol present in this system. The inclusion of polymer chains with such a non-linear conformation may have impaired the ability of the material to undergo elongation.

Values of ultimate tensile strength and 100%, 200% and 300% moduli decreased progressively, and elongation at break increased progressively, as the chain extender composition was changed to the 75%/25% 1,4/-1,2-benzenedimethanol and the
50%/50% 1,4-/1,2-benzenedimethanol compositions. These results were consistent with the results of the other characterisation techniques and could most likely be accounted for by the increasing presence of a second chain extender structure in the system. This could lead to a progressive reduction in the levels of structural coincidence between the hard segment structures and, therefore, cause a reduction in the extent to which the hard segments were able to participate in cohesive inter-hard segment interactions. The consequence would be a decreasing tendency to phase separate and to form a reinforcing hard/soft segment domain morphology.

The material chain-extended with the 50%/50% 1,4-/1,2-benzenedimethanol composition possessed the greatest value of elongation at break and the lowest values of 100%, 200% and 300% moduli of the benzenedimethanol chain-extended elastomers. This implied that this elastomer possessed the least phase-separated, least reinforcing hard/soft segment domain morphology of the benzenedimethanol chain-extended polyurethanes. The presence of such a morphology was indicated by the results of the other characterisation experiments and provided further evidence that the presence of equal proportions of two different chain extender structures may lead to severely compromised inter-hard segment interactions. Despite these results this elastomer did not display the least value of ultimate tensile strength of the benzenedimethanol chain-extended materials. This could probably be ascribed to the occurrence of strain hardening at higher elongations. This was evident from the plots of stress vs strain for the benzenedimethanol chain-extended materials.

Despite possessing similar values of ultimate tensile strength, values of 100%, 200% and 300% modulus of the 25%/75% 1,4-/1,2-benzenedimethanol chain-extended polyurethane were noticeably greater than those of the elastomer prepared with the 10%/90% 1,4-/1,2-benzenedimethanol composition. This may have been due to the presence of a more phase-separated, hard segment domain reinforced morphology in the former material. Such a morphology was indicated by the results of the M-TDSC and the DMTA analyses.

The 100% 1,2-benzenedimethanol chain-extended material generally displayed greater values of 100% and 200% moduli than the rest of the benzenedimethanol chain-extended polyurethanes, with the exception of those containing at least 90% of the
1,4-benzenedimethanol isomer in their chain extender composition. This was observed despite the fact that the 100% 1,2-benzenedimethanol chain-extended elastomer possessed the least value of ultimate tensile strength of all of the benzenedimethanol chain-extended materials. The relatively high values of moduli could most likely be accounted for by the fact that this material possessed a quite highly phase-separated and well defined hard/soft segment domain morphology. The presence of this morphology was also implied by the results of the DSC, DMTA and WAXS analyses, and could have been facilitated by the regular inter-hard segment interactions which should arise from the presence of a single chain extender structure. Such a morphology would, therefore, be able to impart substantial reinforcement to the material. However, the levels of cohesive interaction between hard segments within the hard segment domains were probably relatively low in comparison to those of the materials containing the greatest proportions of the 1,4-benzenedimethanol isomer. This was again suggested by the results of the other characterisation methods employed and was probably due to the non-linear, relatively asymmetrical nature of the 1,2-benzenedimethanol moiety. This, in combination with the fact that such non-linear structures should be less able to undergo strain hardening at higher elongations than more linear ones, would account for the low value of ultimate tensile strength observed for the 1,2-benzenedimethanol chain-extended material. Such an inhibition of strain hardening was evidenced by the stress-strain plot of this elastomer.

9.1.7 Swelling Studies

The results of the swelling studies performed on the benzenedimethanol chain-extended polyurethanes are shown in table 9.5.

