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INFLUENCE OF CHAIN EXTENSION AGENTS

ON THE PROPERTIES OF POLYETHER BASED

URETHANE ELASTOMERS AT ELEVATED TEMPERATURES

by

DAVID CHARLES HARGET, B.A., M.Sc.

A Doctoral Thesis submitted in partial fulfilment of
the requirements for the award of Doctor of Philosophy
of the Loughborough University of Technology,
September 1977.

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Institute of Polymer Technology

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SUMMARY

Previous work has shown that whilst the excellent physical and mechanical properties of polyurethane elastomers can be varied by changes in the molecular structure of their constituent units, these advantages are considerably diminished at elevated temperatures. The present work was carried out to investigate the effect of hard segment chemical structure on the properties of a polyether based polyurethane elastomer, particularly at elevated temperature.

Polyurethane elastomers were prepared by chain extension of a poly(oxytetramethylene)glycol/methylene bis(4 cyclohexylamine) prepolymer in N,N'-Dimethyl formamide. Diamines and diols were investigated as chain extension agents, and reactions were followed by an infra-red spectroscopic technique. Solid elastomeric materials were produced by diamine chain extension, whereas diols generally gave very low extents of reaction in solution and failed to yield useful products.

Molecular weight analysis and solubility indicated polyurethanes to be essentially linear and have molecular weights (Mn) in the region of 20,000-30,000. Infra-red analysis showed evidence for hydrogen bonding of hard segment urea and urethane groups. The proportion of hydrogen bonded NH groups was found to be significantly affected by the symmetry of the chain extension agent molecular structure.
Thermal analysis and X-ray scattering data showed support for a phase segregated morphological structure, where hard segment interactions lead to the formation of non-crystalline domains. Symmetry of hard segments was found to largely affect the extent of interaction and hence the thermal stability of resulting domains.

Physical and mechanical properties of polyurethane elastomers were investigated over a broad temperature range. It was generally shown that greater hard segment symmetry and increased hard segment:soft segment ratio have a marked effect in improving properties and leading to retention of properties at elevated temperature. This was explained by the promotion of hard segment domain formation which results in more thermally stable physical 'tie points'.

To evaluate the effects of the chain extension agent structure on polyurethane performance under possible service conditions, Stress Relaxation, Creep and Hysteresis were investigated. More symmetrical chain extension agents were shown to lead to lower stress relaxation and creep and higher hysteresis loss. It was demonstrated that stress relaxation and creep processes were essentially physical and reflected the role of hard segment interaction. Relatively high hysteresis loss in polyurethanes based on symmetrical chain extension agents, was explained in terms of the high net energy absorption required to reorganise well-ordered domain structures.

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CHAPTER 1

POLYURETHANES

Introduction

The term 'Polyurethane' is conveniently used to describe a wide variety of polymeric materials, including foams (flexible and rigid), elastomers, surface coatings and adhesives. During early development of these commercially important polymers, the predominant chemical group present in the chain was the urethane group (A). However, with the rapid expansion of this class of materials over the past 30 years, the polyurethanes now include those polymers which contain a significant number of urethane groups, together with a variety of other structurally important groups, eg. ester, ether and urea groups.

The growing importance of polyurethane materials is reflected in the rapid rise in demand. From 1960 to 1972, the total market for polyurethanes increased by 1100%, and has continued to increase since. The largest proportion of the market is represented by foamed materials, although elastomers, particularly castables, are finding an increased demand.
The present chapter deals firstly with the background of polyurethanes, with particular emphasis on the development of elastomeric materials. This is followed by a review of the general chemical principles on which these polymers are based.
1.1 Background

In 1937, Bayer and co-workers at I.G. Farbenindustrie AG (Leverkusen), Germany, began a line of research into materials having properties competitive with those of the polyamides patented by Du Pont in America. The reaction between aliphatic diamines and aliphatic diisocyanates yielded polyureas having no useful properties, being infusible and hydrophilic. However, polyurethanes, prepared by reacting aliphatic glycols with aliphatic diisocyanates were found to show more interesting properties. In 1941, these materials were marketed as Perlon U, a fibre forming polymer, and Igamid U, for plastic moulding uses. Potential was also shown for use as adhesives, foams, lacquers, coatings and synthetic leathers. In 1942, German Patent 728,981 was published, covering the basic principles of the processes involved.

During the late 1930's interest grew in the potential of diisocyanate reactions. Pinten of Dynamit A.G. (Germany) investigated the reactions of polyesters with diisocyanates and this formed the basis of the I Gummi class of materials. Trimethylolpropane was incorporated as cross-linking agent, giving rise to materials having high tensile strength and abrasion resistance, but poor tear strength. By 1952, the 'Vulkollan' class of castable polyurethane elastomers had been established in Germany.
These materials were based on the reaction of a polyester with diisocyanate and the subsequent chain extension with glycol. Two major reviews of the work on the 'Vulkollan' development have appeared in the literature describing the variations of composition possible and the effect on the properties of resulting materials. Elastomers with excellent tear and abrasion resistance together with high tensile strengths and good oil resistance, are typical of the Vulkollans, which form the basis for the majority of present day polyurethane composites. A more detailed review of Polyurethane elastomers is presented in Section 1.2. As well as solid elastomeric compositions, polyurethanes have been widely developed to include foams (flexible, semi-rigid and rigid), surface coatings, adhesives and textiles.

1.2 Polyurethane Elastomers

As outlined in Section 1.1, the establishment of the 'Vulkollan' class of castable polyurethane elastomers in Germany in 1952, has since led to widespread development of a large variety of closely related materials. These fall into three main categories:

1. Castable Polyurethanes
2. Thermoplastic Polyurethanes
3. Millable Polyurethanes

A survey of these principal types is given here, together with a brief discussion of various other commercial polyurethane elastomer systems.
1. **Castable Polyurethane Elastomers**

All castable polyurethane elastomers are based on the same chemical principles which were used in the original 'Vulkollan' materials,\(^4\),\(^5\),\(^6\) mentioned above. The systems comprise three major ingredients:

a) A long chain polyol, usually a polyester or a polyether
b) A diisocyanate
c) A chain extension agent, usually a diamine or diol of low molecular weight.

Reaction of an excess of diisocyanate with the long chain polyol produces a prepolymer, which on further reaction (of free isocyanate in the prepolymer) with chain extension agent yields the final elastomeric material. The chemistry of these systems is dealt with more fully in Section 1.3. By variation of the three major ingredients and their molecular ratios, polyurethane elastomers are available covering a very wide range of physical properties. Introduction of crosslinking also provides further control over structure and properties.

Commercially available cast polyurethane systems fall into three groups:

1. Stable Prepolymer
2. Unstable Prepolymer
3. One Shot
Stable prepolymer systems form by far the largest proportion of the cast polyurethane elastomer market. In 1958, details were published by Du Pont in America of the Adiprene L liquid castable polyurethane system. During the years following, the Adiprene system was greatly developed and now covers a wide range of elastomers of varying physical properties. Although many other commercial systems of the stable prepolymer type are currently available, eg. Formrez (Witco), Multrathane (Mobay) and Neothane (Goodyear), the Adiprene L system is typical of the technology involved.

The Adiprene L system is based on a room temperature stable prepolymer made by reaction of a polyether polyol, i.e. poly(oxytetramethylene)glycol (POTMG), with a diisocyanate (toluene diisocyanate). The prepolymer is in the form of a viscous liquid, which requires degassing before the addition of chain extension agent and subsequent casting in a mould prior to cure. Chain extension is normally carried out using a diamine, MOCA (4,4'-methylene-bis(o-chloroaniline), which provides a practical reactivity and good final physical properties. Diols are often used in place of diamines, and these generally give rise to much softer elastomers having rather poorer physical properties. The most common example is 1,4-Butane Diol, which is often used together with a small proportion of trimethylol propane to provide limited crosslinking.
The manufacture of a solid polyurethane elastomer from a typical Adiprene system as outlined above, falls into five main steps. Firstly, the Adiprene prepolymer and the chain extender are heated to the required mixing temperature. The Adiprene is degassed, in order to minimise bubbles and voids in the final elastomer, and the chain extender is then blended in. The resulting mixture is dispensed into heated moulds where curing of the product takes place.

The production of polyurethane elastomer components by this general scheme is usually carried out using fully automated metering and dispensing equipment, in which the prepolymer is degassed, mixed with chain extension agent and dispensed into heated moulds.

The Vulkollan system of polyurethane elastomers is typical of the unstable prepolymer type. This system was developed in the early 1950's and has remained basically unchanged since. It differs from the stable prepolymer (Adiprene) type, in that the fabricator is supplied with a polyol (a polyester) and diisocyanate which must be reacted to form the prepolymer before chain extension and casting. The extra step in the process is necessary because the diisocyanate used is 1,5-Naphthalene Diisocyanate which forms an unstable prepolymer requiring 'in situ chain extension' to avoid further unwanted isocyanate reaction.
A typical Vulkollan system would be based on Desmophen 2000 (linear polyethyleneadipate; Molecular weight ~2000), Desmodur 15 (1,5-Naphthalene diisocyanate) and chain extension agent (normally 1,4-Butane Diol). In order to avoid any reaction of moisture with the diisocyanate, the Desmophen 2000 must be carefully dried. On a large scale, spray drying techniques are widely used for this purpose. Desmodur 15 is then added to the dry Desmophen 2000 at approximately 130°C and the exothermic reaction is taken to completion under vacuum (~10 minutes). Diols, eg. 1,4-Butane Diol, are normally used as chain extension agents and these are mixed with the prepared prepolymer and dispensed automatically into hot moulds (~110°C). The product is removed from the mould as soon as it has solidified and is finally hot air oven cured for approximately 24 hours at 110°C, to develop the final properties.

An alternative method of polyurethane elastomer manufacture is the 'One shot' system. Although not as important commercially as the prepolymer techniques described, it has been considerably developed as a possible method of overcoming the use of relatively unstable prepolymers and the need for accurate temperature control. A typical system is that of the Wyandotte Chemical Corpn., in which a blend of poly(oxypropylene)glycol and diamine is carefully dried, catalyst added and then mixed with toluene diisocyanate at room temperature.
The mixture is then poured into moulds heated to 100°C, and the product is finally cured in a hot air oven to give optimum properties. The major problem associated with this type of system is the need for the use of a catalyst to balance the fast amine-isocyanate reaction with the relatively slow hydroxyl-isocyanate reaction. This has been largely overcome by using diols\textsuperscript{10} as chain extension agents.

By variation of the three major ingredients, cast elastomers manufactured by the techniques discussed cover a wide range of physical properties. They vary from very soft gelatine like materials, to hard products of outstanding strength. They also exhibit excellent oil and abrasion resistance. Because of these outstanding properties, cast elastomers have found successful applications as solid tyres for industrial vehicles, rollers, pulleys, bearings, gear wheels etc.

2. **Thermoplastic Polyurethane Elastomers**

Thermoplastic polyurethane elastomers are a relatively recent development in the field of polyurethane technology. They fall into two main classes:

a) Linear polymers (no covalent crosslinks) soluble in appropriate organic solvents.

b) Lightly crosslinked polymers; virtually insoluble.
Both types are normally prepared by the prepolymer route as in the case of cast polyurethane elastomer systems. Reaction of a linear hydroxy terminated polyether or polyester with excess diisocyanate at approximately 100°C gives rise to the prepolymer system consisting of excess uncombined diisocyanate together with isocyanate terminated polymeric diol. Further reaction with chain extender in equivalent molar properties to the free isocyanate groups available, yields a linear polymer having flexible polyether or polyester chains linked to rigid high melting point polyurethane blocks.¹¹

Use of a slight molar deficiency of chain extension agent, gives rise to an overall excess of isocyanate groups which can take part in branching reactions and hence introduce a small amount of crosslinking into the system.

Commercial thermoplastic polyurethane elastomer systems of the linear soluble type, include 'Estane' (B.F.Goodrich) which is based on a polyester/4,4'-diphenylmethane diisocyanate prepolymer, chain extended with 1,4-Butane Diol. Mechanical properties are very similar to the cast polyurethanes, although set and creep behaviour are generally inferior. Polymers such as 'Estane' are usually sold in granular form, which can then be processed by conventional thermoplastic fabrication techniques such as injection moulding, extrusion, blow moulding, vacuum forming etc.
They can also be used as surface coatings and adhesives since they are completely soluble in several organic solvents.

Thermoplastic polyurethanes of the lightly cross-linked type, also possess properties similar to the cast polyurethane systems, and have improved set and creep behaviour over the linear polymers, due to the introduction of a small amount of crosslinking. It is believed that allophanate crosslinks (formed by isocyanate-urethane branching reactions) present are thermolabile, allowing normal thermoplastic fabrication techniques at elevated temperatures. On cooling, the crosslinks are reformed. After fabrication, these thermoplastic elastomers usually require heating at approximately 110°C for 10 hours, to attain their ultimate properties. Commercial systems of this type include 'Texin' (Mobay Chemical Co), 'Desmopan' (Bayer) and 'Roylar' (U.S. Rubber Co). These systems normally incorporate a ratio of isocyanate:hydroxyl of between 1.0 and 1.1, to achieve optimum properties.

Thermoplastic polyurethanes have found widespread application owing to their excellent mechanical strength, abrasion, oil resistance and ease of processing. Injection moulded articles include seals, gaskets, bearings and shoe heels. In solution, the linear polyurethanes are used as fabric and leather coatings and as adhesives.
3. **Millable Polyurethanes**

The third important class of polyurethane elastomer systems is composed of the storage-stable millable gums. These are essentially based on the prepolymer concept described for cast and thermoplastic elastomers. However, in this case, a slight excess of hydroxyl groups is employed, giving rise to a stable prepolymer in which all the isocyanate groups are fully reacted. Prepolymer of this nature are generally gums having molecular weights around 20,000 which can be handled using conventional rubber processing equipment. In order to build up a network structure similar to the cast elastomers, crosslinking reactions must be introduced. This is generally carried out either by the addition of more diisocyanate, or by the use of conventional rubber curing agents, eg. peroxides or sulphur based. Addition of crosslinking agent to the prepolymer gum on the mill and subsequent compression moulding, allows the production of components not easily made by the casting method.

A typical commercial system of the isocyanate cured millable type is Urepan 600 (Bayer) based on a polyester/Toluene diisocyanate prepolymer. The preferred diisocyanate is dimerised 2,4-toluene diisocyanate (Desmodur TT), which because of its relatively high melting point (145°C), can be mixed on the mill with little likelihood of reaction occurring at this stage.
If harder products of high modulus are required, conventional fillers such as carbon black or silica can also be added at the milling stage. The same effect can also be brought about by incorporation of an aromatic diol in equivalent ratio to the excess diisocyanate added. This gives rise to rigid polyurethane segments throughout the polymer.

For moulding articles, conventional presses and moulds are used, the normal curing cycle being about 130°C for 10 to 15 minutes. Compounded Urepan 600 can also be extruded, although cure must be carried out using hot compressed air and not steam which would react with unreacted isocyanate.

Elastomers of the Urepan 600 type have the high level of mechanical properties characteristic of polyurethane materials, though these are slightly inferior to the cast type.

A typical peroxide cured millable system would be based on a polyester/4,4'-diphenylmethane diisocyanate prepolymer cured with dicumyl peroxide. In a neutral or alkali media, thermal decomposition of dicumyl peroxide gives rise to cumyloxy radicals which abstract hydrogen atoms from the polymer chain allowing formation of a crosslinked network. As decomposition of dicumyl peroxide into free radicals is proportional to temperature, processing at high temperature and short cure time cycles is possible.
Isocyanate cured millable elastomers are very similar in structure to the cast elastomer systems, where long polar chains are held loosely together by allophonate and biuret crosslinks. However, the peroxide cured types are crosslinked by short, strong covalent carbon-carbon chemical bonds which tend to break down the secondary attractive forces predominant in the cast systems. It is due to this basic structural difference that the peroxide cured elastomers have superior set properties to the isocyanate cured and cast systems, but are much softer materials with a lower level of physical properties. In covalently crosslinked urethane elastomers, use of reinforcing fillers is therefore necessary to obtain a useful level of properties.

Sulphur cure of polyurethane millable gums, requires points of unsaturation in the prepolymer system, to enable the crosslinking reaction to take place. Unsaturation is incorporated in the prepolymer by substituting some of the polyol by an unsaturated diol such as glyceryl monoalkylether. As in the case of the peroxide cured elastomer, formation of relatively strong chemical crosslinks reduces the strength of the polymer and the use of reinforcing fillers becomes necessary to give optimum properties. However, the sulphur cured materials do generally give higher tensile and tear properties than the corresponding peroxide cured gums, although they are inferior in compression set and hot air ageing.
Miscellaneous Commercial Polyurethane Elastomer Systems

**Spandex Fibres**

A Spandex fibre is defined as "A manufactured fibre in which the fibre-forming substance is a long chain synthetic polymer comprised of at least 85% of a segmented polyurethane".\(^\text{12}\) Like other polyurethane block copolymers described earlier, these materials are based on polymers having alternating flexible and rigid segments. The flexible segments are usually polyethers or polyesters and they form 60-90% by weight of the final polymer. The rigid segments are composed of the urethane or urea groups produced in the diisocyanate chain extension reactions.

Most commercial systems of this type are based on toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) and chain extension is normally by diamines or diols. Spandex fibres are prepared by the prepolymer technique where the isocyanate terminated polyester or polyether is reacted with diol or diamine chain extender. The three main methods of manufacture are solution spinning, reaction spinning and melt spinning, the choice depending on the reactivity of the chain extender and the final properties desired.

Spandex fibres have replaced natural rubber thread in many applications, particularly as foundation garments. They also have the advantage of being available in finer deniers and are therefore ideal for use in lightweight fabrics.
Spandex fibres generally have higher modulus, tensile strength and abrasion resistance than natural rubber thread as well as improved dyeability and resistance to weathering. However, natural rubber thread shows better elastic recovery and lower hysteresis.

Cellular Polyurethane Elastomers

By incorporation of water or other chemical blowing agents in a polyurethane elastomer system, a microcellular structure can be produced having a specific gravity in the range 0.35 to 0.65. Materials of this type, being softer and more flexible than the solid elastomer, find wide applications in shoe sooling.

Poromeric Polyurethanes

Poromeric polyurethanes are based on polyurethane elastomer systems having a microcellular structure which is permeable to water vapour but not to liquid water. Materials of this type can therefore 'breathe' like leather and find useful applications in the shoe and furnishing industries. Some commercial poromerics contain randomly dispersed fibres (eg. Corfam) whereas others have a microporous unreinforced structure (eg. Porvair).
1.3 Chemistry of the Polyurethanes

A variety of reactions have been used to produce urethanes, such as the reaction of an amine with a chloroformate ester:

\[ R'NH_2 + Cl-C-OR \xrightarrow{\text{H}_2\text{O}} R'N-C-OR + HCl \]

By far the most widely used route to urethanes is through the reactivity of the isocyanate group.

The present section deals firstly with the basic chemistry of isocyanates, and this is followed by a review of the chemistry of polyurethane elastomer systems.

1.3.1 Isocyanate Chemistry

1.3.1.1 Reactions of the Isocyanate Group

Reactions of the isocyanate group fall into three main categories:

a) Intermolecular hydrogen transfer addition
b) Self Addition
c) Miscellaneous Reactions.

In this section, reactions of each type are outlined, with particular emphasis on those reactions relevant to polyurethane chemistry and technology.
a) Intermolecular Hydrogen Transfer Reactions

The isocyanate group is highly reactive towards compounds containing an active hydrogen atom (i.e. hydrogen atom replaceable by sodium), and this reactivity forms the whole basis of polyurethane chemistry. Reactions of this type have been extensively reviewed, attention here being focussed on the four most important primary reactions:

1) Reaction with Alcohols:

\[
R'OH + RNCO \rightarrow R-N-C-O-R' \\
\text{Urethane}
\]

2) Reaction with Amines:

\[
R'NH_2 + RNCO \rightarrow R-N-C-N-R' \\
\text{Urea}
\]

3) Reaction with Carboxylic Acids:

\[
R'C\text{OOH} + RNCO \rightarrow R-N-C-O-C-R' \\
\text{Mixed Anhydride}
\]

In the case of strong acids, the mixed anhydride breaks down to the amide with loss of carbon dioxide:

\[
R-N-C-O-C-R' \rightarrow R-N-C-R' + \text{CO}_2 \\
\text{Amide}
\]
Weaker acids give a mixture of anhydride and urea:

\[
2R-N-C-O-C-R' \rightarrow \left[ \begin{array}{c}
R-N-C-O-C-N-R \\
H O O
\end{array} \right] + R'-C-O-C-R' \rightarrow \left[ \begin{array}{c}
R-N-C-N-R \\
H O H
\end{array} \right] + \text{Anhydride} \\
\text{Urea}
\]

4) Reaction with water:

\[
H_2O + RNCO \rightarrow \left[ \begin{array}{c}
R-N-C-OH \\
H O
\end{array} \right] \rightarrow \text{Unstable carbamic acid} \\
\rightarrow \text{RNH}_2 + CO_2 \\
\text{Amine}
\]

The amine produced, then reacts with more isocyanate:

\[
\text{RNH}_2 + RNCO \rightarrow \left[ \begin{array}{c}
R-N-C-N-R \\
H O H
\end{array} \right] \rightarrow \text{Urea}
\]

Primary isocyanate reaction products which still contain active hydrogen atoms, can react further with isocyanates as follows:

i) Urethane:

\[
R-N-C-OR' + RNCO \rightarrow \left[ \begin{array}{c}
R-N-C-OR' \\
H O
\end{array} \right] \rightarrow \text{Allophonate}
\]
ii) Urea:

\[ R-N-C-N-R' + RNCO \rightarrow R-N-C-N-R' \]

Biuret

iii) Amide:

\[ R-N-C-R' + RNCO \rightarrow R-N-C-R' \]

Acyl Urea

**Mechanism and Reactivity**

Reactivity of the isocyanate group towards compounds containing an active hydrogen atom is most easily explained by considering the possible resonance structures of the isocyanate group:

\[ R-N=C=O \overset{\ddots}{\leftrightarrow} R-N=C=O; \overset{\ddots}{\leftrightarrow} R-N=C=O; \]

Reaction proceeds by attack of a nucleophilic centre upon the electrophilic carbon atom:

\[ R-N=C=O + HX \overset{\ddots}{\leftrightarrow} R-N=C=O \rightarrow R-N-C-X \]

The general reaction scheme is well illustrated by the isocyanate-alcohol reaction. Baker (et al)\textsuperscript{14,15,16} proposed the following reaction mechanism:
Reactions of this type are primarily in the nature of a nucleophilic attack (i.e., electron donation by active hydrogen compound), as opposed to a hydrogen atom donation. This is shown by the effect of substituent groups on the isocyanate and the active hydrogen compound. Electronegative groups on the isocyanate increase the partial positive charge on the carbon atom and lead to faster reaction with nucleophilic compounds. Electropositive groups on the isocyanate give the opposite effect. The following reactivity series illustrates the point.

- t. butyl < cyclohexyl < n-alkyl < benzyl < phenyl < p-nitrophenyl.

In the case of the active hydrogen compounds, electronegative groups decrease the basicity of the nucleophilic centre hence decreasing the reaction rate with isocyanate. If reaction was essentially hydrogen donation, reaction rate would be increased by electronegative substituents on the active hydrogen compound due to increased acidity of the active hydrogen. However, this is not found experimentally.
As well as the electronic effects of substituents on reactivity, steric factors also play an important role. For example, aromatic isocyanates having bulky groups in the ortho position are less reactive than the corresponding unhindered isocyanates. The effectiveness of catalysis can also be affected by the presence of bulky groups shielding the reactive partial positive carbon of the isocyanate.

 Reactivity of the isocyanate group can also be affected by the solvent system used. Solvents which complex with the active hydrogen compound generally slow down the rate of reaction and under certain conditions reaction between isocyanate and solvent may occur.

 The relative reactivity of active hydrogen compounds towards isocyanates generally follows the order\textsuperscript{13}:

 Aliphatic amine > aromatic amine > primary hydroxyl > water > secondary hydroxyl > tertiary hydroxyl > phenolic hydroxyl > carboxylic acid > urea > amide > urethane.

 However, reactivity is very dependent on those factors outlined above, particularly the profound influence of catalysts.

b) **Self Addition Reactions of Isocyanates**

 Self addition reaction of isocyanates can occur under certain conditions. The four most important reactions of this type are as follows:
i) Dimerisation:

\[
2 \text{RNCO} \xrightarrow{\text{pyridine}} \text{R-N} \text{N-R}
\]

Uretidione ring

ii) Trimerisation:

\[
3 \text{RNCO} \xrightarrow{\text{strong base}} \text{R} \text{N-N-R}
\]

Isocyanurate ring

iii) Linear polymerisation:

\[
n \text{RNCO} \xrightarrow{\text{Na, Low Temperature}} \text{R-N-C=NR}_n
\]

A nylon 1

iv) Carbodiimide Formation:

\[
2 \text{RNCO} \xrightarrow{\text{High Temp, (Phospholine Oxide catalyst)}} \text{RN-C=NR} + \text{CO}_2\text{carbodiimide}
\]

Reactions of the third type are of least importance in polyurethane chemistry and require strict experimental conditions. Dimerisation reactions (i) take place only with aromatic isocyanates and the uretidione rings formed dissociate back to isocyanates between 130° and 200°C.
Isocyanurate ring formation (reaction ii) is the most common self addition reaction in practical polyurethane systems, and trimers of this type based on aromatic isocyanates do not begin to decompose until well above 300°C. Carbodiimides (reaction iv) are used as hydrolysis inhibitors in certain polyester urethane systems.

c) Miscellaneous Reactions

Although the reactions covered above are the most important reactions in practical polyurethane systems, the isocyanate group can take part in many other types of reaction.¹³ These include the following:

i) Reaction with S-H group:

\[ \text{eg. } 2 \text{RNCO} + H_2S \rightarrow \text{R-N-C-N-R} + \text{COS} \]

\[ \text{H O H} \]

This reaction is analogous to the reaction with water. Reaction with mercaptans yield thiourethanes:

\[ \text{RNCO} + \text{R'SH} \rightarrow \text{R-N-C-SR'} \]

\[ \text{H O} \]

ii) Reaction with Grignard reagents:

\[ \text{RNCO} + \text{R'MgX} \xrightarrow{\text{H2O}} \text{R-N-C-R'} \]

\[ \text{H O} \]

Amide
iii) Reaction with Halogens:

\[
\text{NCO} + \text{Cl}_2 \xrightarrow{25^\circ C} \text{N-C}=\text{O} \xrightarrow{95^\circ C} + \text{HCl}
\]

Chlorinated Carbamoyl Chloride

At higher temperatures, hydrogen chloride is removed:

\[
\begin{align*}
\text{Cl} & \quad \text{C}=\text{O} \\
\text{NH} & \\
\text{Cl} & \quad \text{NCO} \\
\text{Cl} & \quad + \text{HCl}
\end{align*}
\]

1.3.1.2 Catalysis of Isocyanate Reactions

Isocyanate reactions are catalysed by both acids and bases, the latter generally being much more effective. Tertiary amines and organometallic compounds are the most commonly used catalysts to promote hydrogen transfer addition reactions.

Tertiary Amines

Tertiary amines catalyse all isocyanate hydrogen transfer reactions and the efficiency generally increases with increasing base strength. Steric shielding of the amino nitrogen is also important\textsuperscript{15,17} as shown by the following series.\textsuperscript{18}
Amine Catalyst

<table>
<thead>
<tr>
<th>Amine</th>
<th>Structure</th>
<th>pKa</th>
<th>Catalytic Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Diazabicyclo[2.2.2] octane (DABCO)</td>
<td><img src="image" alt="Structure" /></td>
<td>5.4</td>
<td>23.9</td>
</tr>
<tr>
<td>N,N-Diethylcyclohexylamine</td>
<td><img src="image" alt="Structure" /></td>
<td>10.0</td>
<td>0.7</td>
</tr>
<tr>
<td>N-Methylmorpholine</td>
<td><img src="image" alt="Structure" /></td>
<td>7.4</td>
<td>1.0</td>
</tr>
<tr>
<td>N,N,N',N'-Tetramethyl methane (CH₃)₂NCH₂N(CH₃)₂</td>
<td><img src="image" alt="Structure" /></td>
<td>10.6</td>
<td>0.085</td>
</tr>
</tbody>
</table>

The very high catalytic activity of 1,4-Diazabicyclo[2.2.2] octane is associated with the complete lack of steric hindrance afforded by its cage structure.

Organometallic Compounds

Although many metal complexes have a catalytic effect on reactions of the isocyanate group, organotin compounds are usually preferred for use in polyurethane systems. They are extremely effective in promotion of the isocyanate-hydroxyl reaction. Catalysts of this type include stannous octoate, stannous oleate and dibutyltin dilaurate.
The following table illustrates the much higher catalytic activity of tin complexes over tertiary amine catalysts in an isocyanate-hydroxyl reaction. Combinations of the two types of catalyst give even greater activity as shown by (stannous Octoate/DABCO).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conc. (%)</th>
<th>Order of Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>TMBDA</td>
<td>0.1</td>
<td>56</td>
</tr>
<tr>
<td>DABCO</td>
<td>0.1</td>
<td>130</td>
</tr>
<tr>
<td>DBTDL</td>
<td>0.1</td>
<td>210</td>
</tr>
<tr>
<td>SnOct</td>
<td>0.1</td>
<td>540</td>
</tr>
<tr>
<td>DABCO</td>
<td>0.3</td>
<td>330</td>
</tr>
<tr>
<td>SnOct</td>
<td>0.3</td>
<td>3500</td>
</tr>
<tr>
<td>SnOct + DABCO</td>
<td>0.3+0.3</td>
<td>4250</td>
</tr>
</tbody>
</table>

TMBDA: Tetramethylbutanediamine
DABCO: 1,4-Diazabicyclo[2.2.2]octane
DBTDL: Dibutyltin Dilaurate
SnOct: Stannous Octoate

Tin catalysts also catalyse the isocyanate-water reaction, but with less effect than tertiary amines. The mechanism of isocyanate reaction catalysis by tertiary amines is thought to depend on complex formation, both between amine and isocyanate and between amine and hydroxyl component. Catalysis by metals such as tin has been explained by the formation of ternary complexes. Other explanations are based on the formation of bridge complexes between metal-alcohol and metal-isocyanate complexes.
1.3.2 Chemistry of Polyurethane Elastomers

Before reviewing the effect of structure on properties in polyurethane elastomers, it is worthwhile considering the chemical principles of network formation in these materials.

Elastomers with a high level of mechanical properties are based on block copolymer systems having alternating flexible and rigid segments in the polymer chain. The flexible segments are composed of polyols, generally polyester or polyether, while the hard segments are made up of urethane or urea units formed by the reaction of diisocyanates with diols or diamines. Polyurethane elastomers are composed therefore of three basic intermediates:

1) Polyol

Most commercial polyurethane elastomer systems employ aliphatic hydroxyl terminated polyesters or polyethers of molecular weight between 800 and 3000. Polyesters include Poly(ethylene adipate), Poly(tetramethylene adipate) and Polycaprolactone. They are usually prepared by reaction of dibasic acids with excess diols, as in the case of Poly(ethylene adipate):

\[
(n + 1) \text{HO(CH}_2\text{)}_2\text{OH} + n \text{HOOC(CH}_2\text{)}_4\text{COOH} \downarrow \text{H} \left[ \text{O(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_4\text{CO} \right]_n \text{O(CH}_2\text{)}_2\text{OH} + 2n\text{H}_2\text{O}
\]
Ring opening polymerisation of lactones is also a useful synthetic route, eg. Polycaprolactone:

\[
\text{HO-R-OH + 2n } \overset{\text{glycol}}{\longrightarrow} \text{HO} \left\{ (\text{CH}_2)_5\text{COO} \right\}_n \text{R} \left\{ \text{OOC(}\text{CH}_2) \right\}_n\text{OH}
\]

In some cases, copolyesters are employed, eg. the use of Poly(ethylene-co-propylene adipate) to overcome the cold hardening effect in Poly(ethylene adipate) due to crystallisation.

Polyethers commonly used in commercial polyurethane elastomers include Poly(oxytetramethylene) and poly(oxypropylene). Poly(oxypropylene)glycol is prepared by the base catalysed ring opening polymerisation of propylene oxide:

\[
\text{HO-(CH}_2\text{)}_2\text{-OH + 2n CH}_2\text{-CH-CH}_3 \overset{\text{base}}{\longrightarrow} \text{H(OCHCH}_2\text{)}_n\text{O(}\text{CH}_2\text{)}_2\text{O(}\text{CH}_2\text{CHO})_n\text{H}
\]

Poly(oxytetramethylene) glycol is generally prepared by the cationic ring opening of tetrahydrofuran:

\[
\begin{align*}
\text{CH}_2\text{-CH}_2 \\
\text{CH}_2\text{-CH}_2 \\
\overset{\text{O}}{\longrightarrow} \\
\text{H(}\text{O-(CH}_2\text{)}_4\text{)}_n\text{OH}
\end{align*}
\]

2) Diisocyanate

There are several diisocyanates established in polyurethane elastomer systems. The most common are Toluene diisocyanate (TDI), Diphenylmethane diisocyanate (MDI), Naphthalene diisocyanate (NDI) and Hexamethylene diisocyanate (HDI).
The aromatic diisocyanates give polyurethanes which discolour in ultraviolet light and this has led to the development of more light stable diisocyanates, eg. 4,4'-Dicyclohexylmethane diisocyanate \( (H_{12}MDI) \) and isophorone diisocyanate (IPDI).

Diisocyanates are generally made by the phosgenation of the corresponding amines in an inert solvent. Reaction occurs in two stages, firstly at a temperature of 25-100°C:

\[
RNH_2 + COCl_2 \rightarrow RNHCOCl + HCl
\]

Carbamoyl chloride

\[
RNH_2 + HCl \rightarrow RNH_2 HCl
\]

\[
RNH_2 + RNHCOCl \rightarrow RNH_2 HCl + RNCO
\]

Further phosgenation at a temperature around 160°C follows:

\[
RNH_2 HCl + COCl_2 \rightarrow RNCO + 3HCl
\]

Other preparative methods include the Curtius, Hofmann & Lossen rearrangement reactions, but none of these is of any real commercial importance.

3) **Chain Extension Agents**

Chain extension agents are low molecular weight difunctional compounds, usually diols and diamines. By reaction with free isocyanate groups in a prepolymer system they form rigid segments joining together the flexible polyol segments.
The most widely used diol in solid polyurethanes is 1,4-Butane Dial, prepared by hydrogenation of butynediol. Other diols include ethylene diol and hydroquinone diethylol ether.

Diamines include 3,3′-dichloro-4,4′-diamino diphenyl methane (MOCA), 4,4′-diaminodiphenyl methane (MDA) and 3,3′-dichlorobenzidine.

Chemical Network Formation in Elastomeric Polyurethane Block Copolymers

Most solid polyurethane elastomer systems are based on the prepolymer technique as described earlier. Build up of the final polymeric network falls into three stages:

1) **Synthesis of Prepolymer**

Reaction of excess diisocyanate with polyol gives a prepolymer consisting of isocyanate terminated polyether or polyester and unreacted diisocyanate:

\[(m+2n)OCN-R-NCO + nHO-A-OH \rightarrow mOCN-R-N-C-O-A-O-C-N-R-NCO + \text{Prepolymer} + mOCN-R-NCO\]

Where A = Polyester or Polyether.

2) **Chain Extension**

Further reaction of the prepolymer with chain extension agent gives rise to essentially linear block copolymers in which the flexible polyol units (A) are joined through rigid polyurethane (using diol chain extension agents) or polyurea (using diamine chain extension agents) segments:
If all crosslinking reactions are avoided, linear block copolymers result as shown above. Their structure is also well represented:

a) Diol Chain Extension
\[ \text{(PE) URUR'URUR'URUR'(PE)URUR'URUR' URUR'(PE)} \]

b) Diamine Chain Extension
\[ \text{(PE) URUR'R^2URUR'R^2URUR'(PE) URUR'R^2URUR'R^2URUR'(PE)} \]
where PE = Polyester or Polyether
U = Urethane group
U' = Urea group
R = Diisocyanate residue
R' = Diol residue
R² = Diamine residue

3) Crosslinking Reactions

Formation of a crosslinked polyurethane network can be brought about in four ways:

a) Use of excess diisocyanate over chain extension agent allows reaction with urethane and urea groups in the hard segments. Reactions of this type which give allophonate and biuret groups lead to the formation of crosslinks between adjacent polymer chains:

\[ \sim\{(PE)\ \text{URU}'\text{URAR}'\text{URU}(PE)\}\sim \]

Dial Chain Extension
\[ \sim\{PE\} \text{URUR}'\text{URUR}'\text{URU}(PE)\sim \]
\[ R A = \text{Allophonate group} \]
\[ \sim\{PE\} \text{Ura-R}'\text{URUR}'\text{URU}(PE)\sim \]

Diamine Chain Extension
\[ \sim\{PE\} \text{URUR}'\text{URUR}'\text{BRU}(PE)\sim \]
\[ B = \text{Biuret} \]
\[ \sim\{PE\} \text{URUR}'\text{URBR}'\text{URU}(PE)\sim \]

b) Replacement of a small proportion of difunctional chain extension agent by a trifunctional compound, eg. trimethylol propane, allows branching and crosslinking through reaction with diisocyanate.
c) By using a polyol with a functionality greater than 2, a prepolymer of this higher functionality results and forms a crosslinked network during the chain extension step.

d) In the case of the millable type elastomers, crosslinking is brought about by the use of peroxides or sulphur as described earlier. Incorporation of unsaturation in the polyol creates sites for sulphur crosslinks to form.
CHAPTER 2

GENERAL STRUCTURE - PROPERTY RELATIONSHIPS IN SEGMENTED POLYURETHANE ELASTOMERS

Introduction

Since the early work on the Vulkollan type polyurethane elastomers, several notable reviews have been published on the effect of chemical structure on the final properties of such materials.\textsuperscript{13,25-33} As indicated in Chapter 1, variation introduced by altering the chemical structure of the three basic components, can bring about marked changes in physical properties as well as influencing the technology of the system. Relationships between structure and properties in these materials are most correctly interpreted in terms of chemical structure and supramolecular structure.

The present chapter deals firstly with the structure of segmented polyurethane elastomers, and this is followed by a review of the more important structure-property relationships in these systems. The final section outlines the aims of the present work as related to the relationships discussed.

2.1 Structure in Segmented Polyurethane Elastomers

Polyurethane elastomers comprise one of the most complex classes of polymeric materials in terms of structure and related properties.
Most commercial types of polyurethane elastomers derive their high level of physical properties from their segmented polymer structure, combining strength and flexibility. In order to gain a better understanding of the relationships between structure and physical properties, it is necessary to consider the structure in two ways:

a) Chemical composition of segmented polymer chains.
b) Supramolecular structure formed by polymer chain interactions.

Chemical composition greatly influences the supramolecular structure and hence the physical and mechanical properties of the elastomer.

2.1.1 Chemical Structure of Segmented Polyurethane Elastomers

As described in Section 1.3.3, polyurethane elastomers are generally based on a segmented polymer structure, consisting of alternating hard (rigid) and soft (flexible) segments. The hard segment is either a polyurethane formed by the reaction between a diisocyanate and a diol, or a polyurea formed by the reaction between a diamine and a diisocyanate.

Crosslinking can be introduced by various means (Section 1.3.2), the following two methods being the most important:
a) Incorporation of a trifunctional chain extension agent, eg. Trimethylolpropane.
b) Use of a molar deficiency of difunctional chain extension agent relative to the diisocyanate.

Crosslinks formed by method (a) through urethane or urea branch points represent stronger chemical linkages, particularly at higher temperatures, than those crosslinks formed by method (b) where excess isocyanate reacts to give allophonate or biuret branch points.

From this brief description, it can be seen that the chemical structure present in a segmented polyurethane elastomer system can be varied in several distinct ways:

1) Variation of the chemical structure of the soft segment.
2) Variation of the chemical structure of the hard segment.
3) Variation of the relative sizes of the hard and soft segments.
4) Variation of the degree and type of covalent crosslinking.

These factors all influence the formation of a supramolecular structure and the properties of the elastomer as shown in the following sections.
2.1.2 Supramolecular Structure in Segmented Polyurethane Elastomers

In recent years, much work has been carried out to elucidate the extent of microphase separation and the structure of the resulting components, in segmented polyurethane elastomers. It is now generally accepted that the hard segments separate to form discrete domains in a matrix of soft segments. The rigid domains formed, act both as tie down points (being chemically linked to the soft matrix) and as filler particles, reinforcing the soft segment matrix.

Bonart has investigated the structure of segmented polyurethane elastomers using X-ray diffraction techniques. Polyether (poly(oxytetramethylene)) and polyester (a co-polyester) based elastomers incorporating diphenylmethane diisocyanate (MDI) and extended with ethylene diamine or hydrazine, were chosen for investigation. Diffraction patterns obtained and their interpretation in terms of molecular organisation will be dealt with more fully in Chapter 5 of the present work.

However, it is worthwhile describing here the supramolecular model proposed, both for the elastomer in the relaxed state and under varying degrees of extension.

In the relaxed state, spatially separated hard and soft segments exist in the material. The hard segments are held together in discrete domains through the action of van der Waal's forces and hydrogen bonded interactions.
On extension, soft segment polymer chains undergo various extents of stretching and disentanglement causing the rigid domains to lie in a disorientated manner transverse to the direction of stretching. In the case of polyether based elastomers, extension beyond approximately 150% gives rise to marked elongation crystallisation of the soft segments. (Fig. 2.1). Polyester based elastomers showed a lower level of crystalline order, presumably due to the more irregular chemical structure present. As the elastomer is further elongated up to 500% extension, the orientation of soft segments improves only to a small extent, while the hard segments turn themselves with their longitudinal axes into the direction of elongation. This effect is explained in terms of force strands, i.e. maximally loaded chains in the soft segment which oppose any further extension. Further extension therefore requires sliding processes between hard segments to take place resulting in the formation of new force strands. At 500% elongation, this restructuring process is virtually complete. Treatment of the extended sample with warm water (80°C) for 30 minutes, accelerates the process and also gives rise to an even distribution of forces amongst soft segment chains, resulting in a loss of elongation crystallisation in this region. (Fig. 2.2). Hard segments are now fully orientated in the direction of elongation, and show relatively intense reflexes in the X-ray photographs. On relaxation of the material, soft segments disorientate almost completely, while the hard segments tend to remain in the orientated manner described (Fig. 2.2).
This model of molecular organisation and restructuring on extension, provides a possible explanation of stress softening phenomena and high hysteresis in polyurethane elastomers. This will be discussed more fully in subsequent chapters. Bonart\textsuperscript{36} (et al) has also investigated supra-molecular structure in polyester/MDI based elastomers, extended with 1,4-Butane Diol. Elastomers extended to 400\% showed clear crystal reflexes associated with stress induced crystallisation of the polyester segment. At high levels of hard segment content, reflexes associated with paracrystalline arrangements of hard segments are apparent, while the soft segment organisation appears less complete, i.e. the hard segment is now inhibiting soft segment crystallisation on extension. Interpretation of hard segment reflexes was based on the formation of paracrystalline regions through the hydrogen bonded interactions between urethane CO and NH groups.

The factors contributing to the degree of crystallinity and domain formation in segmented polyurethane elastomers, have received a great deal of attention over recent years. The effects of hydrogen-bonded interactions have been shown to be of particular importance in this context. Infra-red spectroscopic studies\textsuperscript{38} have demonstrated the presence of this type of interaction, and will be discussed more fully in Chapter 4.
It appears that almost all NH groups in segmented polyurethane elastomers are hydrogen-bonded. Hydrogen bonded interactions between urethane groups or urea groups contribute to hard segment domain formation. There is also evidence for hydrogen-bonded interactions between hard segment NH groups and soft segment oxygen atoms (i.e. CO group in polyester and COC group in polyether). This has been explained in terms of incomplete domain separation resulting in hard segments being dispersed in the soft matrix. It is also postulated that part of these interactions may occur at the domain-matrix interface.

Thermal analysis techniques have been widely used to determine the extent of polymer chain interactions and phase separation in polyurethane elastomers. Low temperature transitions are generally associated with the soft segment matrix, while transitions at higher temperatures reflect dissociations of hard block domains. A more detailed review of thermal transition in these materials is presented in Chapter 5.

The phenomenon of microphase separation has been clearly demonstrated by electron microscope techniques. Koutsky (et al) showed the presence of domains in polyester and polyether based elastomers, by staining samples with iodine and observing darkened areas by transmission electron microscopy.

Recent work has shown that the presence of a crystallisable segment in a segmented polyurethane elastomer system, can lead to the development of large scale structure (termed 'Superstructure').
Wilkes (et al) has demonstrated this phenomenon in materials incapable of hydrogen bonding\(^\text{43}\) as well as hydrogen-bonded elastomers.\(^\text{44}\) It appears that the superstructure entities ('spherulites') contain preferentially oriented domains. Spherulitic structure of the soft segment is readily apparent at high soft segment content, whereas at lower soft segment content, spherulites are formed by aggregation of hard segment domains. Slowikowska\(^\text{45}\) (et al) reported the formation of radial spherulites in polyurethane elastomer systems, and showed that increased degree of crosslinking in these systems impedes the ability to crystallise.

Physical and mechanical properties of segmented polyurethane elastomers can often be explained most easily in terms of supramolecular structure as described in the present section, i.e. Hard domains dispersed in a soft segment matrix. The soft matrix having a low T\(_g\) influences properties particularly at low temperatures. Hard segments in the domains, act as tie points as well as reinforcing filler entities, and govern the performance of the material at elevated temperature. The analogy between hard segment domains in polyurethane elastomers and reinforcing fillers in conventional rubbers, provides a useful means of interpreting structure-property relationships in segmented polyurethane elastomers. Thermoplastic elastomers based on various other types of block copolymers appear to derive a high level of physical properties from their domain structure.
These include ABA poly(styrene-b-butadiene) and ABA poly(styrene-b-isoprene). In these materials, incompatibility of the two blocks gives rise to formation of discrete glassy polystyrene domains in a soft rubbery continuous matrix. Obviously, these structures are very similar to that described for polyurethane elastomers, and structure-property relationships are based on the same principles.

Direct comparisons of domain structure reinforcement in phase separated elastomeric block copolymers and filler reinforcement in conventional rubbers have been made by Bishop (et al). He showed that the reinforcement activity of a polystyrene domain is comparable to that of a good reinforcing carbon black (eg. HAF Black).

Increased proportion of hard segment in segmented polyurethane elastomers has been shown to give materials of higher modulus, an effect observed on increasing the filler content of conventional rubbers. The phenomenon of stress softening on repeated extension is demonstrated in segmented polyurethane elastomers and has been attributed to disruption of domain structure, leading to a decrease in the number of effective 'cross-linking' sites. Smith (et al) has demonstrated that at a given strain level, the stress in phase separated elastomeric block copolymers decreases as the temperature is raised, due to melting or softening of domain structures, which therefore become ineffective as tie points and filler particles.

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Introduction of chemical crosslinking, particularly between hard segments, has been shown to lead to less aggregation of hard segments into domains\textsuperscript{52}, resulting in a decrease of physical properties, particularly a lowering of modulus (reflecting the reduced filler reinforcement effect). Ng\textsuperscript{53} (et al) has also demonstrated that domain perfection in segmented polyurethane elastomers is directly related to activity analogous to filler reinforcement in conventional rubbers. It was shown that polymers having a hard segment of narrow molecular weight distribution, had a higher modulus than polymers having structural irregularity due to a wide molecular weight distribution of hard segments.