The lowest values of \( \sigma_s \) observed for the benzenedimethanol chain-extended elastomers were observed for those incorporating the 100% 1,4-benzenedimethanol and the 90%/10% 1,4/1,2-benzenedimethanol compositions. This was in agreement with the results of the other characterisation techniques and again implied that the para-substituted 1,4-benzenedimethanol isomer resulted in effective inter-hard
segment interactions, and the formation of a highly reinforcing hard/soft segment domain morphology. Such a morphology was able to impart significant resistance to solvent induced swelling. The ability of the 1,4-benzenedimethanol isomer to produce a phase-separated domain morphology was such that the presence of 10% of the 1,2-benzenedimethanol isomer in the chain extender composition, did not appear to disrupt significantly the formation of such a morphology. This again reflected the findings of the other characterisation methods.

<table>
<thead>
<tr>
<th>Chain Extender Composition</th>
<th>Volume Fraction of Toluene in the Swollen Elastomer, $\sigma_s (\pm 0.04)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Benzenedimethanol (100%)</td>
<td>0.50</td>
</tr>
<tr>
<td>1,4/1,2-Benzenedimethanol (90% / 10%)</td>
<td>0.52</td>
</tr>
<tr>
<td>1,4/1,2-Benzenedimethanol (75% / 25%)</td>
<td>0.64</td>
</tr>
<tr>
<td>1,4/1,2-Benzenedimethanol (50% / 50%)</td>
<td>0.74</td>
</tr>
<tr>
<td>1,4/1,2-Benzenedimethanol (75% / 25%)</td>
<td>0.63</td>
</tr>
<tr>
<td>1,4/1,2-Benzenedimethanol (10% / 90%)</td>
<td>0.69</td>
</tr>
<tr>
<td>1,2-Benzenedimethanol (100%)</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 9.5. Results of the swelling studies performed on the benzenedimethanol chain-extended polyurethanes.

Values of $\sigma_s$ increased with increasing levels of 1,2-benzenedimethanol in the chain extender composition to reach a maximum value for the 50%/50% 1,4-/1,2-benzenedimethanol chain-extended material. This probably occurred due to the increasingly mixed nature of the composition and the fact that this reduced the levels of hard segment structural regularity and the tendency for the formation of a phase-separated, physically crosslinked hard/soft segment domain morphology. Of the polyurethanes containing between 75% and 100% of the 1,2-
benzenedimethanol isomer in their chain extender composition, that chain-extended with the 100% 1,2-benzenedimethanol composition displayed the lowest value of $\sigma_3$. This indicated the presence of a relatively highly phase-separated domain morphology. Again, this could probably be ascribed to the presence of a single chain extender structure and the formation of a quite well phase-separated domain morphology, with reasonable ability to resist solvent induced swelling.

It was observed that the elastomer chain extended with the 25%/75% 1,4-/1,2-benzenedimethanol chain extender composition possessed a reduced value of $\sigma_3$ in comparison to that containing the 10%/90% 1,4-/1,2-benzenedimethanol composition. This implied that the former possessed a morphology which was more able to resist swelling due to solvent ingress. This was consistent with the results of the other characterisation techniques and may have been possible if the 1,2-benzenedimethanol-containing hard segments in this material underwent aggregation, and if the proportion of remaining 1,4-benzenedimethanol-containing hard segments was sufficient to cause some aggregation of these structures. This could have resulted in a more physically crosslinked, more reinforcing hard/soft segment domain morphology in this material.

### 9.1.8 General Observations

The polyurethanes chain-extended with the 100% 1,4-benzenedimethanol and the 90%/10%, 1,4-/1,2-benzenedimethanol compositions appeared opaque and white to the naked eye. These observations were indicative of the presence of well phase-separated hard/soft segment domain morphologies and were thus consistent with the results of the other characterisation methods used. The opacity could be explained as a consequence of the different densities and refractive indices of the two types of domain present. This would then result in the scattering of incident radiation with visible wavelengths.\(^{(182)}\)

The elastomer containing the 75%/25%, 1,4-/1,2-benzenedimethanol chain extender composition appeared translucent. This indicated the presence of a less perfectly formed, less discrete dual phase domain morphology than the materials containing greater proportions of the 1,4-benzenedimethanol isomer.
All other materials chain-extended with benzenedimethanol compositions appeared colourless and transparent. This indicated that these materials either possessed no hard/soft segment domain morphologies or morphologies containing domains with dimensions substantially less than that of the wavelength of light.