In summary therefore, it appears that segmented polyurethane elastomers derive their high level of physical properties from the formation of discrete domains, which act in an analogous manner to reinforcing filler particles in a continuous soft segment matrix. A regular chemical structure in hard segments will be expected to aid efficient microphase separation and formation of perfect domains. Hydrogen bonding, particularly within hard domains, has been shown to contribute to discrete domain formations. However, domain formation has also been demonstrated in non hydrogen-bonded elastomers\textsuperscript{54}, indicating that other factors are involved (Thermodynamic incompatibility, polar interactions, molecular 'fit' etc).
Properties of segmented polyurethane elastomers at elevated temperature are dependent on the ability of the hard domains to remain associated. Introduction of chemical crosslinking into phase separated systems appears to disrupt the domains present, leading to a general lowering of properties.

2.2 Effect of Chemical Structure on General Properties of Segmented Polyurethane Elastomers

2.2.1 Structure of Soft Segment

The flexible (soft) segments in polyurethane elastomers greatly influence the elastic nature of the material and also the properties at low temperature. Aliphatic polyethers and polyesters are the most important materials used to form the soft segments. They have low glass transition temperatures (below room temperature) and are generally amorphous or have low melting points. Polyethers generally give elastomers having a lower level of physical properties than the polyester based materials due to the weaker interchain attractive forces present. The following table gives the energies of interaction between groups commonly present in polymeric materials.
It can be seen therefore that ester groups have almost three times the energy of cohesion of ether groups. This is readily explained by the presence of the additional carbonyl group giving increased polar interaction. The following values\textsuperscript{27} illustrate the lower tensile strength and modulus possessed by a polyether based elastomer (POTM) compared with a polyester based (PEA) material.

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Mwt.1000</th>
<th>Tensile Strength (MPa)</th>
<th>300% Modulus (MPa)</th>
<th>Elong. % Break</th>
<th>Hardness Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA</td>
<td>48.9</td>
<td>7.6</td>
<td>650</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>POTM</td>
<td>36.6</td>
<td>6.9</td>
<td>725</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>POP</td>
<td>28.9</td>
<td>4.4</td>
<td>800</td>
<td></td>
<td>76</td>
</tr>
</tbody>
</table>

Where PEA = Poly(ethylene adipate)  
POTM = Poly(oxytetramethylene)  
POP = Poly(oxypropylene)

(Above values are for materials prepared from polyol/1,4-Butane Diol/MDI in molar ratio 1:1:2).
Both PEA and POTM materials crystallise on extension due to their structural regularity and this is thought to be an important factor contributing to their high tensile strengths. (POTM gives the best physical properties among polyethers). The higher elongation at break shown by the polyether material can also be explained by the weaker interchain attractive forces present, allowing increased chain slippage and disentanglement.

Introduction of a pendant methyl group onto the polyol chain, as in the case of POP (HO(CH₂CH.CH₃)ₙH), causes increase in chain separation, lowering of interchain attractive forces, and loss of crystallisation on extension. These factors explain the decrease in tensile strength and modulus, and increase in elongation at break compared with the POTM based material.27

The low glass transition temperature (~76°C) of POTM confers better low temperature properties than found in typical polyesters (eg. PEA Tg = -48°C). Polyether based materials also show far superior hydrolytic stability as shown by the following values:

<table>
<thead>
<tr>
<th>Polyol</th>
<th>% Tensile Strength Retained on Hydrolysis (21 days/70°C in H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA</td>
<td>40</td>
</tr>
<tr>
<td>PHA</td>
<td>30</td>
</tr>
<tr>
<td>POTM</td>
<td>88</td>
</tr>
<tr>
<td>PPG (POP)</td>
<td>88</td>
</tr>
<tr>
<td>PHA = Poly(hexamethylene adipate).</td>
<td></td>
</tr>
</tbody>
</table>
This greater resistance to hydrolysis is readily explained by the greater hydrolytic stability of the ether group over that of the ester group.

Variation of polyester structure\textsuperscript{33} has much the same effect on properties as was shown for polyethers, i.e. the general effect of side groups is to prevent or hinder crystallisation on extension and to decrease interchain attractive forces, resulting in lower tensile strength and modulus. Decreased ester group content and the presence of pendant groups on the polyester backbone, cause a decrease in tear strength. Polyesters based on rigid symmetrical structures\textsuperscript{27} (eg poly(1,4-cyclohexyl-dimethylene adipate)) give hard elastomers of low elongation, due to reduced chain flexibility. Permanent set has been shown to increase with increasing ester group content\textsuperscript{58}. This has been explained by the presence of residual polyester crystallinity on relaxation, a view supported by the increased recovery found at higher temperatures\textsuperscript{59} due to the melting of polyester crystallites.

The molecular weight of the soft segment has a marked influence over the final elastomer properties. Increasing the molecular weight relative to the hard segment, produces a fall in modulus and an increase in the elongation at break.\textsuperscript{4} This is explained by the increase in flexibility and the relative reduction in highly polar hard segment interactions. Very low molecular weight of soft segment (\(<600\)) gives poorly elastic, hard materials, whereas high molecular weights give soft materials having poor physical properties.
2.2.2 Structure of Hard Segment

As shown earlier, hard segments in polyurethane elastomers are produced by the reaction of a diisocyanate with a diol or diamine chain extension agent to give a rigid polyurethane or polyurea structure. Interchain attractive forces between these rigid segments are far greater than those present in the soft segments, due to the high concentration of polar groups and the possibility of extensive hydrogen bonding. Hard segments significantly affect mechanical properties, particularly modulus, hardness and tear strength. The performance of elastomers at elevated temperatures is very much dependent on the structure of the hard segment and its ability to remain associated at these temperatures.

The present section deals firstly with the effect of diisocyanate on the general mechanical properties of polyurethane elastomers and secondly with the effect of the chain extension agent.

Diisocyanate

The effect of the diisocyanate structure on the physical properties of polyurethane elastomers has been investigated by several workers. Bulky aromatic diisocyanates having a symmetrical molecular structure have been shown to give elastomers of high modulus and hardness. Table 2.1 illustrates this general relationship.
### TABLE 2.1

**EFFECT OF DiIISO CYANATE STRUCTURE ON PHYSICAL PROPERTIES OF SEGMENTED POLYURETHANE ELASTOMERS**

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Tensile Strength (MPa)</th>
<th>Elong. @ Break %</th>
<th>Tear Strength (kN/m)</th>
<th>300% Modulus (MPa)</th>
<th>Hardness Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PDI</td>
<td>44.1</td>
<td>600</td>
<td>52.5</td>
<td>15.8</td>
<td>72</td>
</tr>
<tr>
<td>1,5-NDI</td>
<td>29.4</td>
<td>500</td>
<td>35.3</td>
<td>20.6</td>
<td>80</td>
</tr>
<tr>
<td>2,4/2,6-TDI</td>
<td>31.4</td>
<td>600</td>
<td>26.5</td>
<td>2.5</td>
<td>40</td>
</tr>
<tr>
<td>MDI</td>
<td>54.4</td>
<td>600</td>
<td>47.1</td>
<td>11.0</td>
<td>61</td>
</tr>
</tbody>
</table>

Where:  
- p-PDI = p-phenylene diisocyanate  
- 1,5-NDI = 1,5-Naphthalene diisocyanate  
- 2,4/2,6-TDI = Mixed isomers of toluene diisocyanate  
- MDI = Diphenylmethane diisocyanate
The bulky 1,5-NDI is shown to give materials of higher modulus and hardness than the single aromatic ring p-PDI and the flexible MDI. Asymmetrical molecules as represented by the 2,4/2,6-TDI combination, give elastomers of low modulus and hardness. Tensile strength and tear strength are also shown to be greater in the case of symmetrical molecules, particularly those based on the 1,4-substituted benzene ring system (p-PDI and MDI).

**Chain Extension Agent**

Chain extension agents most commonly employed in polyurethane elastomer systems are diols and diamines as described in Section 1.3.3. Diols give elastomers having polyurethane hard segments, whereas diamines form essentially polyurea segments. This fundamental structural difference between diol and diamine extended materials generally leads to differences in physical properties between the two classes. Diamine extended materials usually possess a higher level of physical properties due to the strong hydrogen bonded interaction of the urea group. This is shown in Table 2.2 for a polyether/MDI system.
<table>
<thead>
<tr>
<th>Chain Extension Agent</th>
<th>Tensile Strength (MPa)</th>
<th>300% Modulus (MPa)</th>
<th>Elongation at break %</th>
<th>Hardness Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCA</td>
<td>31.7</td>
<td>12.6</td>
<td>450</td>
<td>90</td>
</tr>
<tr>
<td>MOCA/MDA/m-PDA (60/20/20)</td>
<td>31.7</td>
<td>7.3</td>
<td>450</td>
<td>82</td>
</tr>
<tr>
<td>1,4-B.D/TMP (1.0/0.3)</td>
<td>8.9</td>
<td>2.1</td>
<td>560</td>
<td>57</td>
</tr>
<tr>
<td>1,4-B.D/TMP (3.0/1.3)</td>
<td>10.4</td>
<td>2.9</td>
<td>470</td>
<td>60</td>
</tr>
</tbody>
</table>

Where:
- MOCA = 3,3'-Dichloro-4,4'-diaminodiphenylmethane
- MDA = Methylene dianiline
- m-PDA = m-Phenylenediamine
- 1,4-B.D. = 1,4-Butane Diol
- TMP = Trimethylolpropane
In the case of diol extended materials, a significant proportion of crosslinking is often introduced by the use of a triol (eg. Trimethylolpropane) to give improved properties. However, these materials are still of low hardness and strength compared with the diamine extended materials (eg. MOCA extended). Use of ternary amine blends (eg. MOCA/MDA/m-PDA) gives softer materials of lower modulus than those obtained using a single diamine. This is thought to be due to structural irregularity causing decreased intermolecular bonding.

Diols are often preferred as chain extension agents in systems based on symmetrical diisocyanates (eg. MDI and NDI), where intermolecular attractive forces are favoured. Table 2.3\textsuperscript{29} compares the physical properties of a poly(ethylene adipate)/MDI elastomer chain extended with a homologous series of diols and an aromatic diol.
### TABLE 2.3

**EFFECT OF DIOL CHAIN EXTENSION AGENT STRUCTURE ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS**

<table>
<thead>
<tr>
<th>DIOL</th>
<th>Tensile Strength (MPa)</th>
<th>300% Modulus (MPa)</th>
<th>Elongation at break %</th>
<th>Hardness Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Ethane diol</td>
<td>44.8</td>
<td>13.8</td>
<td>500</td>
<td>61</td>
</tr>
<tr>
<td>1,3-Propane diol</td>
<td>45.5</td>
<td>6.6</td>
<td>600</td>
<td>61</td>
</tr>
<tr>
<td>1,4-Butane diol</td>
<td>54.5</td>
<td>6.9</td>
<td>600</td>
<td>61</td>
</tr>
<tr>
<td>1,5-Pentane diol</td>
<td>49.0</td>
<td>6.2</td>
<td>600</td>
<td>62</td>
</tr>
<tr>
<td>1,6-Hexane diol</td>
<td>51.0</td>
<td>5.9</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>p-Xylene-1,1’diol</td>
<td>45.5</td>
<td>15.2</td>
<td>500</td>
<td>73</td>
</tr>
</tbody>
</table>
The effect of changing the diol structure is seen to be relatively small, although much harder materials of higher modulus are given by the aromatic diol, p-Xylene- \( \text{\textbullet \textbullet} \)-Diol. The high modulus of the 1,2-Ethane diol extended material is thought to be due to the presence of the \(-(\text{CH}_2)_{2}\)- group in both the soft block and the hard block, allowing increased structural regularity. Schollenberger\(^{27}\) points out a similar effect in the case of a poly(tetramethylene adipate)/MDI material extended with 1,4-Butane diol.

Investigation of a series of aliphatic diols in the manufacture of a fibre forming composition\(^{58}\) based on poly(tetramethylene adipate)/MDI, showed that 1,2-Ethane diol gives a far superior permanent set over the longer chain diols examined. Use of rigid, bulky diols has been shown to give materials of high hardness and modulus together with good tensile and tear strength as shown by 1,4-Dihydroxy-1,2,3,4-tetrahydronaphthalene (Tetralin Diol).\(^{60}\)

Diamine chain extension agents are often used when an asymmetrical diisocyanate (eg. 2,4-TDI) is employed in a polyurethane elastomer system. Strong intermolecular attractive forces between urea groups compensate for structural irregularities due to the diisocyanate. The most commonly used diamine chain extension agent in commercial elastomer systems is MOCA\(^{8}\) (3,3'-Dichloro-4,4'-diamino diphenyl methane), which combines a practical reactivity rate with a high level of physical properties in the final elastomer.
One major drawback in the use of aromatic diamines for polyurethane elastomer synthesis, is the suspected carcinogenic activity associated with many of these materials, particularly 4,4'-diaminobiphenyl (Benzidine) and its derivatives.\textsuperscript{61,62} Blahak\textsuperscript{63} (et al) has reported the synthesis of polyurethane elastomers based on esters of 3,5-diamino benzoic acid and derivatives of anthranilic acid. These materials are claimed to be free of carcinogenic activity and have good physical properties, although inferior to typical MOCA based materials.

In a fundamental investigation into the effects of diamine structure on the properties of a poly(oxytetramethylene) diol/TDI elastomer Sampson & Blaich\textsuperscript{64} reported the data given in Table 2.4.
TABLE 2.4
EFFECT OF DIAMINE STRUCTURE ON PHYSICAL PROPERTIES
OF POLYURETHANE ELASTOMERS

<table>
<thead>
<tr>
<th>Diamine</th>
<th>Tensile Strength (MPa)</th>
<th>100% Modulus (MPa)</th>
<th>300% Modulus (MPa)</th>
<th>Elong @ Break %</th>
<th>Tear (kN/m)</th>
<th>Hardness Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDA*</td>
<td>30.5</td>
<td>7.9</td>
<td>14.1</td>
<td>520</td>
<td>94.2</td>
<td>86</td>
</tr>
<tr>
<td>MOCA</td>
<td>34.5</td>
<td>6.4</td>
<td>14.5</td>
<td>450</td>
<td>83.4</td>
<td>91</td>
</tr>
<tr>
<td>PAPA</td>
<td>28.2</td>
<td>5.3</td>
<td>28.2</td>
<td>300</td>
<td>113</td>
<td>86</td>
</tr>
<tr>
<td>BB*</td>
<td>29.9</td>
<td>8.2</td>
<td>16.1</td>
<td>470</td>
<td>99.1</td>
<td>86</td>
</tr>
<tr>
<td>DCB</td>
<td>37.6</td>
<td>11.7</td>
<td>28.1</td>
<td>390</td>
<td>109.9</td>
<td>94</td>
</tr>
<tr>
<td>TB</td>
<td>48.3</td>
<td>12.7</td>
<td>21.6</td>
<td>550</td>
<td>118.7</td>
<td>95</td>
</tr>
<tr>
<td>DB</td>
<td>17.0</td>
<td>5.1</td>
<td>7.6</td>
<td>550</td>
<td>72.6</td>
<td>93</td>
</tr>
<tr>
<td>p-PDA*</td>
<td>16.0</td>
<td>10.8</td>
<td>16.0</td>
<td>300</td>
<td>112.8</td>
<td>91</td>
</tr>
</tbody>
</table>

* Prepared by solution method

Where:  MDA = 4,4'-Diamino diphenylmethane
MOCA = 3,3'-Dichloro-4,4'-diamino diphenyl methane
PAPA = Polymethylene Polyaniline
BB = 4,4'-diamino biphenyl
DCB = 3,3'-Dichloro-4,4'-diamino biphenyl
TB = 3,3'-Dimethyl-4,4'-diamino biphenyl
DB = 3,3'-Dimethoxy-4,4'-diamino biphenyl
p-PDA = p-phenylene diamine
Diamines having relatively unhindered amino groups (MDA, B.B. & p-PDA) were too reactive to be used as melts in a bulk polymerisation process. Elastomers were therefore prepared from these diamines by mixing them with the prepolymer in methyl ethyl ketone (65% solids content), casting a 1mm film on glass, and evaporating off the solvent. Films were allowed to cure for 3 hours at 100°C. Diamines having more sterically hindered amino groups were reacted by the conventional bulk polymerisation process, where molten chain extender and prepolymer were mixed at elevated temperature and then press cured for 3 hours at 100°C.

Comparison of MOCA and MDA extended materials, shows that tear strength and elongation are slightly superior in the case of the MDA elastomers, although tensile strength is a little lower. However, it is important to note that MOCA and MDA elastomers were prepared by the different processes outlined above and it may be misleading to compare the properties of these materials. However, the results do show that the benzidine structure generally gives materials of higher modulus, tensile strength, tear strength and hardness than the diphenyl methane structure. This is demonstrated by comparing B.B. with MDA, and DCB with MOCA. The diphenyl methane diamine materials have a higher elongation at break, presumably due to their greater flexibility around the methylene bridge.
Elastomers prepared using PAPA as chain extension agent were thought to have excessive crosslinking due to the high functionality present. This gives rise to material of lower tensile strength, tear strength and elongation at break. The poor tensile strength and elongation of the p-PDA extended material was explained by the presence of gel particles, formed by the extremely fast reaction in 65% solid solution.

Sampson & Blaich showed further evidence for the effect of the benzidine structure in providing a high level of physical properties. They prepared a polyurethane elastomer based on poly(ethylene adipate)/Bitoluene diisocyanate extended with MOCA. This material had a high tensile strength (45 MPa) and high modulus (300% Modulus = 33 MPa), as well as an extremely high tear strength (186 kN/m). However, use of OCB as chain extension agent in this system gave inferior properties to the MOCA extended material. This was thought to be due to the introduction of excessive rigidity (i.e. too high concentration of benzidine groups) in the material.

Haikens et al investigated the properties of a polyester/MDI based elastomer, chain extended with a series of linear diamines of varying chain length. Tensile strength and elongation at break were shown to be higher when a diamine having an odd number of carbon atoms was used. Modulus was found to be higher in the case of the diamines having an even number of carbon atoms.
Polyamides have been shown to act in a similar manner, where crystallite formation is favoured by regular groups of an even number of carbon atoms. Bonart (et al) provided further evidence for this effect in polyurethane elastomers, by showing that diamines having an even number of carbon atoms, give materials with a higher hard segment softening point, reflecting their superior hard segment domain formation.

Commercial polyurethane elastomers are generally prepared by the conventional melt polymerisation methods. Chain extension agents are therefore limited to diols and diamines which are liquids, or solids of relatively low melting point (eg. 1,4-B.D., MOCA, MDA). However, polyurethane elastomers prepared in solution (as represented by solution spun and reaction spun spandex fibres) allow the use of a much wider range of chain extension agents including those having high melting points and those of high reactivity. In general, fibres formed using chain extension agents of aromatic or cycloaliphatic nature, are harder and have higher melting points than those fibres based on straight chain diamines (eg. ethylene diamine). The formation of high melting point hard segments in these fibres, leads to improved mechanical properties at higher temperatures. However the presence of aromatic groups causes discolouration on exposure to light, and so most commercial materials are based on aliphatic systems.
2.2.3 Effect of Segment Size on Properties of Polyurethane Elastomers

Several investigations into the effect of varying the size of the hard and soft segments in polyurethane elastomers, have been made. In a poly(oxypropylene) glycol/TDI material \(^{68}\) extended with MOCA, increased molecular weight of the polyether soft segment was found to give a decrease in tensile strength, modulus, hardness and tear strength, but increased abrasion resistance. In a water extended poly(ethylene-co-propylene adipate)/MDI system, Little \(^{69}\) (et al) showed that increased polyester molecular weight is accompanied by a decrease in modulus. Bylsma \(^{70}\) reported the effect of variation in polyurethane concentration on tensile strength in a system based on poly(oxypropylene) glycol/TDI. Increased polyurethane concentration gave materials of increased tensile strength, a correlation which was not found between degree of crosslinking and tensile strength. These results indicate the general increase in strength properties (modulus, tensile strength, hardness, tear strength) associated with increased urethane concentration in polyurethane elastomers. Investigation by Pigott \(^{71}\) (et al) into a polyester/MDI system extended with 1,4-B.D., support this general picture although in this case a gradual decrease of tensile strength with increasing urethane concentration was found.
Tear strength was found to increase to a maximum and then decrease with further increase in urethane concentration, presumably due to the disruptive effect of excessive bulky MDI groups. Elongation set was found to increase with increasing urethane content. Mohajer et al demonstrated an optimum hard segment/soft segment ratio for elastic and work recovery in a poly (ethylene adipate)/MDI elastomeric fibre extended with 1,4-B.D. Increase in hard segment size above the optimum led to a gradual decrease in elastic recovery (ie. increased elongation set).

Smith & Magnusson have studied the effects of urethane concentration and crosslinking on properties of polyurethane elastomers. They showed that the increase in Tg with increasing urethane concentration for poly (oxypropylene) glycol based elastomers, gives rise to an increase in tensile strength measured at ambient temperature. Crosslinking was found to have much less effect on Tg and hence on the tensile strengths measured at ambient temperature.

The effect of hard segment size and molecular weight distribution has been investigated in polyurethanes having carefully controlled chemical structure. Polymers were based on a poly(oxytetramethylene) soft segment and a piperazine/1,4-B.D. hard segment.
Unlike most practical polyurethane elastomer systems, these polymers provide no possible sites for hydrogen-bonded interactions. Polymers having a narrow hard segment molecular weight distribution were found to have a higher modulus than polymers with a wide molecular weight distribution. Tensile strength and elongation at break were found to be highest for polymers having a narrow soft segment molecular weight distribution. Permanent set was found to increase as the molecular weight distributions of hard and soft segments were narrowed. By preparing blends of polymers with different size hard segments, it was found that compatibility depended on the relative sizes of the hard segments combined. A more recent investigation into the dynamic mechanical properties and thermal behaviour of these materials has been made. Explanation of the increase in modulus found for materials of higher hard segment content and narrower hard segment molecular weight distribution was given in terms of improved phase separation and domain formation (see Section 2.1.2).

2.2.4 Effect of Crosslinking on Properties of Segmented Polyurethane Elastomers

Chemical crosslinking in segmented polyurethane elastomers falls into two main classes:

a) Crosslinking by the use of a trifunctional chain extension agent, eg. Trimethylolpropane.

b) Crosslinking by reaction of excess isocyanate to give biuret or allophanate linkages.
Even more important than these primary covalent (chemical) crosslinks, are the non-covalent inter-molecular attractive forces such as hydrogen bonding. Havlik & Smith\textsuperscript{74} demonstrated the importance of these non-covalent interactions in a soluble polyurethane elastomer based on poly(oxypropylene)glycol/2,4-TDI extended with 2,4-toluene diamine. This material showed a high modulus compared with a chemically crosslinked elastomer based on the same system. This effect has been explained by the disruption of non-covalent inter-molecular forces by the introduction of chemical cross-links which cause spatial separation of polymer chains.

Pigott\textsuperscript{33} (et al) investigated the effect of chemical crosslinking on properties in a poly(ethylene adipate)/MDI system extended with 1,4-B,D. The extent of cross-linking was increased by using varying amounts of TMP combined with 1,4-B,D. chain extension agent. Results showed that increased degree of crosslinking in this system is accompanied by a decrease in tensile strength, elongation at break, modulus, hardness and tear strength. Elongation set and compression set are lower (i.e. increased elasticity) in the more highly crosslinked materials. Volume swelling of elastomers in dimethyl acetamide decreased as expected with increasing degree of crosslinking. Modulus and tensile strength were found to decrease to a minimum and then increase (sharply in the case of modulus) at very high degree of crosslinking.
This behaviour of polyurethane elastomers is in sharp contrast to conventional hydrocarbon rubbers which show increased modulus and strength as crosslinking is incorporated. These results could be interpreted in terms of evidence for the presence of non-covalent intermolecular attractive forces which lose their effectiveness as increased chemical crosslinking causes increased chain separation. At very high levels of chemical crosslinking, modulus increases due to the excessive density of crosslinks hindering molecular motion. Measurements were also made of the Clash-Berg torsional modulus of a series of elastomers of varying crosslink density. Results showed that materials of higher crosslink density maintained their modulus to a higher temperature than did the more lightly or non-crosslinked materials. This evidence presumably reflects the greater thermal stability of the chemical crosslinks (formed by the triol-diisocyanate reaction) over that of the non-covalent interactions and allophonate type linkages.

Polyether based elastomers extended with diols have been found to show increased hardness and modulus with increased degree of crosslinking. This is in contrast with the diol extended polyester materials as described above, and can be attributed to the lack of intermolecular polar interactions which are present in the polyester based materials.
However, use of a diamine chain extension agent eg. MOCA, provides increased intermolecular non-covalent interactions (by increased hydrogen bond formation through urea groups), resulting in behaviour similar to the polyester based elastomers, ie. decreased modulus as degree of crosslinking increases.

Smith and Magnusson\textsuperscript{72} investigated the effect of crosslinking on Tg in a series of poly(oxypropylene)/TDI based elastomers using TMP as a crosslinking agent. They found no significant effect on Tg as the degree of crosslinking increased. Tensile strength was found to vary only slightly, whereas the modulus increased and the elongation at break decreased.

From the above considerations, it is seen that the effect of chemical crosslinking on the properties of polyurethane elastomers is influenced largely by the presence of non-covalent intermolecular attractive forces in the linear polymer. Elastomers having strong secondary interactions tend to suffer a general decrease in physical properties as the extent of crosslinking increases, eg. Polyester based materials. Elastomers which have relatively weak secondary interchain interactions, eg. polyethers extended with diols, and polyols with pendant methyl groups, show a general increase in physical properties with increasing crosslink density.
Investigations into the effect of crosslinking on the dynamic properties of polyurethane elastomers derived from a poly(ethylene adipate)/MDI prepolymer extended with mixtures of 1,4-B.D. and TMP, have been reported. At low degrees of crosslinking, both for allophanate and TMP crosslinked materials, compression flex fatigue resistance was poor. Increased crosslinking gives rise to improved flex fatigue resistance, although heavily crosslinked materials show a fall off in this property. Elastomers crosslinked by allophanate type crosslinks showed properties inferior to those based on TMP. It appears therefore, that elastomers lightly crosslinked by the use of a triol with the chain extension agent give optimum flex fatigue properties.

Weisfeld (et al) calculated the contribution of covalent and secondary polar type crosslinks to the modulus of a polyurethane elastomer based on poly (ethylene-co-propylene adipate)/MDI extended with MOCA. By variation of the NH₂/NCO molar ratio (kept below 1.0), materials of varying degrees of crosslinking through biuret linkages were prepared. The modulus of elasticity was assumed to be represented:

\[
\frac{\sigma}{\nu} = ART e^{-\frac{E_a}{RT}} + \left(\frac{\nu e}{\nu}\right) RT
\]

where \( \frac{\sigma}{\nu} \) is the stress per unit deformation.
\( \frac{\gamma a}{V} \) is the term attributed to primary covalent crosslinks as derived in the statistical theory of rubber elasticity.

\[ \frac{-E_a}{RT} \]

\( \text{ART} e \) is the term attributed to secondary polar type crosslinks assuming an Arrhenius Law temperature dependence.

A \( = \) a constant
R \( = \) gas constant
T \( = \) absolute temperature
Ea \( = \) activation energy of secondary bonds
\( \frac{\gamma a}{V} \) = density of primary crosslinks

Assuming all amine groups react with isocyanate groups to give urea linkages and excess isocyanate groups react with urea groups to give biuret groups, the concentration of urea groups and biuret groups was calculated. As the extent of primary crosslinking decreases, the contribution of non-covalent secondary crosslinks to the modulus was shown to increase, together with the overall experimentally measured modulus. These results provide further evidence for the disruption of polar interactions by chemical crosslinks leading to a decreased modulus.

Sasaki\textsuperscript{75} (et al) has investigated the effect of isocyanurate crosslinks in a poly(oxyethylene)glycol based elastomer.

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Modulus was found to increase linearly with crosslink density, and it was suggested that this effect was due to formation of isocyanurate rings into rigid domain aggregations. (However, it seems more probable that domain formation is inhibited by the chemical crosslinks formed and the increased modulus is due to the high chemical crosslink density).

2.3 Aims of the Present Work

Segmented polyurethane elastomers have been shown to possess excellent physical and mechanical properties, particularly at or near ambient conditions. However, at elevated temperatures, properties appear to fall off rapidly. Saunders\textsuperscript{30} points out that the chemical design of the hard segment is probably the most important factor in determining the retention of properties at elevated temperatures. He concludes that symmetrical hard segments having good 'fit' would be anticipated to form a basis for higher temperature resistant polymers.

The aim of the present work is to investigate the effect of the chemical structure of the hard segment on mechanical properties at elevated temperatures. The structure of the hard segment is varied by the incorporation of different chain extension molecules. Polymerisation in solution allows the use of bulky aromatic diamines of high melting point, which owing to their rigid structure, might be expected to assist retention of properties at elevated temperatures in a segmented polyurethane elastomer system.
Structure-property relationships have predominantly concentrated on the relation between chemical structure and general mechanical properties, i.e. tensile strength, modulus, hardness etc (Section 2.2). The present work aims to extend these relationships to include properties which are important under possible service conditions, namely:

a) Stress relaxation and creep
b) Hysteresis
FIG. 2.1
ELONGATION CRYSTALLISATION OF POLYETHER SOFT SEGMENTS IN A SEGMENTED POLYURETHANE ELASTOMER AT 200% EXTENSION (REF. 35)
FIG. 2.2
SEGMENTED POLYURETHANE ELASTOMER AT 500% EXTENSION AND PLACED IN WARM WATER AT 80°C (REF. 35)

Crystalline lattice planes

ca. 12 Å
ca. 100-200 Å
ca. 25 Å
3.1 Introduction

Polyurethane elastomers are usually prepared by bulk polymerisation techniques, where the prepolymer and chain extension agent are mixed in the molten state at elevated temperature. Cure in a mould is normally carried out by heating in the temperature range 50-110°C for several hours. Precise conditions require optimisation for the chemical system under consideration. Although this procedure has become established for many commercial elastomers where a solvent-free system provides relative ease of handling and processing, several disadvantages are apparent:

a) The choice of diisocyanate is restricted to those having a relatively low melting point, eg. MDI (38°C), TDI (liquid at room temperature), HDI (liquid at room temperature) and 1,5-NDI (127°C).

b) Chain extension agents must also be liquids or low melting point solids, eg. 1,4-BDo. (liquid at room temperature) and MOCA (approximately 109°C).

c) The reactivity of the chain extension agent with the diisocyanate must be low enough to allow efficient mixing of the chain extension agent with the prepolymer prior to casting.
This effect has been demonstrated in a commercial polyether based urethane elastomer. Chain extension with MOCA gives a pot life (time during which mixture is liquid castable) of 5 minutes at 85°C. However, chain extension with the more reactive MDA, gives a pot life of less than 10 seconds at 70°C.

d) Production of uniform, homogeneous elastomeric materials depends largely on the efficient dispersion of reactants during the mixing stage. However, chain extension agents are often insoluble in the prepolymer and may only form a fine suspension. It is likely therefore that localised reaction will occur in the system, leading to the formation of gelled regions through branching and crosslinking reactions.

Efficient dispersion of reactants is also hindered by the relatively high viscosity of the molten mixture. In systems where use of a reactive chain extension agent leads to a short pot life, efficient mixing is either not possible or very difficult due to the short time available.

By use of solution polymerisation techniques, these problems can largely be overcome. A much wider range of diisocyanates and chain extension agents can be used, including those having high melting points and high reactivity.
This is reflected in the wide variety of materials used in the production of solution spun spandex fibres. Use of a solvent system also gives rapid and efficient dispersion of reactants, leading to more uniform reaction throughout the medium.

Several investigations have been reported on the synthesis of polyurethanes by solution techniques. Lyman prepared homopolyurethanes by reaction of ethylene glycol with various diisocyanates, in a series of solvents. Polar solvents, particularly dialkyl amides and dialkyl sulphoxides were found to provide the most suitable conditions for efficient polymerisation. Lyman noted four important aspects of the solution polymerisation method:

1. The solvent must be a non-reactive medium, in which diisocyanate, chain extender and polyurethane product, are all readily soluble.
2. The solvent must not contain any active hydrogen atoms.
3. The solvent must be pure, i.e. it must contain no monofunctional impurities which might act as chain stoppers, and no acidic or basic impurities which could promote side reactions.
4. The solvent must be dry to prevent water-isocyanate reactions from occurring.

It has been shown that under certain conditions, solvents which are apparently non-reactive towards the isocyanate group, can react to a certain extent.
Reaction of N,N-dialkyl amides with the highly reactive p-toluenesulphonyl isocyanate to give N,N-dialkyl-N'-
(p-toluenesulphonyl) amidines, has been reported.\textsuperscript{78} Sorenson\textsuperscript{79} reported a side reaction between phenyl isocyanate and dimethylsulphoxide.

3.2 Preliminary Investigations

It was required to prepare essentially linear elastomeric polyurethane materials for fundamental investigations into structure-property relationships, particularly at elevated temperatures. Diamines and diols of bulky aromatic molecular structure, were investigated as possible chain extension agents in a poly(oxytetramethylene)/H\textsubscript{12}MDI based system.

N,N-Dimethylformamide (DMF) was found to be a suitable solvent for all chain extension reagents investigated and for the prepolymer system used. On stirring prepolymer in purified DMF for 24 hours at 90°C, no apparent decrease in isocyanate content (measured by infra-red analysis - Section 3.3.4) was found, indicating negligible solvent-isocyanate side reaction.

The optimum chain extension reaction temperature was found to be 90°C giving a reasonable diamine/prepolymer reaction rate, without allowing significant allophanate or biuret formation. A total solids content of 33% was found to give a castable polymer solution during chain extension with reactive diamine.
A 50% solution however yielded a highly viscous solution, containing a small amount of gelled material, presumably formed by localised reaction.

In order to compare the effect of a variety of chain extension agents on the properties of the final material, the chain extension reaction must be taken to completion in each case. It is necessary therefore to follow the course of each reaction. An infra-red spectroscopic technique was developed (Section 3.3.4), requiring only very small proportions of reaction solution and giving absolute values of isocyanate concentration with time of reaction.

On completion of reaction, solutions were cast on a polished glass surface at 50°C. Use of a release agent was found to give rise to an uneven surface on the resulting polymer film. Solution casting on a mercury bed was also investigated, but mercury was found to adhere to polymer films on removal, apparently due to dust particles on the mercury surface. Toxic hazards associated with mercury vapour also proved to be a drawback to this method.

Solutions cast at 50°C provided a low rate of solvent evaporation. Use of higher temperatures was found to have two main deleterious effects:

a) An uneven film surface due to solvent evaporating off too quickly.

b) Inefficient removal of solvent from the film due to a high rate of solvent evaporation from the surface of the liquid layer, leading to the formation of a 'skin'.
In the light of suspected health hazards associated with isocyanates and aromatic diamines, reagents were used only in a well ventilated area. Disposable gloves were worn when handling these materials.

3.3 Experimental
3.3.1 Materials

Prepolymer

A polyether based prepolymer, Poly(oxytetramethylene) glycol/H_{12}MDI (E I du Pont de Nemours Co Inc.) was used in the preparation of all elastomers investigated. In order to minimise any possible isocyanate reactions (eg. self-addition reactions), the prepolymer was stored in a refrigerator until required.

Diisocyanate

4,4'-dicyclohexylmethane diisocyanate (ie. Hydrogenated MDI - termed H_{12}MDI) was used as supplied. (E I du Pont de Nemours Co. Inc.).

Solvent

N,N-Dimethylformamide (DMF) (Fisons - SLR grade) was dried over molecular sieve (Type 4A) and distilled through a Claisen Column at 80°C under reduced pressure (80 Torr), using a fine bleed of dry nitrogen. The middle fraction was collected and used immediately.

Catalyst

A stabilised stannous octoate catalyst, ie. Stannous 2-ethyl hexoate (designated Nuocure 28, Durham Chemicals Ltd) was used as supplied.
Nitrogen

White spot nitrogen (B.O.C.) was used throughout and further dried by passing through silica gel guard tubes.

Chain Extension Agents

The following diamines and diols were investigated as possible chain extension agents (supplied by the Aldrich Chemical Company, unless stated).

a) Diamines:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Phenylenediamine</td>
<td>138 - 143</td>
</tr>
<tr>
<td>o-Phenylenediamine</td>
<td>100 - 102</td>
</tr>
<tr>
<td>1,5-Diaminonaphthalene</td>
<td>185 - 187</td>
</tr>
<tr>
<td>3,6-Diaminoacridine</td>
<td>270 (Dec)</td>
</tr>
<tr>
<td>3,3'-Dichloro-4,4'-diaminodiphenylmethane (MOCA)</td>
<td>109 (E I du Pont de Nemours Co Inc)</td>
</tr>
<tr>
<td>2,3-Diaminofluorenone</td>
<td>192 - 195</td>
</tr>
<tr>
<td>2,7-Diaminofluorene</td>
<td>166 - 167</td>
</tr>
<tr>
<td>2,4-Diamino-6-phenyl-s-triazine</td>
<td>226 - 228</td>
</tr>
</tbody>
</table>

b) Diols:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Butane Diol</td>
<td>15 - 19         (General Aniline &amp; Film Ltd)</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>172 - 173 (Dec)</td>
</tr>
<tr>
<td>1,5-Dihydroxynaphthalene</td>
<td>259 - 261 (Dec)</td>
</tr>
<tr>
<td>2,3-Dihydroxynaphthalene</td>
<td>162 - 164</td>
</tr>
<tr>
<td>2,6-Dihydroxyanthraquinone</td>
<td>&gt; 320</td>
</tr>
</tbody>
</table>
1,4-Butane Diol was distilled at reduced pressure under dry nitrogen and stored under dry nitrogen in a glass tube fitted with a suba seal stopper. All other chain extension reagents were dried in a vacuum oven at 50°C for a short period immediately before use.

In order to avoid any unwanted side reactions due to trace impurities, all glassware was carefully washed in fresh chromic acid followed by repeated washings with deionised water, and finally left to dry at 100°C in a drying cabinet.

3.3.2 Chain Extension Reactions

Prepolymer was melted in an oven at 50°C and the required amount weighed into a three-necked round bottomed flask. The flask was equipped with a water condenser, pressure equalising dropping funnel and a PTFE paddle stirrer. (Fig 3.1). The stirrer was driven by a variable speed Citenco electric motor and was connected to the flask through an oil sealed ground glass stirrer gland. PTFE tape was wound round all quickfit cone joints, giving tight connections which were unaffected by solvent vapour. A steady flow of dry nitrogen was passed through the apparatus via the dropping funnel. 60mls of freshly distilled DMF were added to the prepolymer and the apparatus was clamped in an oil bath at 90°C.
The oil was stirred continuously by means of a motor driven stirrer and the temperature was maintained at 90°C ± 2°C by using a Fi-Monitor attachment on a mercury thermometer immersed in the oil by the side of flask A. The prepolymer readily dissolved in the DMF and was stirred rapidly.

The required amounts of chain extension agent and catalyst were weighed accurately into a small beaker and 30mls of DMF added. If necessary the beaker was warmed gently on a hot plate until all solid had dissolved. The solution was then poured into the pressure equalising dropping funnel and the nitrogen inlet quickly replaced. Any remaining solution in the beaker was washed into the dropping funnel with 5mls DMF. The solution of chain extension agent was heated to approximately 60°C by means of a band heater wrapped around the dropping funnel. The hot solution of chain extension agent was then added dropwise (at a fairly fast rate) to the vigorously stirred solution of prepolymer. Any remaining solution in the dropping funnel was washed through with 5mls DMF. The dropping funnel was removed from flask A and the nitrogen inlet quickly attached directly to the flask at the Quick-fit joint.

The extent of reaction was followed by an infra-red spectroscopic technique as described in Section 3.3.4. On completion of reaction, polymer films were cast as described in Section 3.3.3.
Quantities and Ratios of Reactants Used

The available isocyanate content of the prepolymer was specified in the accompanying Du Pont literature as 4.75 ± 0.15%. This value was checked by the standard di-n-butylamine back titration method (see Appendix 1) and found to be correct for the material used.

ie. 100g Prepolymer contains 4.75g NCO; ie. \( \frac{4.75}{42} \) moles NCO.

45g Prepolymer was used in each reaction, ie:

\[
\frac{4.75 \times 45}{42 \times 100} = 5.09 \times 10^{-2} \text{ moles NCO.}
\]

For 100% chain extension reaction using a difunctional chain extension agent, 45g Prepolymer required

\[
\frac{4.75 \times 45 \times 1}{42 \times 100 \times 2} \text{ moles chain extension agent. ie:}
\]

\[
2.54 \times 10^{-2} \text{ moles.}
\]

For 95% chain extension reaction, \( (2.41 \times 10^{-2}) \) moles chain extension agent are required.

For 90% chain extension reaction, \( (2.29 \times 10^{-2}) \) moles chain extension agent are required.

Reactions were carried out in 100mls DMF, ie. approx. 33% solids content. Several polymers were prepared using prepolymer of higher isocyanate content. It was required to prepare prepolymer of 10% and 15% available isocyanate content, by adding excess \( H_2 \text{MDI} \) to the 4.75% NCO prepolymer (herein referred to as Prepolymer-4.75 NCO).
The following formula was used to calculate the proportions of \( \text{H}_{12} \text{MDI} \) and prepolymer-4.75 NCO required:

\[
\% \text{ NCO} = 100 \left( \frac{\left( \frac{4.75}{100} \right) y + \left( \frac{84}{262} \right) x}{y + x} \right)
\]

where \( x \) = weight (g) \( \text{H}_{12} \text{MDI} \) required.
\( y \) = weight (g) prepolymer-4.75 NCO used.

The following formulations are derived using this equation:

a) 10% available NCO Prepolymer (herein referred to as Prepolymer-10 NCO):

400g Prepolymer-4.75 NCO + 95g \( \text{H}_{12} \text{MDI} \)

b) 15% available NCO Prepolymer (herein referred to as Prepolymer-15 NCO):

400g Prepolymer-4.75 NCO + 240g \( \text{H}_{12} \text{MDI} \).

Prepolymer-10 NCO and Prepolymer-15 NCO were prepared by stirring the above formulations for 1 hour at 50°C under dry nitrogen. The viscous solutions obtained were stored in tins under nitrogen. Isocyanate content was determined by the di-n-butylamine back titration method (Appendix 1) before use, giving the following results.

Prepolymer-10 NCO, contained 11.35% available NCO.
Prepolymer-15 NCO, contained 16.28% available NCO.
Using these accurately determined values of NCO content, polymers were prepared using 45g prepolymer and 95% chain extension agent. (Molar quantities were calculated as shown for Prepolymer-4.75 NCO). Table 3.1 summarises the ratios and molar quantities of reactants used:

TABLE 3.1

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>Available NCO (%) Determined (by titration)</th>
<th>45g Prepolymer NCO (moles) (x10^-2)</th>
<th>Chain Extension Agent (moles) (x10^-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>90%</td>
</tr>
<tr>
<td>Prepolymer-4.75 NCO</td>
<td>4.75</td>
<td>5.09</td>
<td>2.29</td>
</tr>
<tr>
<td>Prepolymer-10 NCO</td>
<td>11.35</td>
<td>12.16</td>
<td>-</td>
</tr>
<tr>
<td>Prepolymer-15 NCO</td>
<td>16.28</td>
<td>17.44</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3.3 Casting of Polymer Films

On completion of reaction, the polymer solution was allowed to cool down to 50°C (with continued stream of nitrogen passing over). The condenser, stirrer and dropping funnel were removed and the flask quickly transferred to a vacuum oven at 50°C. The solution was degassed under vacuum to remove any entrapped gas which might lead to bubbles in the polymer film.
A square glass plate with a silicon rubber border was used as a mould. The surface was thoroughly cleaned with DMF followed by distilled water, and the plate allowed to dry in a drying cabinet. The surface was then highly polished and the glass plate levelled carefully (using a bubble level) in a hot air circulating oven at 50°C. The degassed polymer solution was carefully applied evenly over the surface of the glass plate, taking care not to entrap any air bubbles in the liquid film as these would give rise to voids in the solid product.

The film was left in the oven at 50°C for 24 hours, allowing DMF to evaporate off at a fairly slow rate leaving a solid film of approximately 0.5mm thickness. By using a drop of water at the glass/film interface, the film was peeled away from the glass surface. Films were stored at constant temperature (23°C) and humidity (67% RH) by hanging in a glass tank (kept in a constant temperature room) containing a dish of saturated sodium nitrite solution. Films were left for at least two weeks before testing.

3.3.4 Extent of Chain Extension Reaction

The molecular structure of the chain extension agent governs the rate of reaction with prepolymer. It was necessary, therefore, to follow the extent of each reaction prior to casting the solution. The following infra-red spectroscopic technique was adopted:
Procedure

At timed intervals during the chain extension reaction (Section 3.2.2), 1ml samples of the reaction solution were removed from flask A by means of a clean, dry pippette. Samples were diluted to 10% by stirring well in excess DMF in a clean dry beaker. Two sodium chloride discs were cleaned thoroughly in DMF, dried and placed in a vacuum oven at 50°C. A single drop of the 10% reaction solution was placed on each disc and the DMF evaporated off at 50°C under vacuum. The sodium chloride discs were then clamped together in the sample cell of a double beam infra-red spectrophotometer (Unicam SP200G. Grating Infra-Red Spectrophotometer). Using air in the reference beam, spectra were recorded between 2.5\mu m (4000 cm\(^{-1}\)) and 5.0\mu m (2000 cm\(^{-1}\)) at a medium scanning speed. A typical spectrum is shown in Fig. 3.2 (Reaction of p-Phenylenediamine and Prepolymer-4.75 NCO, at 90°C for 1 hour).

Reaction was followed by observing the disappearance of the characteristic (-N=C=O) absorption band (4.4\mu m i.e. 2270 cm\(^{-1}\)) with time of reaction. Using the (-CH) absorption band (2935 cm\(^{-1}\)) as an internal reference to overcome the problem of variation in sample thickness, the concentration of isocyanate was calculated as follows:
Beer-Lambert's law of absorption states:

\[ A = \log_{10} \left( \frac{I_o}{I} \right) = ECL \quad (1) \]

Where:

\[ A = \text{Absorbance} \]
\[ I_o = \text{Intensity of incident radiation} \]
\[ I = \text{Intensity of transmitted radiation} \]
\[ E = \text{Extinction coefficient} \]
\[ C = \text{Concentration} \left( \text{moles} \, \text{L}^{-1} \right) \]
\[ L = \text{Path length} \left( \text{cm} \right) \]

A standard solution of Prepolymer (45g) in DMF (100 mls) was prepared and the infra-red spectrum recorded as above. This sample represents the 100% NCO standard, having a relative (NCO)/(CH) absorbance (using equation (1)) given by:

\[ \left[ \frac{A_{\text{NCO}}}{A_{\text{CH}}} \right]_s = \frac{E_{\text{NCO}} (C_{\text{NCO}}) L_s}{E_{\text{CH}} (C_{\text{CH}}) L_s} = \frac{E_{\text{NCO}} (C_{\text{NCO}}) s}{E_{\text{CH}} (C_{\text{CH}}) s} \quad (2) \]

Similarly, for a sample of the reaction solution:

\[ \left[ \frac{A_{\text{NCO}}}{A_{\text{CH}}} \right]_r = \frac{E_{\text{NCO}} (C_{\text{NCO}}) L_r}{E_{\text{CH}} (C_{\text{CH}}) L_r} = \frac{E_{\text{NCO}} (C_{\text{NCO}}) r}{E_{\text{CH}} (C_{\text{CH}}) r} \quad (3) \]

Combining equations (2) and (3) and assuming:

\[ (C_{\text{CH}})_s = (C_{\text{CH}})_r \]

% Unreacted NCO in reaction solution:

\[ \frac{(C_{\text{NCO}}) r}{(C_{\text{NCO}}) s} \times 100 = \left[ \frac{A_{\text{NCO}}}{A_{\text{CH}}} \right]_r \times 100 \frac{A_{\text{NCO}}}{A_{\text{CH}}} \left[ \frac{A_{\text{NCO}}}{A_{\text{CH}}} \right]_s \quad (4) \]
Values of \( \text{ANCO} \) and \( \text{ACH} \) were calculated from the infra-red spectra using the 'baseline density' method\(^8\) as shown in the following example:-

From Fig. 3.2.,

\[
\text{ANCO} = \log_{10} \left( \frac{I}{I_0} \right)_{\text{NCO}} = \log_{10} \left( \frac{AC}{BC} \right) \quad \text{(5)}
\]

and,

\[
\text{ACH} = \log_{10} \left( \frac{I}{I_0} \right)_{\text{CH}} = \log_{10} \left( \frac{XZ}{YZ} \right) \quad \text{(6)}
\]

hence,

\[
\begin{bmatrix}
\text{ANCO} \\
\text{ACH}
\end{bmatrix}
\]

can be calculated from equations (5) and (6).