### 9.2 Conclusions

Variations in the isomeric composition of benzenedimethanol chain extenders were found to have a significant effect on the morphologies and properties of the resulting polyurethane elastomers.

It was found that the benzenedimethanol chain extended polyurethanes chain-extended with the 100% 1,4-benzenedimethanol and 90%/10% 1,4-/1,2-benzenedimethanol compositions appeared to possess the most phase-separated hard/soft segment domain morphologies. This was probably due to the presence of high levels of the 1,4-benzenedimethanol isomer in these materials and the fact that the linear, highly symmetrical structure of this compound probably promoted the occurrence of particularly regular and cohesive inter-hard segment interactions. Consequently, the level of thermodynamic incompatibility between hard and soft segment structures would be relatively high and the driving force for phase separation great.

The elastomers incorporating the 75%/25%, 1,4-/1,2-, the 25%/75%, 1,4-/1,2- and the 100% 1,2-benzenedimethanol chain extender compositions were observed to possess somewhat reduced levels of phase separation. In the case of the 100% 1,2-benzenedimethanol chain-extended material, this was most likely a consequence of the fact that chain extension was being performed with a less symmetrical, non-linear moiety which would result in less effective inter-hard segment interactions. For the 75%/25%, and the 25%/75%, 1,4-/1,2-benzenedimethanol chain-extended materials the mixed nature of the chain extender compositions probably resulted in less effective inter-hard segment interactions. These structural factors would, therefore, produce reduced thermodynamic driving forces for phase separation to occur. However, these polyurethanes did possess quite well phase-separated domain morphologies. In the
case of the 75%/25% 1,4-/1,2-benzenedimethanol chain extended elastomer this was probably due to the relatively high proportion of 1,4-benzenedimethanol present in the composition. This should facilitate quite effective inter-hard segmental interactions and lead to significant hard/soft segment thermodynamic incompatibility. For the 25%/75%, 1,4-/1,2-benzenedimethanol chain-extended elastomer this morphology may have been the result of segregation of the predominant 1,2-benzenedimethanol-containing hard segment structures, thereby allowing phase separation of the remaining 1,4-benzenedimethanol-containing hard segments. The domain morphology of the 100% 1,2-benzenedimethanol chain-extended polyurethane was most likely due to the fact that chain extension was being performed with a single chain extender structure. This would tend to lead to relatively high levels of hard segment structural coincidence, inter-hard segmental interaction and phase separation. The material chain-extended with the 10%/90% 1,4-/1,2-benzenedimethanol composition was found to possess a poorly phase-separated hard/soft segment domain morphology. This was probably a consequence of the fact that this material both contained a mixed chain extender composition and also a high proportion of the 1,2-benzenedimethanol isomer. Such a combination could have combined to reduce the levels of structural regularity amongst the hard segment structures and, therefore, to impair the ability of effective inter-hard segment interactions to occur. The elastomer chain extended with the 50%/50% 1,4-/1,2-benzenedimethanol chain extender composition, was found to possess the least phase-separated, least well defined hard/soft segment domain morphology of the benzenedimethanol chain-extended polyurethanes. This was most likely due to the presence of equal proportions of two benzenedimethanol isomers, which would tend to reduce severely the ability of effective inter-hard segment interactions and phase separation to occur. It was observed that polyurethanes exhibiting the most phase-separated domain morphologies displayed inter-urethane hydrogen bonding interactions with similar or reduced strengths to elastomers with significantly less phase-separated morphologies. It could be inferred from this that the extent of phase separation achieved was determined by the general ability of the hard segment structures to interact, rather than to participate in inter-urethane hydrogen bonding interactions specifically.
Chapter 10

General Conclusions and Recommendations
10.1 General Conclusions

Variations in the chemical structure of the chain extender compounds employed in the synthesis of thermoplastic polyurethane/polyurethaneurea elastomers were found to profoundly influence the morphologies and properties of these materials. As a result of the investigations performed on the various groups of chain-extended elastomers, it was generally inferred that the morphologies and properties of these materials were predominantly determined by the presence of effective/cohesive interactions between hard segments and, therefore, the degree of hard/soft segment thermodynamic incompatibility. It was found that the general occurrence of effective inter-hard segment interactions was of importance, rather than that of inter-hard segment hydrogen bonding interactions specifically. It was also apparent that the symmetry and structural regularity of the hard segment structures significantly affected the ability of such interactions and phase separation to occur.