Similarly \[
\begin{bmatrix}
\text{ANCO} \\
\text{ACH}
\end{bmatrix}
\]
was calculated from the spectrum of the standard solution, and '% unreacted NCO in the reaction solution' determined using equation (4).

Results and Discussion

By plotting 'Unreacted NCO (%)' versus 'Reaction Time', the time of reaction necessary for complete chain extension reaction can be determined. For relatively slow reactions (e.g. 1,5-DAN), reaction times were estimated by extrapolation of the curves obtained. Reaction times used are given in Table 3.2 (Section 3.4).

Graphs 3.1 - 3.6 illustrate the resulting curves for chain extension of prepolymer-4.75 NCO, using chain extension agents given in Table 3.2 (Section 3.4).
It would appear from Graph 3.1 that the more bulky chain extension agents give considerably slower reaction than the single ring phenylenediamines. This can be explained by the high steric hindrance presented by the bulky molecular structures.

0-Phenylenediamine and 2,3-Diaminofluorene were found to give unexpectedly high rates of reaction (Graphs 3.5 and 3.6). It would be anticipated that an amine group ortho to a urethane group would provide a very low rate of reaction with isocyanate groups. This would be predicted considering the high steric interference and the deactivating effect of the urethane group. One possible explanation of the observed phenomenon is the formation of hydrogen bonded complexes between amine groups and dimethylformamide carbonyl groups. In the case of chain extension agents having well separated amine groups (eg. 2,7-DAF), both amine groups are readily complexed and hence amine-isocyanate reactions are hindered. However, where amine groups are closer together (eg. 2,3-DAF), complexing of both amine groups is difficult and hence a high proportion of free amine groups are available for reaction with isocyanate.

Graph 3.2 illustrates the effect of catalysis on three chain extension reactions.
The extremely low extent of reaction can again be attributed to high steric hindrance in the case of MOCA and 2,4-Diamino-6-phenyl-s-triazine. The low reactivity of 1,4-B.D. is thought to be due to the low reactivity of the hydroxyl group with diisocyanate in solution. By using the highly active stannous octoate catalyst (1.0%), reaction rate is increased in all three cases.

Graph 3.3 illustrates the increased rate of reaction given by increased tin catalyst concentration in p-Phenylenediamine extended polyurethane. Rate of reaction is also increased with increased proportion of chain extension agent, as shown in Graph 3.4.

3.4 Summary of Polyurethane Materials Prepared

Table 3.2 summarises the reactions found to produce solid polyurethane materials. A nomenclature is adopted, whereby the polyurethane is labelled according to the chain extension agent incorporated.

Reactions of all diols investigated, with the exception of 1,4-B.D., were found to be extremely slow even in the presence of high tin catalyst concentration (1.5 - 2.0%). Solutions cast from the 1.0% catalysed 1,4-B.D. reaction produced solid elastomeric films, whereas other diols investigated yielded no useful solid materials (even after several days reaction).
It is suggested that the negligible chain extension reaction found for bulky diol reagents is due to several factors:

1. The OH/NCO reaction is very slow compared with the NH₂/NCO reaction.
2. The reactivity of H₁₂MDI is very low compared with most other commercial diisocyanates. This will lead to a particularly low OH/NCO reactivity.
3. Polymerisation in solution leads to a much slower chain extension reaction than bulk polymerisation, due to the higher dispersion and separation of reactant molecules.
4. Steric hindrance presented by the bulky diol molecules will also inhibit chain extension reaction in solution.

In view of the low reactivity of bulky diols under the experimental conditions used, attention was focussed on the diamine extended materials together with the 1,4-Butane Diol extended polymer (Table 3.2). The structure of these materials is represented by the formulae in Table 3.3.
# TABLE 3.2

## POLYURETHANES PREPARED BY SOLUTION POLYMERISATION

<table>
<thead>
<tr>
<th>CHAIN EXTENSION AGENT</th>
<th>POLYURETHANE NOMENCLATURE</th>
<th>PREPOLYMER (-NCO)</th>
<th>CHAIN EXTENSION AGENT (%)</th>
<th>CATALYST (%)</th>
<th>REACTION TIME (HRS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (10NCO)</td>
<td>10</td>
<td>95</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (15NCO)</td>
<td>15</td>
<td>95</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (90)</td>
<td>4.75</td>
<td>90</td>
<td>0.0</td>
<td>5.5</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (100)</td>
<td>4.75</td>
<td>100</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (0.1C)</td>
<td>4.75</td>
<td>95</td>
<td>0.1</td>
<td>3.0</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (0.5C)</td>
<td>4.75</td>
<td>95</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (1.0C)</td>
<td>4.75</td>
<td>95</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>p-PDA (1.5C)</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>1,5-Diaminonaphthalene</td>
<td>1,5-DAN</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>50.0</td>
</tr>
<tr>
<td>1,5-Diaminonaphthalene</td>
<td>1,5-DAN (10NCO)</td>
<td>10</td>
<td>95</td>
<td>0.0</td>
<td>50.0</td>
</tr>
<tr>
<td>1,5-Diaminonaphthalene</td>
<td>1,5-DAN (15NCO)</td>
<td>15</td>
<td>95</td>
<td>0.0</td>
<td>50.0</td>
</tr>
<tr>
<td>3,6-Diaminoacridine</td>
<td>3,6-DAA</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>40.0</td>
</tr>
<tr>
<td>3,6-Diaminoacridine</td>
<td>3,6-DAA (10NCO)</td>
<td>10</td>
<td>95</td>
<td>0.0</td>
<td>40.0</td>
</tr>
<tr>
<td>3,6-Diaminoacridine</td>
<td>3,6-DAA (15NCO)</td>
<td>15</td>
<td>95</td>
<td>0.0</td>
<td>40.0</td>
</tr>
<tr>
<td>2,7-Diaminofluorene</td>
<td>2,7-DAF</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>10.0</td>
</tr>
<tr>
<td>2,3-Diaminofluorene</td>
<td>2,3-DAF</td>
<td>4.75</td>
<td>95</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2,4-Diamino-6-phenyl-s-triazine</td>
<td>2,4-DPT</td>
<td>4.75</td>
<td>95</td>
<td>1.0</td>
<td>30.0</td>
</tr>
<tr>
<td>3,3'-Dichloro-4,4'-diaminodiphenylmethane</td>
<td>MOCA</td>
<td>4.75</td>
<td>95</td>
<td>1.0</td>
<td>15.0</td>
</tr>
<tr>
<td>1,4-Butane Diol</td>
<td>1,4-B.D.</td>
<td>4.75</td>
<td>95</td>
<td>1.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>
TABLE 3.3
CHEMICAL STRUCTURE OF
POLYURETHANE ELASTOMERS

a) Diamine Extended :

\[
\left[ A-O-C-N-R-N-C \{ N-R' \cdot N-C-N-R-N-C \}_x \right]_y
\]

b) Diol Extended :

\[
\left[ A-O-C-N-R-N-C \{ O-R'-O-C-N-R-N-C \}_x \right]_y
\]

Where :

\[
A = \left( \begin{array}{c} \text{Polyether ; } \\ \text{Soft Segment} \\ O-C-C-C-C_n \end{array} \right)
\]

\[
R = \left( \begin{array}{c} \text{Diisocyanate (H}_{12}\text{MDI) } \\ \text{Residue} \\ \text{Diamine Residue} \\ \text{Diol Residue} \end{array} \right)
\]
<table>
<thead>
<tr>
<th>TABLE 33 (cont'd)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diamine Extended</strong></td>
</tr>
<tr>
<td><strong>Polyurethane</strong></td>
</tr>
<tr>
<td>P-PDA</td>
</tr>
<tr>
<td>o-PDA</td>
</tr>
<tr>
<td>1,5-DAN</td>
</tr>
<tr>
<td>3,6-DAA</td>
</tr>
<tr>
<td>2,7-DAF</td>
</tr>
<tr>
<td>2,3-DAF</td>
</tr>
<tr>
<td>2,4-DPT</td>
</tr>
<tr>
<td>MOCA</td>
</tr>
</tbody>
</table>

| **Diol Extended** |
| **Polyurethane** |
| 1,4-BD            | ![chemical structure] |
Fig: 3.1

CHAIN EXTENSION REACTION - APPARATUS

KEY:
A. 250 ml. round bottomed, three-necked flask.
B. Glass stirrer rod fitted with PTFE paddle.
C. Cold Water condenser, fitted with silica gel guard tube.
D. Pressure equalising dropping funnel, wrapped in heater band.
Fig. 3.2

INFRARED SPECTRUM OF p-PDA CHAIN EXTENSION SOLUTION AFTER REACTION FOR 1 HOUR AT 90°C

N-H  C-H  -N=C=O

Transmittance (%)  100  75  50  25

Baseline

Wavenumber (cm⁻¹)  4000  3500  3000  2500  2000
Wavelength (µm)  2.5  3  3.5  4  5
GRAPH 3.1 - Uncatalysed Diamine Chain Extension Reactions of Prepolymer-4.75NCO in DMF

KEY:
- △ 1,5-DAN
- □ 3,6-DAA
- ○ 2,7-DAF
- ○ p-PDA
- ▽ o-PDA
- ○ 2,3-DAF

Unreacted NCO (%) vs. Time (Hours)
GRAPH 3.2 - Catalysis of 2,4-DPT, 1,4-B.D. and MOCA Chain Extension
Reactions of Prepolymer-4.75NCO in DMF.

KEY:
- 2,4-DPT
- 1,4-B.D.
- MOCA
- 2,4-DPT (1.0% catalyst)
- MOCA (1.0% catalyst)
- 1,4-B.D. (1.0% catalyst)
GRAPH 3.3 - Catalysis of p-PDA Chain Extension Reactions of Prepolymer-4.75NCO in DMF

KEY:
- p-PDA
- p-PDA (0.1C)
- p-PDA (0.5C)
- p-PDA (1.0C)

Unreacted NCO (%) vs Time (Hours)
GRAPH 3.4 - Effect of Stoichiometry on p-PDA Chain Extension
Reactions of Prepolymer-
4.75NCO in DMF

KEY:
- p-PDA (90)
- p-PDA
- p-PDA (100)

Unreacted NCO (%) vs. Time (Hours)
GRAPH 3.5 - Comparison of p-PDA & o-PDA Chain Extension Reactions of Prepolymer-4.75NCO in DMF

KEY:

- ▼ o-PDA
- ○ p-PDA
GRAPH 3.6 - Comparison of 2,7-DAF & 2,3-DAF Chain Extension Reactions of Prepolymer-4.7S NCO in DMF

KEY:
- □ 2,7-DAF
- ○ 2,3-DAF

Unreacted NCO (%) vs. Time (Hours)
CHAPTER 4

POLYURETHANE CHARACTERISATION

4.1 Introduction

After conditioning for at least two weeks at constant temperature and humidity (Section 3.3.3), polymer films were characterised by molecular weight determination and infra-red spectroscopic analysis. Solubility of films in DMF were determined, and densities were measured using a density gradient column.

Molecular weight determination was necessary in order to show any marked variation in average molecular size between polymers derived from different chain extension agents. It has been shown that the physical and mechanical properties of polyurethane elastomers (as in the case of all other polymeric materials) are dependent on molecular weight\textsuperscript{29}, particularly at lower values. As the present work is concerned with the effect of molecular structure on properties, any significant variation in molecular weight must be taken into account, as this may greatly influence the properties of the material.

The molecular structure of solid polyurethane materials was investigated by infra-red spectroscopic analysis. Spectra were examined for characteristic group absorption bands due to component groups present in the polyurethane structure.
Solubility was estimated in order to investigate the extent of crosslinking present in the polyurethanes prepared. It was shown in Chapter 2, that properties of polyurethane elastomers are dependent on the degree of crosslinking present. It is necessary therefore in the present work, to estimate the extent of crosslinking and the resulting contribution to physical properties.

4.2 Infra-Red Studies of Hydrogen Bonding in Segmented Polyurethane Elastomers

Several notable investigations into the nature and extent of hydrogen bonding in segmented polyurethane elastomer systems have been reported. Tanaka\textsuperscript{86} (et al) estimated that at least 85\% of NH groups were hydrogen bonded in a solid polyurethane based on TDI. Trifan and Terenzi\textsuperscript{34} reported essentially complete hydrogen bonding in polyurethanes based on an aliphatic diisocyanate, and Nakayama\textsuperscript{87} (et al) reported the same result in MDI based elastomers.

Infra-red spectroscopic techniques have been used to determine the groups involved in hydrogen bonding in these materials. While the majority of hydrogen bonding occurs between hard segments, it appears that a significant proportion also occurs between the hydrogen atom of the NH group (in the polyurea or polyurethane hard segment) and the ether oxygen of the polyether soft segment.
Similarly, in polyester based urethanes, hydrogen bonding occurs between the NH groups and the soft segment ester carbonyl oxygen atoms.

Paik Sung and Schneider\textsuperscript{39} investigated hydrogen bonding in polyether/TDI based polyurethanes, extended with 1,4-Butane Diol. Three major absorption regions were investigated:-

a) N-H stretching band in the region of 3300 cm\textsuperscript{-1}

b) C=O stretching band in the region of 1700-1740 cm\textsuperscript{-1}

c) COC stretching band in the region of 1000 cm\textsuperscript{-1}

The major NH band at 3300 cm\textsuperscript{-1} is attributed to the hydrogen bonded NH groups, while a shoulder on the high frequency side (near 3460 cm\textsuperscript{-1}) is assigned to the non-bonded NH groups. By comparison of the relative absorbances of these groups, using values of extinction coefficients reported on a model TDI system, Paik Sung and Schneider showed that 95\% of all NH groups are hydrogen bonded in the solid state at room temperature.

Splitting of the carbonyl band (1700-1740 cm\textsuperscript{-1}) due to hydrogen bonding has been reported by Seymour\textsuperscript{38} (et al) for a polyether/MDI based elastomer. A band at 1733 cm\textsuperscript{-1} was attributed to free carbonyl groups, while a band at 1703 cm\textsuperscript{-1} was assigned to hydrogen bonded carbonyl groups. Similarly, Paik Sung and Schneider\textsuperscript{39} reported splitting of the carbonyl band for their polyether/TDI materials.
2,4-TDI based polymers were assigned a hydrogen bonded absorption at 1720 cm\(^{-1}\) and an absorption due to free carbonyl groups at 1740 cm\(^{-1}\). Spectra of 2,6-TDI based polymers showed a band at 1700 cm\(^{-1}\), assigned to bonded carbonyl groups, and a band at 1740 cm\(^{-1}\) assigned to free carbonyl groups. Assuming the extinction coefficients of the bonded and free carbonyl groups are equal, it was shown that 50\% of the urethane carbonyl groups for 2,4-TDI polyurethane samples and 80\% for 2,6-TDI samples are hydrogen bonded to the urethane NH groups. If it is assumed that the only other proton acceptor in this system is the ether oxygen, then the remainder of the NH groups must be hydrogen bonded to the ether groups, thus giving an estimate of the extent of hard/soft segment interaction.

However, it was shown that although essentially all NH groups are hydrogen bonded in model hard segment copolymers (prepared from diisocyanate and diol), a significant proportion of carbonyl groups remain free. This result demonstrates the presence of NH groups hydrogen bonding with the urethane alkoxyl oxygen. An estimate of this type of interaction in the segmented materials was not possible, as it requires analysis of the absorption bands in the ether region (approximately 1000 cm\(^{-1}\)) which presents complexities from bands such as those due to the asymmetric ester stretching vibration.
Tanaka\textsuperscript{83} (et al) showed that in polyether based polyurethane materials, the primary acceptor in hydrogen bonding depends on the size of the soft segment (polyether). As the size of the polyether segment increases, there is increased hydrogen bonding between NH groups and ether groups, and a decrease in the bonding between NH groups and hard segment carbonyl groups. Further evidence of this effect is provided by the results of Nakayama\textsuperscript{87} (et al) on polyether/MDI based materials, extended with ethylene diamine. Polymers having high molecular weight polyether segments ($\overline{M}_n = 8390$) showed no splitting of the carbonyl band at 1727 cm$^{-1}$, indicating that the majority of NH groups must be hydrogen bonded with the polyether oxygen atoms.

4.3 Experimental

4.3.1 Molecular Weight Determination

The Number Average Molecular Weight, $\overline{M}_n$ (Appendix 2), of each polymer film was determined by either Vapour Pressure Osmometry or Membrane Osmometry. The choice of technique depends on the molecular weight range under investigation; Vapour Pressure Osmometry is suitable for values of $\overline{M}_n$ less than approximately 20,000, whereas Membrane Osmometry is used for values of $\overline{M}_n$ greater than approximately 20,000.
a) **Vapour Pressure Osmometry**

**Basic Principles**

The Vapour Pressure Osmometer consists essentially of a constant temperature compartment containing a saturated atmosphere of solvent vapour. Two thermistor beads connected at the end of a probe, are situated in the solvent vapour atmosphere. A drop of pure solvent is placed on one of the beads, and a drop of polymer solution of known concentration is placed on the other. The small temperature difference resulting from different rates of solvent evaporation from and condensation onto the two droplets, is then measured. Assuming this temperature difference is proportional to the vapour pressure lowering of the polymer solution at equilibrium, the Number Average Molecular Weight can be determined (See Appendix 2). A series of measurements using polymer solutions of different concentration are made, and the results extrapolated to zero concentration.

**Experimental**

A Knauer Vapour Pressure Osmometer (connected to a potentiometric chart recorder) was used to measure values of $\bar{M}_n$. Measurements were made using chloroform as solvent at 37°C. The glass solvent reservoir and syringes were thoroughly cleaned in chloroform and dried in a drying cabinet, before use.
A calibration constant was determined, using benzil as a standard of known molecular weight (Appendix 2). Polymer solutions of accurately known concentration in the range 10^-40 g.l.\(^{-1}\) were used in the determination of \(\bar{M}_n\). Solutions of at least four different concentrations were used for each polymer.

The method of calculation of \(\bar{M}_n\) from the data obtained is given in Appendix 2.

b) **Membrane Osmometry**

**Basic Principles**

A membrane osmometer consists basically of two compartments separated by a semipermeable membrane through which only solvent molecules can pass. Each compartment is closed except for capillary tubes. With pure solvent at one side of the membrane, and polymer solution at the other, solvent molecules diffuse through the membrane, creating a hydrostatic pressure (i.e., the level of liquid in the solution capillary becomes greater than that in the pure solvent capillary). This hydrostatic pressure causes an increase in solvent activity on the solution side. An equilibrium is reached therefore, at which the hydrostatic pressure is equal to the pressure created by diffusion of solvent molecules from the solvent compartment. This pressure is termed the Osmotic Pressure.

By measuring the Osmotic pressure of a polymer solution at various concentrations, \(\bar{M}_n\) can be determined (See Appendix 2).
Experimental

Values of $M_n$ were determined using a Knauer Membrane Osmometer connected to a potentiometric chart recorder. (The instrument was used according to the procedure outlined in the manufacturer's handbook). Freshly distilled DMF was used as solvent and was degassed before use, to avoid the inclusion of small air bubbles in the system. Measurements of Osmotic pressure were made at $37^\circ C$ using a cellulose membrane (Schleicher & Schüll Selectron-filter, 0.005/μm). Membranes were conditioned in alcohol/DMF solutions of increasing DMF concentration and finally in 100% DMF immediately before use. Measurements were taken on polymer solutions of accurately known concentration in the range 5-20g.l⁻¹. At least four solutions of different polymer concentration were used for each polymer. Values of $M_n$ were calculated from the Osmotic pressure at zero concentration (obtained by extrapolation) as shown in Appendix 2.

4.3.2 Infra-Red Spectroscopic Analysis

Basic Principles

When electromagnetic radiation falls on a material, energy is absorbed due to molecular transitions between quantum states corresponding to different internal energies. The energy of most molecular vibrations corresponds to that of the infra-red region of the electromagnetic spectrum.
Molecular vibrations in most organic materials, including polymers, generally occur in the wavelength range 2.5 μm to 15 μm (1 μm = 10^-6 m), i.e. 4000 cm^-1 to 660 cm^-1 (cm^-1 = reciprocal of wavelength). Functional groups of a molecule possess characteristic vibrational frequencies, and by observing these absorption frequencies, information on the overall molecular structure can be obtained.

Infra-red spectra are normally observed using a double beam infra-red spectrophotometer. This consists basically of a source of infra-red radiation, and a dispersion system to give a spectrum of varied wavelength radiation. Prisms of inorganic salts and diffraction gratings are commonly used as dispersion agents. The beam of monochromatic radiation is split into two beams of equal intensity by means of a system of mirrors. One beam is arranged to pass through the sample, and the other through a suitable reference medium.

If the frequency of a vibration of the sample molecule falls within the range of the instrument, the molecule will absorb energy at this frequency, resulting in a difference in the intensities of the sample and reference beams which is detected by a photocell system. The final spectrum is recorded on a chart recorder which is coupled to the dispersion and detection systems. Spectra show peaks, corresponding to absorption, plotted against wavelength (or frequency).
In the system outlined above, absorption of infrared radiation by the sample can be brought about using two techniques:

a) Transmission of radiation through the sample.

b) Reflection of radiation from the sample.

Transmission techniques are most commonly used, in which infrared radiation is passed directly through the sample. Solutions, vapours, liquid films and mulls provide suitable samples for this technique. Solid samples, particularly polymeric films and sheets, can be readily investigated using infra-red reflection methods:

**Infra-Red Reflection Spectroscopy**

Multiple Internal Reflectance (MIR) spectroscopy, also termed Attenuated Total Reflectance (ATR) spectroscopy, is a relatively recent technique. The infra-red ATR unit consists essentially of a flat crystal (usually Thallium iodide), arranged in the sample beam of the spectrophotometer so that infra-red radiation can pass through it by total internal reflection (see Fig. 4.1). Samples are clamped firmly on either surface of the crystal. When radiation is totally internally reflected at the surface of the crystal, a small proportion actually passes through the surface of the sample, and may be absorbed. On repeated internal reflection along the crystal, the sum intensity of absorption increases.
Therefore the emerging radiation has a lower intensity than the reference beam, and a spectrum is obtained in the usual way.

**FIG. 4.1**

**Experimental**

Spectra of solid polyurethane elastomer films were recorded using a Beckman TR-9 ATR unit (giving 9 internal reflections), installed in a Perkin-Elmer 457 Grating Infra-red Spectrophotometer. Samples of polymer film (approximately 0.5mm thick) were cut so as to cover the two surfaces of the crystal. Samples were dried in a vacuum oven at 50°C immediately before investigation, to remove any surface moisture which would give rise to characteristic -OH absorption bands. With film samples clamped firmly against the crystal surfaces, spectra were recorded between 600 cm\(^{-1}\) and 4000 cm\(^{-1}\) (16.5\(\mu\)m to 2.5\(\mu\)m), using a medium scanning mode.
The 100% adjustment was set at maximum to give zero obscuration of the sample beam, and a wide slit (setting 7) was used to give a sample beam of maximum energy. The reference beam was attenuated using an RIIC AT-04 attenuation device, to give a baseline at around 80% Transmittance.

For comparison, reference spectra of individual components in the elastomer systems were recorded by the normal transmission techniques, i.e. by applying a thin liquid film on sodium chloride discs. Spectra of solvent (DMF), catalyst (Stannous Octoate), prepolymer systems and diisocyanate (H_{12}MDI) were recorded in this way.

The MIR infra-red technique applied to solid films, essentially gives a spectrum of the molecular structure of the surface layers of the material. It was necessary therefore to observe the transmission spectra of several polymer films for comparison. Transmission spectra were obtained by casting 10% DMF solutions of polymer samples onto sodium chloride discs, evaporating off the solvent at 50°C in vacuo and recording the spectra in the usual way.

4.3.3 Solubility of Polyurethane Elastomers

Experimental

Samples of polymer films were weighed into graduated flasks, and dry DMF added to give solutions of concentration 20g.l^{-1}. Solutions were agitated at room temperature by means of a flask shaker, and the solubility of the films observed.
If necessary, solutions were heated gently on a hot plate.

4.3.4 Density Measurement

Experimental

The approximate densities of polymers were measured by means of a simple density gradient column, i.e. a column of liquid having a linear relation between density and height of the liquid in the tube. The column was prepared by very slowly adding 125ml Xylene (S.G. = 0.86) to 125ml carbon tetrachloride, (S.G. = 1.59) in a 250ml measuring cylinder clamped in a thermostatically controlled water bath at 23°C. When all the Xylene had been added, the interface between the two liquids was broken by rotating a long glass rod in the liquid column. The cylinder was stoppered and left for several hours to reach equilibrium. Coloured glass beads of accurately known density were then carefully lowered into the liquid column and left for 1 hour to settle at a constant height in the column. Care was taken not to allow any air bubbles to be introduced along with the beads, as these would lead to inaccurate results by apparently lowering the bead density. Having settled at constant levels, the calibration bead heights in the column were measured by means of a cathetometer. A calibration plot of density vs. height was plotted.
Samples of polyurethane films approximately 2 x 2 x 0.5mm were introduced into the column and allowed to settle to a constant height. Three samples of each film were used. By measuring the height of each sample in the column using a cathetometer, the sample density can then be obtained from the calibration plot by recording the density corresponding to the height measured.

4.4 Results and Discussion

4.4.1 Molecular Weight

Values of the Number Average Molecular Weight ($\bar{M}_n$) of polyurethane materials investigated are given in Table 4.1. Values were determined by membrane osmometry except where stated. The majority of $\bar{M}_n$ values lie in the region of 20,000-30,000. MOCA, 2,4-DPT, 3,6-DAA (10 NCO) and 3,6-DAA (15 NCO) are of significantly lower molecular weight and this factor should be taken into account when comparisons of physical property data are made. It is suggested that these relatively low values of $\bar{M}_n$ are due to low molecular weight fractions resulting from a predominance of amine 'capping' reactions compared with amine 'extension' reactions.
TABLE 4.1

NUMBER AVERAGE MOLECULAR WEIGHTS
OF POLYURETHANE ELASTOMERS

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Number Average Molecular Weight (Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PDA</td>
<td>28,000</td>
</tr>
<tr>
<td>o-PDA</td>
<td>19,400</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>24,000</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>22,000</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>30,000</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>19,000</td>
</tr>
<tr>
<td>1,4-B.D.</td>
<td>20,000</td>
</tr>
<tr>
<td>MOCA</td>
<td>11,500 φ</td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>12,000 φ</td>
</tr>
<tr>
<td>p-PDA (0.1C)</td>
<td>27,000</td>
</tr>
<tr>
<td>p-PDA (0.5C)</td>
<td>19,500</td>
</tr>
<tr>
<td>p-PDA (1.0C)</td>
<td>17,000</td>
</tr>
<tr>
<td>p-PDA (10 NCO)</td>
<td>18,000</td>
</tr>
<tr>
<td>p-PDA (15 NCO)</td>
<td>19,000</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>26,000</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>23,500</td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)</td>
<td>22,000</td>
</tr>
<tr>
<td>1,5-DAN (15 NCO)</td>
<td>19,000</td>
</tr>
<tr>
<td>3,6-DAA (10 NCO)</td>
<td>13,000 φ</td>
</tr>
<tr>
<td>3,6-DAA (15 NCO)</td>
<td>12,000 φ</td>
</tr>
</tbody>
</table>

φ Determined by Vapour Pressure Osmometry.
4.4.2 MIR Infra-Red Spectroscopic Analysis

Spectra of all polyurethane elastomers were found to be very similar to that of p-PDA as shown in Figs. 4.2 and 4.3. Assignments of the most pronounced absorption bands in p-PDA are given in Table 4.2. Four major absorption regions are apparent:

1. 3320 cm\(^{-1}\) N-H stretch
2. 2790-2935 cm\(^{-1}\) CH\(_2\) stretch
3. 1635-1725 cm\(^{-1}\)
   - 1510-1570 cm\(^{-1}\) Amide (-NHCO-) characteristic vibrations
   - 1220 cm\(^{-1}\)
4. 1110 cm\(^{-1}\) Ether (-COC-) characteristic vibrations

All polyurethane elastomers gave absorptions in these characteristic regions.

The spectrum below 1500 cm\(^{-1}\) is the "Fingerprint" region, is characteristic of the individual molecular structure it represents. Assignment of absorption bands in this region to particular functional group vibrations can be misleading, especially as combination and overtone bands may be present. However the assignments of the more intense bands (Table 4.2) are helpful in characterisation of the material under investigation. Only minor variations between spectra of elastomers were found in the fingerprint region. These variations were due mainly to the variation in structure of the chain extension agent.
For example, the absorption band at 1410 cm\(^{-1}\) assigned to the aromatic ring (C-C) stretching vibration in p-PDA, is absent in the 1,4-B.D. elastomer spectrum. Also, variation in absorption bands below 900 cm\(^{-1}\) can be attributed to the different substitution pattern ring structures of the chain extension agents in different elastomers, e.g. p-PDA gives bands at 830 cm\(^{-1}\) and 810 cm\(^{-1}\) due to the characteristic (CH) bending mode of two adjacent H atoms on a benzene nucleus, while o-PDA gives bands at 760 cm\(^{-1}\) and 740 cm\(^{-1}\) due to the characteristic (CH) bending mode of four adjacent H atoms.

The spectrum of 1,4-B.D. shows the absence of a distinct band at 1635 cm\(^{-1}\), assigned to the urea (C=O) stretching mode. This is reasonable, as only urethane groups would be anticipated in the 1,4-Butane Diol extended material.

As the size of the hard segment in the elastomer increases, the following principal changes were observed in the infra-red spectra:

1. The bands at 1450 cm\(^{-1}\) (CH\(_2\) bend) and 1370 cm\(^{-1}\) (CH\(_2\) wag) decrease in intensity.
2. The bands at 1725 cm\(^{-1}\) and 1700 cm\(^{-1}\) (both urethane Amide C=O stretch) decrease in intensity.
3. The band at 1635 cm\(^{-1}\) (Urea Amide C=O stretch) increases in intensity.

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This effect was shown in p-PDA, 1,5-DAN and 3,6-DAA elastomers of increasing hard segment size (ie. derived from 4.75, 10 and 15% NCO prepolymer), and is consistent with the increased urea/urethane and urea/CH₂ ratios anticipated due to the increase in urea group concentration.

Films of p-PDA prepared using different catalyst concentration (ie. 0.1, 0.5, 1.0% stannous octoate) showed no apparent variation in spectra, all giving absorption corresponding to those of the uncatalysed p-PDA spectrum. Spectra of p-PDA (90) and p-PDA (100) also gave spectra identical to p-PDA.

All polyurethane elastomers gave spectra showing the absence of an isocyanate (-NCO) absorption band at 2270 cm⁻¹, indicating the complete reaction of H₁₂MDI. Comparison of spectra with the solvent (DMF) reference spectrum showed no evidence of residual solvent.

Transmission spectra were found to be identical with MIR infra-red spectra of elastomers, indicating that the MIR technique gives rise to absorption spectra representative of the internal structure (as well as the surface layers) of the materials investigated.
**TABLE 4.2**

**MAJOR ABSORPTION ASSIGNMENTS IN MIR INFRA-RED SPECTRA OF POLYURETHANE ELASTOMERS**

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Relative Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3320</td>
<td>M</td>
<td>U/UT (N-H) stretch</td>
</tr>
<tr>
<td>2935</td>
<td>S</td>
<td>POTM/H₁₂MDI (CH₂) stretch</td>
</tr>
<tr>
<td>2855</td>
<td>S</td>
<td>POTM/H₁₂MDI (CH₂) stretch</td>
</tr>
<tr>
<td>2790</td>
<td>M</td>
<td>POTM (CH₂) stretch</td>
</tr>
<tr>
<td>1725</td>
<td>M</td>
<td>UT Amide I (C=O) stretch</td>
</tr>
<tr>
<td>1700</td>
<td>M</td>
<td>UT Amide I (C=O) stretch</td>
</tr>
<tr>
<td>1635</td>
<td>M</td>
<td>U Amide I (C=O) stretch</td>
</tr>
<tr>
<td>1510-1570</td>
<td>Several bands M/S</td>
<td>U/UT Amide II</td>
</tr>
<tr>
<td>1450</td>
<td>M</td>
<td>POTM/H₁₂MDI (CH₂) bend</td>
</tr>
<tr>
<td>1410</td>
<td>M</td>
<td>Benzene ring (C-C) stretch</td>
</tr>
<tr>
<td>1370</td>
<td>M</td>
<td>POTM/H₁₂MDI (CH₂) wag</td>
</tr>
<tr>
<td>1310</td>
<td>M</td>
<td>Benzene ring (CH) bend</td>
</tr>
<tr>
<td>1220</td>
<td>S</td>
<td>U/UT Amide III</td>
</tr>
<tr>
<td>1110</td>
<td>S</td>
<td>POTM (C-O-C) stretch</td>
</tr>
<tr>
<td>900</td>
<td>Several bands M/W</td>
<td>Benzene ring (CH) bend</td>
</tr>
</tbody>
</table>

φ  S = Strong, M = Medium, W = Weak
φφ  U = Urea, UT = Urethane, POTM = Poly(oxytetramethylene), H₁₂MDI = Hydrogenated Diphenylmethane diisocyanate.
4.4.2.1 Extent of Hydrogen Bonding in Polyurethane Elastomers

From Fig. 4.2, the characteristic NH absorption band at around 3320 cm\(^{-1}\) is seen to have a shoulder at approximately 3450 cm\(^{-1}\). The band at 3320 cm\(^{-1}\) is assigned to hydrogen bonded NH groups, and the shoulder at 3450 cm\(^{-1}\) to free NH groups. The effect of different chain extension agents on the extent of hydrogen bonding and hence on the splitting of the NH absorption band, is illustrated in Figs. 4.4 and 4.5. A simple estimation of the extent of hydrogen bonded NH interactions was made as follows:

By using the baseline method (Section 3.3.4), the absorbances at the absorption maxima were calculated. The absorbance, \(A_b\), of the hydrogen bonded absorption maximum is given by:

\[ A_b = E_b C_b L_b \]

Similarly, for the free NH absorption maximum:

\[ A_f = E_f C_f L_f \]

Where \(E_b\), \(E_f\) = Extinction coefficients of the bonded and free NH absorption maxima respectively.

\(C_b\), \(C_f\) = Concentration of the bonded and free NH groups respectively.

\(L_b\), \(L_f\) = Radiation path length through the bonded and free NH group absorbing medium respectively.
As an approximation, assuming $E_b = E_f$, then:

$$A_b = kC_b$$

and $A_f = kC_f$  
(Where $k$ is a constant)

The proportion of bonded NH groups is then given by:

$$\text{Hydrogen Bonded (NH) %} = \left( \frac{A_b}{A_b + A_f} \right) \times 100$$

Using this approximation, the values given in Table 4.3 were calculated from the spectra of polyurethane materials.

Polyurethanes of larger hard segment size (ie. p-PDA (10 NCO); p-PDA (15 NCO); 1,5-DAN (10 NCO); 1,5-DAN (15 NCO); 3,6-DAA (10 NCO); 3,6-DAA (15 NCO)), all showed little evidence of a free NH absorption band at 3450 cm\(^{-1}\), indicating essentially complete hydrogen bonding in these materials.

From Figs. 4.4 and 4.5 and the values given in Table 4.3, it would appear that there is little significant variation in the proportion of hydrogen bonded interactions in most of the polyurethane elastomers investigated. However, 2,4-DPT and 2,3-DAF elastomers do exhibit a marked decrease in hydrogen bonding, and it would appear that the majority of NH groups do not take part in hydrogen bonding in these materials. This can be explained by considering the molecular geometry of the polyurea hard segments. In both cases, a bulky aromatic pendant group is present (due to the structure of the chain extension agent).
It is suggested that the presence of these pendant groups causes increased separation of the hard segments to such an extent, that hydrogen bond formation between carbonyl groups and NH groups is impaired.

**TABLE 4.3**

**EXTENT OF HYDROGEN BONDING IN POLYURETHANE ELASTOMERS**

<table>
<thead>
<tr>
<th>Polyurethane Elastomer</th>
<th>Hydrogen bonded NH groups (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PDA</td>
<td>68</td>
</tr>
<tr>
<td>o-PDA</td>
<td>66</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>70</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>64</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>65</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>41</td>
</tr>
<tr>
<td>1,4-8.0.</td>
<td>63</td>
</tr>
<tr>
<td>MOCA</td>
<td>64</td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>46</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>65</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>61</td>
</tr>
<tr>
<td>p-PDA (0.1C)</td>
<td>69</td>
</tr>
<tr>
<td>p-PDA (0.5C)</td>
<td>64</td>
</tr>
<tr>
<td>p-PDA (1.0C)</td>
<td>62</td>
</tr>
</tbody>
</table>
The splitting of the carbonyl group band to give a maximum at 1700 cm\(^{-1}\) and a maximum at 1725 cm\(^{-1}\) (Fig. 4.3, Table 4.2) can be assigned to hydrogen bonded and free urethane carbonyl groups respectively. However poor resolution of the two bands and confusion due to the adjacent urea amide band, make estimation of the extent of carbonyl hydrogen bonded interactions very difficult. Also the majority of hydrogen bonding would be expected to occur between NH groups and urea amide carbonyl groups, as these are present in greater concentration. However, no easily resolved splitting of the urea amide band at around 1640 cm\(^{-1}\) could be detected.

4.4.3 Solubility

The majority of polyurethane materials were found to be soluble in DMF after shaking for 24 hours at room temperature. 1,5-DAN and 2,7-DAF required heating to 60°C and were found to dissolve completely at this temperature. 1,5-DAN (10 NCO) and 1,5-DAN (15 NCO) dissolved on heating, leaving a small amount of gel phase, which was thought to be due to a fraction of crosslinked material.

The solubility of the polyurethane elastomers provides evidence of the essentially linear molecular structure of these materials.
4.4.4 Density

Using the simple density gradient column described, no apparent variation in polyurethane density was found within the limits of accuracy of the method.

All materials were found to have densities of $1.1\text{g cm}^{-3}$. 


FIG. 4.2
MIR INFRA-RED SPECTRUM OF p-PDA ELASTOMER;
2,000-4,000 cm\(^{-1}\)

- N-H

- CH\(_2\)
FIG. 4.3
MIR INFRA-RED SPECTRUM OF p-PDA ELASTOMER;
600-2,000 cm\(^{-1}\)
FIG. 4.4 - EFFECT OF CHAIN EXTENSION AGENT STRUCTURE ON SPLITTING OF THE NH ABSORPTION DUE TO HYDROGEN BONDING

1,4-BD

p-PDA

o-PDA

1,5-DAN

3,6-DAA

Wavenumber (cm⁻¹)
FIG. 4.5 - EFFECT OF CHAIN EXTENSION AGENT STRUCTURE ON SPLITTING OF THE NH ABSORPTION DUE TO HYDROGEN BONDING

- 2,7-DAF
- 2,3-DAF
- 2,4-DPT
- MOCA

Wavenumber (cm$^{-1}$)
CHAPTER 5

THERMAL ANALYSIS AND X-RAY SCATTERING INVESTIGATIONS

5.1 Introduction and Literature Review

The effect of chain extension agent on thermal transition behaviour and X-ray scattering was investigated in a series of polyurethane materials. By comparing results from thermal analysis and X-ray scattering, information on crystallinity and molecular organisation can be derived. Orientation and crystallinity in stretched elastomers were investigated by X-ray scattering. The effect of increasing hard segment size was observed in materials based on prepolymer of higher isocyanate content.

Thermal analysis was carried out using two complementary techniques, i.e. Differential thermal analysis (DTA) and Thermomechanical analysis (TMA). Schneider (et al) has demonstrated the importance of using more than one technique in giving reliable assignments to thermal transition behaviour. Wide-angle X-ray scattering (WAXS) techniques were used to detect the presence of molecular organisation, as shown by the X-ray patterns obtained.

As outlined in Section 2.1.2, much work has been carried out over recent years to elucidate the structure of segmented polyurethane elastomers.
It is generally accepted that phase segregation of soft and hard segments resulting in the formation of hard segment domains dispersed in a rubbery matrix is responsible for the high level of physical and mechanical properties. Thermal analysis and X-ray scattering techniques have proved particularly useful in these investigations, although much controversy still exists, especially concerning the role of hydrogen bonded interactions in structural formation.

**Thermal Analysis**

Miller and Saunders\(^{40,41,90}\) carried out a series of investigations into the effect of structure on the thermal transition behaviour of segmented polyurethane elastomers. The effect of changing the diisocyanate structure\(^{41}\) in a system based on poly(ethylene adipate) and 1,4-Butane diol was investigated. Diisocyanates included MDI, TDI, hydrogenated MDI, hydrogenated TDI and hexamethylene diisocyanate (HDI). All diisocyanates were found to give a first order transition at approximately \(-40^\circ C\) (except TDI, \(-18^\circ C\)), which was associated with the glass transition temperature of poly(ethylene adipate). A transition found between \(70^\circ C\) and \(83^\circ C\) for all polymers was thought to be due to the disruption of soft/hard segment hydrogen-bonded interactions, while a transition between \(160^\circ C\) and \(183^\circ C\) was associated with the disordering of hard segments.
The latter assignment was based on transitions observed\textsuperscript{40} in poly(ethylene adipate)/MDI elastomers extended with 1,4-B.D., and samples representing the soft and hard segments. MDI/1,4-B.D. (1:1) samples (ie. hard segment) showed melting transition behaviour between 275\textdegree{}C and 300\textdegree{}C, whereas MDI/Poly(ethylene adipate) (1:1) samples (ie. soft segment) showed softening around 45\textdegree{}C. The intermediate transition of 170\textdegree{}C found for the segmented polyurethane was therefore associated with interference by the polyester soft segment, preventing high ordering of the hard segment and hence reducing the melting temperature.

A transition between -130\textdegree{}C and -141\textdegree{}C,\textsuperscript{41} as found by differential scanning calorimetry, was attributed to the true glass transition temperature of the polyurethanes. In materials extended with 1,4-B.D. and using HDI, this transition rises to -93\textdegree{}C. This effect was explained as due to the expected change in glassy behaviour which accompanies an increase in crystallisation of the bulk elastomer.

A comparison of the high temperature transitions in elastomers based on MDI and hydrogenated MDI showed a lower temperature transition in the case of hydrogenated MDI. This was associated with the poorer 'fit' of the cyclohexyl units compared with that of the phenylene units, resulting in poorer packing of the hard segments.
It was suggested that the poor 'fit' of the cyclohexyl units may be partly due to the asymmetry introduced by the mixed cis/trans isomers of hydrogenated MDI. Similarly, the relatively low melting transition found for TDI elastomers was associated with the poor 'fit' due to the mixed 2,4 and 2,6 disubstitution patterns in TDI. Inefficient hydrogen bonding between hard segments results, and hence increased hydrogen bonded interactions between hard and soft segments is possible, leading to the higher observed value of the soft segment glass transition temperature (ie. -18°C).

Miller & Saunders\textsuperscript{41} demonstrated therefore, that all thermal transitions can be attributed to either the soft segment, the hard segment or interactions of the two. The following effects were suggested as being possible in segmented polyurethane materials:

1. The soft segment transition (particularly Tg) may be unaffected by copolymerisation.
2. Interference by the hard segments may lead to a reduction of soft segment transition behaviour.
3. Tg of the soft segment may be increased by hydrogen bonding with the hard segment.
4. The melting transition of the polyurethane hard segments may fall due to interaction with soft segments.
5. Transition of the hard segments may be low compared with the pure polyurethane due to short segment length.

6. Hard segments of sufficient length may form ordered (truly crystalline) regions giving transitions comparable to the pure polyurethane.

Clough & Schneider\(^9\) investigated thermal transition behaviour in 1,4-B.D. extended polyurethane elastomers based on poly(1,4-Butylene adipate)/MDI and poly (oxytetramethylene)/MDI. TMA and DSC (Differential scanning calorimetry) results for the polyester based elastomer were found to be in good agreement with the expansion and tensile results obtained by Miller and Saunders\(^4\) for a similar material.

The polyether based elastomer showed three major transitions by TMA. A transition at -85°C (termed \(T_1\)) was attributed to the \(T_g\) of the polyether soft segment, related to the onset of bond rotation. A transition at 60°C (termed \(T_2\)) was assigned to the dissociation of urethane-ether hydrogen bonded interaction, and a transition at 153°C (\(T_3\)) was attributed to the dissociation of hard segment hydrogen bonding and domain structure. \(T_2\) and \(T_3\) transitions were also found by DSC, although not as well defined as the TMA penetration results. The possibility of the \(T_3\) transition being due to allophonate or biuret bond dissociation, was discounted on the grounds of the low rate constant reported for this decomposition process at 150°C.
The $T_3$ transition was found to be sharper and more pronounced in the case of the polyether elastomer where it was suggested that inter-urethane hydrogen bonding was greater.

The polyester based elastomer showed a sharper $T_2$ transition, indicating more hard/soft segment association. Polymers with longer hard segments showed enhanced $T_3$ transitions, apparently due to better organised and more stable domain structures. This explains the increased modulus between $T_2$ and $T_3$ for these materials and the relatively low modulus above $T_2$ and poorly defined $T_3$ found for polymers of short hard segment length. It also explains the report by Colodny $^{92}$ (et al) that polymers with only a single hard segment unit flowed at temperatures above $T_2$. Clough and Schneider $^{91}$ also found small transition peaks by DSC around 205$^\circ$C for the polyether material and suggested that these may be due to the presence of spherulitic structures.

Ng $^{53}$ (et al) investigated thermal transition behaviour by DSC in polyurethanes based on poly (oxytetramethylene) soft segments and well defined hard segments composed of the piperazine/1,4-Butane diol bischloroformate reaction product. Hydrogen bonding is absent in these materials as there are no NH groups available.
A transition at approximately -70°C was associated with the glass transition temperature of the soft segment, and a poorly defined transition around 40°C was associated with the glass transition temperature of amorphous hard segment. Endotherms in the range 100°C - 190°C were thought to be due to melting of hard segment crystallites. Comparison of the transition behaviour of these materials with the hydrogen bonded polyurethanes of Huh\textsuperscript{93} (et al) demonstrates the increased soft segment Tg value in the hydrogen bonded systems associated with hard/soft segment hydrogen bonded interactions. Increased hard segment content in the piperazine elastomers was found to give higher soft segment glass transition temperatures. This was explained in terms of the interaction of hard segment domains with the soft matrix, i.e. the domains act as filler particles in the system. A poorly defined DSC transition at approximately 60°C was found to move to higher temperatures and finally merge with the higher temperature transition on annealing the sample. Similar behaviour has been reported in hydrogen bonded systems by Seymour\textsuperscript{94,95} (et al). The effect was explained by assigning a disordering of the more poorly ordered hard segments to the transition at 60°C. Annealing causes improved morphology reflected in the increased hard segment ordering and the rise in transition temperature.
Schneider\textsuperscript{89} (et al) investigated the effect of symmetrical (2,6-TDI) and asymmetrical (2,4-TDI) diisocyanate structures incorporated in a poly (oxytetramethylene) based polyurethane extended with 1,4-B.D. Thermal transition behaviour was observed by DSC and TMA (penetration) techniques. As DSC showed only poorly defined transitions, attention was focussed on TMA results. Three major transitions were observed, comparable to those reported by Clough and Schneider\textsuperscript{91}, and designated $T_1$, $T_2$ and $T_3$. The $T_1$ transition, associated with the soft segment glass transition temperature was found to increase with increasing hard segment content. $T_1$ for 2,6-TDI samples was lower by 50°C than the corresponding 2,4-TDI transitions. In 2,4-TDI materials a $T_2$ transition around 60°C was observed although no similar transition was found for 2,6-TDI samples. All 2,6-TDI polyurethanes displayed a repeatable transition ($T_3$) in the range 126-160°C, whereas only 2,4-TDI samples with highest urethane content showed a $T_3$ transition ($>150$°C). The $T_2$ transition in 2,4-TDI samples was taken to indicate domain structure with limited short range order. Increasing values of $T_2$ with increasing hard segment length was explained in terms of improved stability and organisation of domain structure. The absence of a $T_2$ transition in 2,6-TDI samples and the presence of an endothermic peak at $T_3$ in DSC traces was taken to indicate domain structure of a microcrystalline nature.
Annealing treatment of a 2,4-TDI sample was found to have no effect on the intermediate $T_2$ transition, in contrast to the effect observed in MDI polyurethanes. This apparent absence of a range of stable intermediate states of hard segment order was thought to be due to the inability of the asymmetrical 2,4-TDI structure to promote hard segment crystallisation processes. Defects in MDI polyurethane domain organisation can however be removed by annealing, owing to the symmetrical phenylene units in the hard segment.