In the case of the C₄ α,ω-diol chain-extended polyurethanes it was observed that phase separation and domain formation tended to be increased in the case of chain extension with the most linear and structurally regular diols. It was also found that two-shot reaction processes and increased cure temperatures favoured more perfectly ordered domain structures.

Polyurethaneureas synthesised from hydroxyamine chain extenders were observed to possess more phase separated hard/soft segment domain morphologies than polyurethanes chain-extended with the equivalent diols.

For aromatic diamine chain-extended elastomers, the presence of polar link groups and link groups that were thermodynamically incompatible with the soft segments were discovered to result in enhanced phase separation.

The tendency for phase separation and domain formation to occur in 2,4-pentanediol
chain-extended polyurethanes was progressively reduced as the number of enantiomers/stereoisomers involved was increased from one to three.

In the case of chain extension with isomers of benzenedimethanol it was found that increased linearity of the isomer resulted in increased levels of phase separation. It was also noted that the use of mixed isomers caused reduced phase separation/domain formation.

Endothermic features observed at relatively low temperatures in the DSC results of a number of elastomers and attributed to relatively imperfectly ordered hard segment domain structures were coincident with a scattering feature in the results of the WAXS analyses. This indicated that such features were due to morphological structures which displayed periodicity on a scale of approximately 0.7-0.9 nm.

10.2 Recommendations for Further Study

It would be of interest to synthesise the C₄ α,ω-diol chain-extended polyurethanes over a broader range of cure temperatures. This may facilitate the determination of optimum cure temperatures in terms of the development of specific properties. An analysis of the effects of post-cure annealing treatments on the morphology and properties of these materials would also be valuable for similar reasons.

An additional processing variable which could be explored would be the effect of synthesis via a quasi-prepolymer method. This would enable a comparison of properties resulting from this technique with those from the one- and two-shot processes.

An investigation of the effect of chain extension with secondary amine-functionalised hydroxyamine compounds would also be of interest in order to draw comparisons with the equivalent primary diamine-functionalised compounds. The former may display processing advantages due to the reduced reactivity usually evident for secondary amines. In addition, the synthesis of materials chain-extended with the equivalent
primary and secondary diamine compounds could be performed for further comparison.

Additional characterisation techniques which could be employed to provide further information on the morphologies and properties of the materials synthesised include transmission electron microscopy (TEM), atomic force microscopy (AFM), solid-state NMR spectroscopy and micro-thermal analysis (μ-TA). Techniques such as FTIR spectroscopy as a function of temperature/strain and also simultaneous SAXS/DSC could be used to provide information on the behaviour of the materials and their morphologies when subjected to thermal and mechanical stresses.

It would also be of interest to perform other mechanical tests on the elastomers. These could include measurements of hardness, abrasion resistance and tear resistance.
References

Appendix I

Plot of percentage free isocyanate vs time for the prepolymer synthesis reaction.

The isocyanate content appeared to be constant after a period of approximately fifty minutes.
Appendix II

(a) Solubility parameters of solvents used in the swelling experiments performed on the elastomers.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility Parameter, $\delta$ / (J cm$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>14.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>16.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.2</td>
</tr>
<tr>
<td>Butan-2-one</td>
<td>19.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.4</td>
</tr>
<tr>
<td>Butan-2-ol</td>
<td>22.0</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>23.4</td>
</tr>
</tbody>
</table>

(b) Plot of degree of swelling vs solvent solubility parameter for the 1,4-butanediol chain-extended polyurethane processed via the two-shot, 60°C cure reaction procedure.
Appendix III

An example of the DSC data used to analyse the reaction kinetics of the C4 α,ω-diol chain-extended polyurethanes. The data shown was obtained for the trans-2,3-dibromo-but-ene-1,4-diol chain-extended polyurethane.