**X-Ray Scattering**

In a series of publications, Bonart (et al) reported the investigation of structure in polyurethane elastomers using X-ray scattering techniques. A polyurethane based on poly(oxytetramethylene)/MDI and extended with hydrazine was investigated by wide-angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) techniques. Unstretched samples demonstrated no evidence of crystallinity in the WAXS photographs, showing a broad amorphous halo at 4.5Å. A weak interference ring at 12Å and a diffuse SAXS interference at around 130Å were also observed. WAXS photographs of samples extended to 500% showed clear fibre type diagrams having highly orientated crystal reflexes.
Comparison of these diagrams with the reported crystalline poly(oxytetramethylene) X-ray scattering data\textsuperscript{98-100} showed that the soft segments undergo crystallisation on extension. Strong crystal reflexes at 4.5Å and 3.7Å were associated with the (100) and (010) crystal indexes respectively. Polyurethane samples maintained at 500% extension and treated with warm water showed WAXS patterns having only an amorphous halo indicating the disappearance of soft segment crystallinity. The 12Å interference was found to persist however and was attributed to the hard segment. Samples extended to 500% and then relaxed, showed no evidence of soft segment crystallinity but the hard segment interference still indicated remaining orientation in this region. The 12Å spacing is too small to be associated with periodicity within the hard segments (approximately 25Å) and was therefore attributed to interplanar spacings associated with a defined lateral assemblage of hard segments based on a system of hydrogen bonded bridges.

X-ray scattering investigations were also carried out\textsuperscript{36} on poly(ethylene adipate) based elastomers using MDI and 1,5-Naphthalene diisocyanate (1,5-NDI) extended with 1,4-B.D. Elongated samples showed a 'd' spacing of 11.7Å which was thought to be less than the structural period of 12.2Å in the fully extended polyester, due to a twisting of the ethylene glycol component.
Polyurethane samples with longer hard segments showed hard segment reflexes in the unstretched state, and less complete stress induced crystallisation of the polyester soft segments on extension. It was suggested that the average length of 120Å estimated for these longer hard segments is high enough to allow true crystallisation. DTA results showed two major high temperature transitions. A transition at 170°C was associated with paracrystalline long range ordering through hard segment hydrogen bonded interactions, and a transition at 230°C was associated with true crystalline melting behaviour.

1,5-NDI elastomers did not show an intense reflex in the SAXS pattern as was found for MDI materials, and WAXS patterns of 1,5-NDI elastomers showed no hard segment interferences. This was thought to be due to the presence of crosslinking through biuret and allophanate groups in 1,5-NDI materials and extensive hard/soft segment mixing.

Hard segment interferences in MDI elastomers were interpreted as being due to paracrystalline long range ordering between densely packed but not crystallised hard segments. A model of short range ordering based on hydrogen bonded bridges was proposed, leading to a long range order pattern corresponding to the experimental results.
As this model only allows approximately 50% of all C=O and N-H groups to form hydrogen bonded bridges, it was suggested that hydrogen bonded bridges also form in a plane perpendicular to the two-dimensional plane of the model.

A comparison of aliphatic diol (eg. 1,4-B.D.) and aliphatic diamine (eg. hydrazine) chain extended polyurethanes by SAXS showed a retention of phase segregation at lower hard segment sizes in the diamine materials and a loss of phase segregation in the diol materials. This effect was thought to be due to the excess -NH groups present in the diamine extended materials, resulting in the interaction of C=O groups with at least two NH groups through hydrogen bonding in different directions. A model was proposed, in which each hard segment within a domain is found at the intersection of two crosslinking planes. This model explains why no evidence of phase segregation is found for 1,4-B.D. extended materials unless a molar ratio of 1:2:3 (soft segment:chain extender:MDI) or greater is used. At lower ratios, no free NH groups are available to form transverse crosslinking. However, diamine extended polyurethanes using a molar ratio of 1:1:2 can still form transverse crosslinking through excess NH groups as described above.

A SAXS study of polyether/MDI and polyester/MDI elastomers extended with hydrazine showed no decisive differences in domain segregation which might explain the higher heat distortion temperature of the polyether material.
It was concluded that the molecular weight distribution of the soft segment may be the most important factor. Evidence showed that a substantial amount of soft segment is included in the hard segment domains. Clough\textsuperscript{101} (et al) carried out SAXS investigations on polyether and polyester based elastomers and correlated patterns observed with the thermal transition behaviour reported\textsuperscript{91} for these materials. Soft segment crystalline scattering was found in polymers having a high molecular weight soft segment as well as in elongated samples. X-ray scattering in the temperature range 25°C-110°C (ie. from below the $T_2$ transition to between the $T_2$ and $T_3$ transitions) showed that in samples with longer hard segments, an interference greater than 100Å persists above $T_2$. This evidence suggests that the $T_3$ transition is associated with the hard segment domains. Samples of lower hard segment size gave no significant SAXS patterns, presumably because the length of the hard segments is too low to promote domain formation. Results also indicated greater phase segregation in polyether samples compared with polyester materials of similar composition. WAXS investigations\textsuperscript{91} on poly(oxytetramethylene)/MDI elastomers extended with 1,4-B. D. showed no evidence of crystalline scattering reflexes. Extended samples (>180%) gave scattering patterns with three equatorial peaks at 4.41Å, 3.57Å and 2.34Å, corresponding to those of crystalline high molecular weight poly(oxytetramethylene).
Samuels and Wilkes\(^4\) investigated the structure of non hydrogen-bonded piperazine polyurethanes (i.e. the materials used for thermal analysis by Ng\(^5\) (et al)) using WAXS and SAXS techniques. A well defined small angle interference corresponding to a Bragg spacing of approximately 100Å was thought to indicate domain structure. WAXS patterns showed an increase in sharp crystalline reflexes with increasing hard segment length. This was suggested to be due to the formation of larger crystalline components. Orientation of hard segments was found to be retained on relaxation of stretched samples.

Chang and Wilkes\(^4\) reported X-ray studies on a series of polyether (poly(oxyethylene) and poly (oxypropylene)) based elastomers. Hard segments were composed of H\(_{12}\)MDI and diamines of varying structures. A series of poly(oxyethylene)/H\(_{12}\)MDI/p-PDA materials of varying soft segment/hard segment relative sizes were investigated. Only samples with high molecular weight soft segments gave crystalline reflexes. All other samples showed no evidence of crystallinity. A broad band around 10-20Å was observed for each sample and was thought to be due to the existence of certain short-range ordering. A band at 4.5 - 5Å was associated with amorphous scattering. With increasing hard segment content, this band appeared to sharpen suggesting that some short-range ordering of this dimension is caused by hard segments.
SAXS patterns of the same series indicated the presence of domain structures with less well developed phase separation as the hard segment content is reduced.

A series of polyurethanes of similar composition, but using ethylene diamine as chain extension agent instead of p-PDA, gave WAXS patterns closely resembling those of the p-PDA series. However, two apparent differences were found. Firstly, the broad band around 10-20Å was found to decrease in intensity with increasing polyether content in ethylene diamine samples. This behaviour was not apparent in p-PDA samples, indicating that this periodicity is much more affected by soft segment content as a result of using ethylene diamine. It was suggested that the presence of the -(CH₂)₂- unit in both the soft segment (poly(oxyethylene)) and the hard segment (ethylene diamine residue) would lead to greater compatibility and hence reduced domain formation and segregation in the ethylene diamine samples. SAXS patterns also indicated less well-developed domain morphology as compared with the p-PDA materials. The second noticeable difference between the WAXS patterns of the two series, was the higher extent of short-range (4-6Å) ordering in the ethylene diamine series. No explanation of this effect was given, but it may be that some crystalline hard segment regions are present. Polyurethanes were also investigated using various other aromatic diamine chain extension agents, although it was reported that variations in crystallinity and domain structure were not intense enough to be detected.
Schneider et al. found that WAXS patterns of relatively asymmetrical polyurethanes based on 2,4-TDI showed only a broad amorphous ring. The more symmetrical 2,6-TDI polyurethanes of increased hard segment length, showed crystalline scattering. Reflexes at 3.44Å, 3.93Å, 4.62Å and 10.79Å were all associated with hard segment crystallinity as none of these spacings correspond to those expected for poly(oxytetramethylene) soft segment crystallinity.

5.2 Experimental
5.2.1 Thermal Analysis

Introduction

When a polymeric material is subjected to a broad range of temperature variation, several changes in physical and chemical properties may occur. Physical changes include changes in crystallinity associated with melting transitions and changes in molecular mobility such as the change in localised molecular motion associated with the glass transition temperature. Chemical changes include oxidation and degradation. As a result of these changes on a molecular level, experimentally detectable variations in certain properties occur. For example, heat may be evolved or absorbed by the material, the physical dimensions may alter, or the weight vary. By observing such variations, much information can be obtained about the extent of molecular ordering and the thermal transition behaviour exhibited by a polymeric material.
5.2.1.1 Differential Thermal Analysis

Basic Principles

In differential thermal analysis (DTA), small temperature changes of the sample material are monitored. These changes are due to heat being evolved or absorbed because of exothermic or endothermic activity in the sample, or they are due to distinct changes in the heat capacity of the sample.

In a typical DTA experiment, the sample and an inert reference material (which undergoes no thermal transition in the temperature range investigated) are heated at the same constant rate in close proximity. The temperature difference between the sample and the reference is measured using thermocouples connected in opposition. When the temperature of the sample is equal to that of the reference, the two thermocouples produce identical voltages and therefore the net voltage equals zero. When the temperatures differ, this is reflected by a resulting net voltage differential which is proportional to the difference in temperature. The net voltage differential is amplified and plotted on the vertical axis (y axis) of an x-y recorder. The temperature of the sample and reference environment, which is varied at a programmed constant rate, is monitored on the x axis.
Experimental Procedure

DTA thermograms of polyurethane materials were recorded using a Du Pont 900 Thermal Analyzer equipped with a standard Du Pont heating cell. Samples were used in the form of single pieces weighing approximately 15mg, encapsulated in small closed aluminium pans. Air, in an otherwise empty pan, was used as the reference.

With the reference placed on the right hand thermocouple of the heating cell and the sample on the left hand thermocouple, the cell was cooled to approximately -120°C by pouring liquid nitrogen into a surrounding steel jacket. Care was taken not to allow liquid nitrogen to flow outside the cooling jacket into the cell, as the resulting formation of ice would lead to unwanted transitions associated with the melting and boiling behaviour of H₂O. Having completed the cooling procedure, the cooling jacket was quickly removed and replaced by a steel cover and a pyrex glass surround. The cell was heated at a programmed constant rate of 20°C/min, with a steady purge of pure dry nitrogen flowing through. A sensitivity of 0.2°C/in. was found to be most suitable, giving optimum resolution on the y axis of the thermogram. Thermograms were recorded between -100°C and +300°C.
5.2.1.2 Thermomechanical Analysis

Basic Principles

In thermomechanical analysis (TMA), small changes in physical dimensions and mechanical response of the sample are monitored under varying temperature conditions. For example, changes in volume, stress-strain behaviour and penetration (i.e. compression behaviour) can be determined, reflecting molecular changes as outlined previously.

In a typical penetration TMA experiment, a probe is positioned on the sample surface and loaded to give a constant stress. A record of the penetration of the probe into the sample is obtained as a function of temperature. Movement of a metal core connected to the probe, is measured by means of a linear variable transformer providing an output proportional to the linear displacement of the core. The sample is heated at a programmed constant rate using a cylindrical furnace and the temperature of the sample is monitored using a thermocouple attached to the sample-holder tube stage. The resulting TMA thermogram consists of a plot of probe displacement vs. sample temperature.

Experimental Procedure

TMA thermograms of polyurethane materials were recorded using a Du Pont 941 Thermomechanical Analyzer connected to the Du Pont 900 temperature programmer-controller and x-y recorder.
A quartz probe with a 0.025 inch diameter flat tip was used in the penetration mode. Samples in the form of small squares approximately 3mm x 3mm and 0.5mm thick were used.

With the sample in position on the quartz sample-holder tube stage and the probe adjusted so that the tip just contacts the sample, the sample was cooled to approximately -120°C by means of a Dewar vessel of liquid nitrogen. Using a load of 10g on the probe, samples were heated at a rate of 20°C/min. Sensitivity of the recorder on the y axis was set at 0.008mV/in and TMA thermograms were recorded from -100°C to approximately +200°C. Investigation of materials of increased hard segment size, required the use of a 100g load to give marked penetration below 0°C.

5.2.2 X-Ray Diffraction Studies - Wide Angle X-Ray Scattering

Basic Principles

X-Ray diffraction provides a useful method for investigating the presence of ordered arrangements of atoms and molecules within a solid substance. X-Rays are produced when high-speed electrons strike a metal target causing ionisation of surface atoms and subsequent jumping of electrons into vacant orbitals. By this process, radiation is produced consisting of several distinct wavelength maxima, and by use of suitable filters, radiation of a well defined specific wavelength is obtained.
As the wavelengths of X-rays are comparable to interatomic distances, diffraction effects will occur when X-rays are focussed on a solid substance containing regularly arrayed atoms.

For constructive interference of X-rays reflected from parallel atomic layers, Bragg's Law must be obeyed:

\[ 2d \sin \theta = n\lambda \]  ---- (1)

where:
- \( d \) = distance between the atomic layers
- \( \theta \) = angle of incidence and reflection of X-rays at the atomic layers
- \( n \) = a constant = 0, 1, 2, 3 etc.
- \( \lambda \) = wavelength of X-rays

In a typical X-ray scattering experiment, the solid sample is placed in the path of the X-ray beam and a photographic plate is arranged to receive scattered radiation. Knowing the distance between the sample and the camera plate, the angle \( \theta \) can readily be determined. Using equation (1) and inserting the value of \( \lambda \) for the radiation used and also the appropriate value of \( n \), the \( d \) spacing can be obtained.

Wide-angle X-ray scattering (WAXS), where \( 2\theta \) is greater than \( \sim 3^\circ \), gives information describing the spatial arrangements of atoms in a solid material. More recently, small-angle X-ray scattering (SAXS) techniques have been employed, where \( 2\theta \) is less than \( \sim 3^\circ \). SAXS is useful in detecting larger periodicities such as morphological features at a higher dimensional level.
Experimental Procedure

WAXS photographs of all polyurethane samples were taken using a JEOL DX-GE-2S X-ray generator operating at 30kV and 30mA. Nickel filtered copper Kα radiation (λ = 1.5406Å) was used throughout, photographs being obtained using a flat plate camera. Samples in the form of films 10mm x 5mm and 0.5mm thick were mounted in the path of the X-ray beam with the face of largest surface area perpendicular to the beam. Photographs were taken using a sample to camera distance of 8.8cm, which was found to give well spaced and clearly defined scattering patterns for all polymers.

WAXS photographs of several stretched polyurethane elastomers were also taken. Elastomer samples in the form of long strips 5mm wide and 0.5mm thick were stretched to the desired elongation (measured using bench marks) and clamped on a perspex mounting bracket. The bracket is so designed that the stretched sample passes across a hole in the perspex, through which the X-ray beam is arranged to pass (Plate 1). For extensions greater than approximately 200%, this procedure was found to be inadequate due to slippage of the polyurethane film in the clamps. A bracket was therefore designed and built, to allow photographs of stretched ring samples to be taken (Plate 2).

Exposed X-ray films were developed in the normal way, so that areas of scattered radiation showed up as darkened regions.
Intensity measurements of these darkened regions were made by scanning each film using a Joyce-Loebel double-beam microdensitometer. Essentially, a collimated beam of light from a slit (2mm x \( \frac{1}{2} \) mm) is arranged to pass through the film which moves horizontally across the light path. The intensity of light transmitted through the film is compared with a reference beam, thus giving a measure of light obscuration due to the film. A gear ratio of 3:1 was used so that a trace of 'intensity' vs. '3 x distance across the film' was obtained.

5.3 Results and Discussion

Thermal Analysis

The major thermal transitions observed by DTA and TMA are summarised in Table 5.1. DTA transition temperatures were taken from the peak values of the broad endotherms and TMA transition temperatures were recorded as the intersection of the tangents to the two different slopes over the region of transition. Transition temperatures reported are corrected for chromel-alumel thermocouples using standard correction tables.

Polyurethanes prepared using different chain extension agents and based on prepolymer - 4.75 NCO, all showed a major DTA transition below 60°C. This is thought to be associated with the glass transition of the poly(oxytetramethylene) soft segment.
A typical DTA trace is illustrated by p-PDA (Fig. 5.1). The absence of any major endothermic behaviour, other than the low temperature transition, indicates that no crystallinity is present in these materials. The presence of small peaks above 200°C (see p-PDA, Fig. 5.1) has been reported previously in polyether based polyurethane elastomers. The origin of these minor transitions is not at all clear, although Clough and Schneider have suggested that they are due to the melting of polyether spherulites.

1,4-B.D. samples however, did show DTA endothermic behaviour above the glass transition of the soft segment (see 1,4-B.D., Fig 5.1). A broad multiple transition was observed between 65°C and 140°C, with endotherm maxima around 102°C and 114°C. This behaviour was tentatively assigned to melting phenomena associated with mixed soft-hard segment crystallinity. Unlike the polyurethanes prepared using various diamine chain extension agents, the (CH₂)₄ unit is common in both the hard segment and the soft segment and can be expected to give rise to relatively poor phase segregation. The resulting compatibility of soft and hard segments and the presence of the common (CH₂)₄ unit may then allow the formation of crystalline entities whose melting behaviour is broad and lies between the melting temperature of pure crystalline soft segment (approx. 43°C for poly(oxytetramethylene)) and the melting temperature of hard segment crystallites (in the order of 200°C)*.
Fig. 5.1 also illustrates the effect of increasing the size of the hard segments in p-PDA samples. 1,5-DAN showed similar behaviour. Two broad endotherms are seen to appear in p-PDA (10 NCO) and p-PDA (15 NCO) in the region of 160°C and 250°C. Definition is much improved in samples of highest hard segment size (ie. 15 NCO polymers). The following assignments would seem reasonable in view of the work reviewed in similar systems. Firstly, the transition at 160°C is thought to be associated with the disruption of paracrystalline regions formed through hydrogen-bonded hard segment aggregates. Secondly, the particularly high (250°C) temperature behaviour is associated with the melting of true crystalline hard segment regions. Aggregation of hard segments to form these crystalline entities is possible due to the increased size of hard segments in these materials compared with hard segments in materials based on prepolymer - 4.75 NCO.

TMA results show three major transitions in most of the polyurethanes investigated (Table 5.1 and Fig 5.2). These transitions correspond to those reported by Clough and Schneider and were, therefore, similarly designated $T_1$, $T_2$ and $T_3$.

* An approximate value based on the melting transitions of 230°C and 272°C reported for MDI/1,4-B.D. hard segment crystallites.
The low temperature transition $T_1$, is thought to represent the glass transition temperature of the polyether soft segment, and corresponds to the low temperature transition behaviour found by DTA. An intermediate transition $T_2$ can be attributed to the dissociation of soft-hard segment hydrogen bonded interactions, while the $T_3$ transition is thought to be due to the dissociation of hydrogen bonded hard segment domain structures.

1,4-B.D. polyurethane samples show only two transitions by TMA, i.e. a $T_1$ transition at -75°C and a second transition at approximately 75°C. The latter transition is thought to be essentially a $T_2$ transition, occurring at a slightly higher temperature than found in the case of other polyurethanes due to the actual crystalline regions present in the mixed soft-hard segments. This transition was designated ($T_2$) (Fig. 5.2).

2,4-DPT and MOCA polyurethanes show only broad transitions above room temperature at around 30°C, indicating substantial hard-soft segment mixing but relatively little physically bonded interaction between the two segment types.

p-PDA (10 NCO and 15 NCO) and 1,5-DAN (10 NCO and 15 NCO) show little evidence of $T_2$ transition behaviour. This suggests that the extent of hard-soft segment mixing is relatively low in these materials and the greater hard segment content aids the formation of a segregated domain structure. 3,6-DAA (10 NCO and 15 NCO) however did show $T_2$ transition behaviour.
This can be explained by the relatively asymmetric structure built into the hard segment by the bulky 3,6-diaminoacridine chain extension agent compared with the structures formed by p-phenylene diamine and 1,5-diaminonaphthalene. Asymmetry in the hard segments would lead to poor domain formation and segregation and hence a significant mixing of soft and hard segments, even at higher hard segment content.

DTA transitions were generally found to be represented by broad endotherms and TMA showed only gradual transitions. In view of this absence of sharp characteristic transitions, it was thought unwise to place too much emphasis on minor variations found between transition temperatures in various polyurethanes. However, several marked variations and trends do appear to arise from the polyurethanes investigated. The $T_1$ transition was found to occur in the region of $-70^\circ\text{C}$ for most samples. However, polyurethanes containing highly asymmetric groups, i.e. 2,3-DAF and 2,4-DPT show significantly higher values ($-42^\circ\text{C}$ and $-38^\circ\text{C}$ respectively). These results are supported by those of Schneider$^{89}$ (et al) on TDI materials and can be explained by the relatively poor 'packing' of hard segments containing asymmetric units. This results in mixing of hard segments with the soft matrix, causing inhibition of soft segment bond rotation through hydrogen bonded interaction.
The glass transition of the polyether segment, associated with T$_1$, is therefore raised. MOCA samples show a similar effect, which it is thought may be due to the bulky chlorine atoms introduced into the hard segment by the chain extension agent.

Variation in the symmetry of the chain extension agent also appears to have a marked effect on T$_3$. o-PDA, 3,6-DAA and 2,3-DAF show relatively low values of T$_3$ compared with the more symmetrical molecular structures of p-PDA, 1,5-DAN and 2,7-DAF. This effect can readily be explained by the ability of the latter structures to form more closely 'packed' hard segment domain structures having a high degree of hydrogen bonded interactions. 1,4-B.D., 2,4-DPT and MOCA show little evidence of a T$_3$ type transition, indicating poor hard segment domain formation.

Increasing the hard segment content (ie. % NCO) was found to cause an increase in the T$_3$ temperature for p-PDA, 1,5-DAN and 3,6-DAA. It is thought that this is due to the ability of the longer hard segments present to form larger domains with greater extents of hydrogen bonding. Hence a higher temperature is required to disrupt these improved domain structures. Improved domain structure in p-PDA and 1,5-DAN leads to negligible T$_2$ transition behaviour, whereas this still persists in the more bulky asymmetrical 3,6-DAA as explained previously.
### TABLE 5.1

**MAJOR THERMAL TRANSITIONS IN POLYURETHANE ELASTOMERS**

<table>
<thead>
<tr>
<th>POLYURETHANE</th>
<th>DTA*</th>
<th>TMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T1</td>
</tr>
<tr>
<td>p-PDA</td>
<td>-64</td>
<td>-71</td>
</tr>
<tr>
<td>o-PDA</td>
<td>-65</td>
<td>-66</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>-73</td>
<td>-75</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>-65</td>
<td>-79</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>-65</td>
<td>-69</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>-74</td>
<td>-42</td>
</tr>
<tr>
<td>1,5-B.D.</td>
<td>-64</td>
<td>-75</td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>-67</td>
<td>-38</td>
</tr>
<tr>
<td>MOCA</td>
<td>-76</td>
<td>-42</td>
</tr>
<tr>
<td>p-PDA</td>
<td>-64</td>
<td>-</td>
</tr>
<tr>
<td>p-PDA (10 NCO)</td>
<td>-61</td>
<td>159</td>
</tr>
<tr>
<td>p-PDA (15 NCO)</td>
<td>-80</td>
<td>167</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>-73</td>
<td>-</td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)</td>
<td>-67</td>
<td>167</td>
</tr>
<tr>
<td>1,5-DAN (15 NCO)</td>
<td>-65</td>
<td>162</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>-65</td>
<td>-</td>
</tr>
<tr>
<td>3,6-DAA (10 NCO)</td>
<td>-67</td>
<td>-</td>
</tr>
<tr>
<td>3,6-DAA (15 NCO)</td>
<td>-69</td>
<td>-</td>
</tr>
</tbody>
</table>

* Values reported are taken from the endotherm maxima.
Φ TMA (penetration) transitions recorded using a load of 100g. All other TMA (penetration) transitions recorded using a load of 10g.
Wide-angle X-ray Scattering

WAXS photographs illustrating the different scattering patterns observed are given in plates 3-10. Photographs presented were obtained by contact printing from the original exposed X-ray plates, and so scattered X-rays show up as light regions on a dark background.

Figs. 5.3 and 5.4 give results obtained from microdensitometer scans of original X-ray plates. The intensity values plotted on the 'y' axis are highly dependent on X-ray exposure time and sample thickness. As a certain amount of variation in exposure time (generally 10-15 minutes) was found necessary to give clear scattering patterns for different polyurethanes, no useful information can be derived from absolute values of scattering intensity or from comparison of the intensity of a particular reflection for different polyurethanes. However, the relative intensities of reflections for a particular polymer and the Bragg spacings associated with these reflections, do provide useful information. The angle of scatter (2θ) was calculated using the following relationship:-

\[ \tan (2\theta) = \frac{R}{x} \]

where: \( R \) = radius of scattered reflection (cm), as measured from densitometer scan.

\( x \) = sample to camera distance = 8.8cm.
Using Bragg's Law (Section 5.2.2) and inserting the calculated $\theta$ value together with the wavelength of the radiation used and the appropriate value of $n$ (= 1 for 1st order reflections), the d spacing can readily be obtained.

All polyurethane elastomers based on 4.75% NCO prepolymer, with the exception of 1,4-B.D., show WAXS patterns similar to that given by p-PDA (Plate 3 and Fig. 5.3). The presence of only a diffuse halo at 4.5Å indicates the absence of crystallinity in these materials. Scattering from the beam stop (indicated by the broken line in Figs 5.3 and 5.4) tends to obscure any reflections which may occur due to spacings greater than 10Å. 1,4-B.D. gave a WAXS pattern (Plate 8 and Fig. 5.4) having distinct crystalline scattering rings at approximately 3.6Å, 4.8Å and 6.9Å, as well as the broad amorphous type halo at 4.5Å. Rings discernable only on the original X-ray photograph are represented by the symbol (▽) in Fig. 5.3. Although the 3.6Å reflex appears close to the reported spacing\textsuperscript{35} of 3.7Å for the crystalline poly(oxytetramethylene) (010) index, the reflexes at 4.8Å and 6.9Å do not correlate with this type of crystalline structure. It would appear therefore, that crystalline entities occurring in the mixed soft-hard regions are responsible for this scattering.
The effect of increasing the hard segment content in p-PDA and 1,5-DAN is shown in Figs 5.3 and 5.4, and Plates 9 and 10. A crystalline ring at 4.1Å was found in p-PDA (15 NCO), while crystalline scatter in the region of 5.0Å and 18.0Å was found in 1,5-DAN (15 NCO). It is thought that these reflexes are associated with crystalline hard segment regions which are promoted by increased hard segment content and size. 3,6-DAA (15 NCO) however, showed no evidence of crystalline X-ray scatter, indicating the absence of hard segment crystallisation even at high hard segment content. This can be explained in terms of the relatively bulky, asymmetric structure of the hard segment, hindering crystalline formation.

Plates 3 to 7 illustrate the effect of elongation on the WAXS pattern of p-PDA. Samples extended 100% (Plate 4) show scattering giving distinct arcs, indicating the onset of molecular orientation. By 200% extension (Plate 5), a clear fibre diagram is given representing elongation crystallisation of the polyether soft segment. At 350% extension (Plate 7), the soft segment reflexes at 4.3Å and 3.6Å can be seen as intense spots. These reflexes correspond to the (100) and (010) indices respectively of crystalline poly(oxytetramethylene)\textsuperscript{35}. 

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FIG. 3.1
DIFFERENTIAL THERMAL ANALYSIS TRANSITIONS IN POLYURETHANE ELASTOMERS

- p-PDA
- p-PDA (10 NCO)
- p-PDA (15 NCO)
- 1,4-BD

Temperature (°C)
FIG. 5.2 - THERMOMECHANICAL ANALYSIS TRANSITIONS IN POLYURETHANE ELASTOMERS

Temperature (°C)

Relative Probe Displacement

T₁, T₂, T₃, (T₂)

1,4-B.D.
FIG. 5.3
MICRODENSITOMETER SCANS OF POLYURETHANE
WAXS PATTERNS: INTENSITY (I) VS. 2θ

INTENSITY

2θ (Deg)
FIG. 5.4
MICRODENSITOMETER SCANS OF POLYURETHANE WAXS PATTERNS: INTENSITY (I) VS. 2θ
PLATE 1: Wide Angle X-Ray Scattering (WAXS)
   Equipment with Strip Sample Elongation
   Bracket in Position.

PLATE 2: Wide Angle X-Ray Scattering (WAXS)
   Equipment with Ring Sample Elongation
   Bracket in Position.
PLATE 3: WAXS Photograph of Relaxed p-PDA Elastomer.

PLATE 4: WAXS Photograph of p-PDA Elastomer at 100% Extension.
PLATE 5: WAXS Photograph of p-PDA Elastomer at 200% Extension.

PLATE 6: WAXS Photograph of p-PDA Elastomer at 300% Extension.
PLATE 7: WAXS Photograph of p-PDA Elastomer at 350% Extension.

PLATE 8: WAXS Photograph of Relaxed 1,4-B.D. Elastomer.
PLATE 9: WAXS Photograph of Relaxed p-PDA (15 NCO) Elastomer.

PLATE 10: WAXS Photograph of Relaxed 1,5-DAN (15NCO) Elastomer.
CHAPTER 6

GENERAL MECHANICAL PROPERTIES

6.1 Introduction

The present chapter deals with the effects of structural variation on the general mechanical properties of segmented polyurethane elastomers. A review of the literature is given with particular emphasis on the effect of hard segment structure. The effect of chain extension agent on the following properties has been investigated:

a) Tensile properties
b) Tear strength
c) Tension set
d) Hardness

Tensile properties were measured over the temperature range of -25°C to +150°C, in order to correlate hard segment structural variation with strength properties particularly at elevated temperatures.

6.1.1 Literature Review

The effect of variation of the chemical structure of polyurethanes on the mechanical properties of the resulting material has been extensively reviewed in the literature 13,29,64 (see Chapter 2).
More recently attention has been focussed on the effects of chemical structure on the overall morphology in segmented polyurethanes and the influence of the resulting structural entities on properties.\textsuperscript{102-104}

Saunders\textsuperscript{30} pointed out that the retention of properties at elevated temperatures is governed by three main factors:

1. Chemical crosslinking
2. Intermolecular attractive forces.
3. Presence of stiff segments in the chain.

While chemical crosslinking may be formed in either the hard or soft segments, factors 2 and 3 are generally associated with the hard segment. By correct 'design' of hard segments the formation of domain structures may be promoted, which then serve as physical crosslinks throughout the system. By incorporation of long hard segments based on symmetrical groups having good 'Fit' and strong intermolecular attraction, the strength of domain structures can be enhanced. This effect was demonstrated\textsuperscript{30} in a polyester based material by varying the 2,4'/4,4' isomer ratio of MDI. As the proportion of asymmetrical 2,4' isomer is increased, the heat distortion temperature of the elastomer was found to decrease. Dunleavy\textsuperscript{31} (et al) measured the tensile properties of diol and diamine extended poly-caprolactone based materials at elevated temperatures.
Results showed that the amine extended polyurethanes exhibited greater high temperature strength retention, presumably reflecting the greater intermolecular attraction of urea groups compared with urethane groups.

Chang & Wilkes \textsuperscript{44} correlated morphological structure in segmented polyurethanes with stress-strain behaviour. They showed that the modulus decreases and extensibility increases with decreasing hard segment content in poly(ethylene oxide) based elastomers extended with either ethylene diamine or p-phenylene diamine. The trends were explained in terms of greater degree of domain formation and perfection with increasing hard segment content. At low hard segment content (<\sim 10\%), poor domain formation results and crystallisation of the soft segment accounts for the unexpectedly high modulus observed. Comparison of both modulus and breaking stress in ethylene diamine and p-phenylene diamine extended materials showed higher values for p-phenylene diamine. This would be predicted as p-phenylene diamine was shown to give greater phase separation and enhanced domain formation.

Estes \textsuperscript{102} (et al) has also shown an increase in modulus and tensile strength with increasing hard segment content in a polyether based material. Measurement of tensile properties over a broad temperature range demonstrated a decrease of stress at a given strain with increasing temperature.
The negative temperature coefficient of stress was explained in terms of the viscoelastic softening of hard segment domains resulting in a decrease in effective physical crosslinks.

Smith\textsuperscript{103,104} has reviewed the factors which contribute to strength and toughness in polyurethane elastomers with particular emphasis on the role of the dispersed phase. It was pointed out that tear strength is affected in a similar manner to tensile strength. The following strengthening processes are thought to be effective in a two phase system:

\begin{center}
\begin{tabular}{ll}
Matrix & Dispersed Phase \\
1. Viscoelastic dissipation of energy near crack tip & 1. Increased dissipation of energy \\
2. Strain induced crystallisation & 2. Deflection and bifurcation of cracks \\
3. Development of high orientation & 3. Induce cavitation \\
& 4. Plastic deformation of domains
\end{tabular}
\end{center}

Depending on the structure of an elastomer, several or possibly all of these processes may be active. For an elastomer to exhibit retention of strength over an extended range of temperature, it is necessary for a dispersed phase to be present. This will normally either take the form of strain-induced crystalline entities, or else the presence of finely divided filler particles. It is thought that domain structures in segmented polyurethane elastomers also act in this latter manner.
Morton\textsuperscript{105, 106} (et al) investigated the reinforcement characteristics of spherical polystyrene particles dispersed in SBR vulcanisates. Results demonstrated that the tensile strength increases with increased concentration and decreased size of particles. By using different plastics as filler, it was also shown that increased modulus of the filler improves the tensile strength of the filled vulcanisates. Analogously the concentration, size and perfection of hard segment domains influence the properties of a polyurethane elastomer.

At elevated temperatures it is thought\textsuperscript{103} that the strength of polyurethane elastomers is dependent primarily on changes in the viscous nature of the matrix and the stress required to induce plastic flow of domain structures. Smith\textsuperscript{103} investigated the change in tensile strength over a broad temperature range (-40°C to +160°C) for various two phase materials. Results showed that in the case of triblock elastomers, the tensile strength falls rapidly in a relatively narrow temperature range depending on the softening temperature of domains. Segmented polyurethane elastomers exhibit a rather less pronounced decrease in tensile strength presumably due to the presence of more poorly ordered domain structure and a small proportion of covalent crosslinking. Nevertheless, substantial increase in tensile strength with reduction in temperature may be primarily attributed to the progressive increase in domain toughness in polyurethane elastomers.
An increase in the viscous characteristics of the matrix is thought to provide a secondary strengthening process.

Results also demonstrated the relative reinforcement behaviour of MDI/1,4-B.D. and TDI/MOCA hard segment domains in a poly(oxytetramethylene) matrix. It was found that the MDI/1,4-B.D. gives rise to substantially lower strength elastomers and exhibits a rapid decrease in tensile strength at temperatures well below those which cause the TDI/MOCA domain reinforcement to deteriorate. This effect is thought to be primarily due to the relative lowering of the cohesive energy of hard segments by incorporating butane units. A greater extent of hydrogen bonding between urea groups compared with urethane groups may also play an important role.

Morbitzer and Hespe investigated the effects of chemical structure on extension set in poly(ethylene adipate) based polyurethane elastomers. Set was attributed to two main factors; strain-induced crystallisation and deformation of plastic domains. The contributions of these two factors were separated by measuring set before and after heating samples above the melting point of strain-induced crystallites. Results showed that elastomers containing higher hard segment content gave greater set.
On heating above the melting temperature of strain-induced crystallites, materials of relatively low hard segment content were found to lose almost all their residual extension, whereas materials of increased hard segment content retained a significant proportion. It can be concluded therefore, that plastic domain deformation plays only a minor role in extension set of polyurethane elastomers, but becomes increasingly more significant with increased hard segment content.

6.2 Experimental

Tensile Properties - Sample Geometry

Myers & Wenrich\textsuperscript{108} have recently compared tensile stress-strain data taken on elastomeric materials using three different sample geometries:

1. Standard tensile dumbbell
2. Ring
3. Oval

It is worthwhile considering the comparison of material deformation obtained using the widely accepted tensile dumbbell and the ring sample (used in the present work). By using a thermoplastic polyurethane material, points of stress concentration in samples were detected by observing the stress-whitening effect at elongations above 300\%. 

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In the case of dumbbell samples, it was found that the extensometer clamps act as stress concentrators, and that extensive deformation in the dumbbell tab leads to a varying strain rate. On initial deformation, ring samples exhibit tensile loading of material at the inner radius between the grip pins and at the outer radius over the pins. Material at the outer radius between the pins and the inner radius in contact with the pins, undergoes compressive loading. This strain gradient persists throughout the test. It was found that higher values of stress and strain at failure were obtained using dumbbell specimens. This was explained as being primarily due to the uniaxial nature of the dumbbell test compared with the ring test where material in contact with the pins experiences non-uniaxial deformation leading to failure in these regions.

In the present work, ring samples were used throughout. Preliminary investigations with both types of sample showed:

1. Dumbbell specimens tend to undergo slippage in standard grips. This is particularly true in a cyclic type of test (Chapter 8).
2. Ring samples allow the use of a variable temperature chamber, whereas dumbbells, requiring the attachment of an extensometer for accurate strain determination, cannot easily be adapted to variable temperature investigations.
3. By using specially designed ring sample grips having a total of four freely rotating pins, stress concentrations around pins were minimised.

Tensile Properties - Experimental Procedure

Tensile properties were measured on polyurethane samples in the form of rings of internal diameter 23mm and external diameter 27mm. Rings were cut by means of a fly press from cast films approximately 0.5mm thick, using a specially designed cutting tool (Plate 11). A floor-standing Instron model machine was used to determine stress-strain data over the range, -25°C to +150°C. The following brief description of the apparatus and the mode of operation used is now given.

The Instron tensile testing machine consists essentially of a horizontal beam crosshead which is arranged to move vertically at a constant rate, and above which is connected a sample grip. A second grip is suspended above the first and attached to a fixed load cell. A sample held between the grips is elongated at a constant rate of extension, and the force applied is detected by the load cell. Separation of the grips, related to sample strain, is recorded directly on the X axis of an X,Y chart recorder, and the applied force related to the stress on the sample, is recorded on the Y axis.

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In order to determine stress/strain data over a broad temperature range, the Instron was equipped with a variable temperature chamber (Plate 13), connected to a Eurotherm temperature control unit. Control of temperature within ±1°C was obtained, air being circulated in the chamber by means of a fan positioned at the rear. Temperatures below ambient were achieved by connection of the Eurotherm unit to a valve head attached to a pressurised dewar vessel of liquid nitrogen. A constant temperature was maintained by the periodic release of a stream of liquid nitrogen into the chamber. Samples were allowed to equilibrate for 5 minutes at test temperature prior to testing.

Tensile measurements were made using a CTM load cell, giving a maximum load sensitivity of 100kg. A crosshead speed of 10cm min⁻¹ was used throughout. Grips were designed (Plate 12) to give good distribution of stress in ring samples on elongation by positioning the rings around four freely rotating spindles (Plate 14). From the Load (Kgf)/Extension (mm) curves obtained, the following tensile parameters were calculated (See Appendix 3):

1. Ultimate Tensile Strength
2. Modulus at 10%, 100% and 300% extension
3. Elongation at Break (%)
Tension Set

Set in polyurethane samples subjected to a constant elongation for a fixed length of time, was measured by the following procedure based on BS.903 (Part A5 1958). Strips of polyurethane materials, of approximate dimensions 100mm x 2mm x 0.5mm, were cut from cast films using a cutting tool having two parallel knife blades. Benchmarks 40mm apart were made on each sample which was then extended at a constant rate of 10cm min\(^{-1}\) to 100% extension, using pneumatically closed tensile grips on the Instron tensile machine. Samples were held at 100% extension for a timed interval of 10 minutes and were then relaxed at 20cm min\(^{-1}\), thus giving quick release without snap back. Set was determined by measuring the residual extension (to the nearest 0.5mm) after 2, 10, 30 and 60 minutes.

Tear Strength

A 'Trouser' type tear test based on ASTM D-470 was used to determine the tear properties of polyurethane elastomers. Rectangular test pieces, of approximate dimensions 37.4mm x 12.5mm x 0.5mm, were die-cut from cast films. A slit, of length 25mm was made centrally from midway along the shorter edge of each sample by means of a razor blade (Fig 6.1). The thickness of each test piece at the point of tear initiation (ie. at the slit/elastomer interface) was determined using a thickness gauge to the nearest 0.01mm.
Pneumatic grips were used on the Instron tensile machine and samples were extended at a rate of 20 cm min^{-1} in the manner indicated in Fig 6.1.

**Hardness**

The hardness of all polyurethanes was determined using a Wallace Microhardness Meter. Essentially, this is a measure of the penetration of a rigid probe into the sample under a fixed load and for a constant length of time. Polyurethane samples in the form of discs 23 mm in diameter were used. A thickness of approximately 1.0 mm was achieved by using doubly plied test pieces. Values of hardness in International Rubber Hardness Degrees (IRHD) were obtained.

6.3 Results and Discussion
6.3.1 Tensile Properties

The results of tensile properties determined over the temperature range -25°C to +150°C are presented in graphs 6.1 through 6.19. Although it would not be meaningful to attempt to correlate relatively minor variations in properties shown by different chain extension agents, it is worthwhile observing trends arising from this data.

Graphs 6.1 through 6.4 show variation of ultimate tensile strength with temperature. From Graph 6.1, it can be seen that materials studied fall into two basic groups.
2,7-DAF, p-PDA and 1,5-DAN all have high tensile strengths at ambient temperature. With increasing temperature, tensile strength falls off, although a significant proportion is retained even at 150°C.

o-PDA, 2,3-DAF, 2,4-DPT, 1,4-B.D. and MOCA exhibit relatively low tensile strength at ambient temperature, with little retention of strength at temperatures of 50°C and above. 3,6-DAA appears to give properties which fall between these two extremes. The first group consists of polymers having highly symmetrical groupings in the hard segment (Table 3.3 Chapter 3). These groupings apparently lead to ordered domain structure resulting in a high level of physical properties. At 150°C, domain structure is still not completely disrupted and hence a significant strength is retained. The second group consists essentially of polymers incorporating asymmetrical hard segment units, i.e. o-PDA, 2,3-DAF and 2,4-DPT. Poor ordering results in these systems yielding polymers of low room temperature strength and almost total loss of strength at elevated temperatures. The poor tensile strength of MOCA is thought to be due to its relatively low molecular weight (Table 4.1 Chapter 4). This may also partly account for the low strength of 2,4-DPT.

It may be anticipated that 1,4-B.D. would yield good hard segment domain formation due to the regular structural unit involved.
However, the low level of tensile strength properties exhibited by this material indicates the presence of a disordered system having mixed hard and soft segments. It is suggested that mixing is promoted by the common -(CH₂)₄-D- group in both hard and soft segments. 3,6-DAA shows a level of tensile strength below that of the symmetrical materials over the whole temperature range. This is reasonable, as the bulky three ring unit presents a certain amount of steric hindrance between adjacent hard segments due to the 3,6 substitution pattern.

Graph 6.2 illustrates the effect of catalyst level on the tensile strength of p-PDA elastomers. With increased catalyst concentration tensile strength decreases over the entire temperature range. It is thought that this may be due to the promotion of biuret formation during the chain extension reaction. Resulting biuret groups lead to poor hard segment domain formation by disrupting physical crosslink sites. This effect may also be an important factor contributing to the low tensile strengths of MOCA, 1,4-B.D. and 2,4-DPT (Graph 6.1), all of which were catalysed at 1.0% stannous octoate.

The effect of variation in percentage chain extension agent is illustrated for p-PDA in Graph 6.3. It can be seen that optimum strength properties result using 95% stoichiometric chain extension agent.
At this ratio, it is thought that the introduction of a small amount of covalent crosslinking through biuret formation helps reinforce the two phase polymer structure. Higher levels of biuret crosslinking, as would be anticipated using only 90% chain extension, lead to disruption of the ordered two phase structure by interfering with physical crosslink sites. This results in lower tensile strength materials. 100% chain extended materials give essentially no reinforcement from covalent crosslinking and hence have lower strength than elastomers incorporating 95% chain extension agent.

Graph 6.4 illustrates the effect of hard segment content on tensile strength for p-PDA. At ambient, p-PDA (5% NCO) elastomers exhibit significantly higher tensile strength than materials based on higher NCO systems. This is explained by the higher elongation achieved in p-PDA (5% NCO) and the much greater ratio of soft segment to hard segment. Both these factors give rise to the relative ease of soft segment crystallisation in p-PDA (5% NCO) resulting in a particularly high tensile strength. With increasing temperature, retention of tensile strength becomes higher in the case of p-PDA (10 NCO) and p-PDA (15 NCO), due to the greater reinforcement afforded by the strong domain structures derived from the long hard segments present.
Graphs 6.5 through 6.15 illustrate the effect of each of the above variables on 10%, 100% and 300% modulus values over the temperature range -25°C to +150°C. In general it can be seen that the same trends arise as were observed for tensile strength. A notable exception is the effect of hard segment content as illustrated in Graphs 6.8 and 6.12. 10% and 100% modulus values increase with increased hard segment content at all temperatures. It would appear that crystallisation of the soft segment plays only a minor role at both 10% and 100% elongation and that the physical association of hard segments is the important reinforcing factor. At temperatures below the melting point of crystalline POTM (43°C), modulus is therefore proportional to hard segment content. At higher temperatures this relationship still holds true, as the thermal stability of the hard segment aggregates is greater for materials of higher hard segment content.

Graph 6.13 illustrates similar trends to those observed for tensile strength (Graph 6.1). Symmetrical bulky groups yield materials having high modulus whereas asymmetric bulky groups yield low modulus materials. It can be concluded that good phase segregation and domain formation are essential for high modulus elastomers.

The effect of hard segment structure on 'Elongation at Break' (EB) is illustrated in Graphs 6.16 through 6.19.
From -25°C all materials show increased EB with increased temperature. Asymmetric groups exhibit higher elongation initially but fail at relatively low temperatures, eg. o-PDA, 2,3-DAF, 2,4-DPT. More symmetrical groups give lower initial elongation, but continue to increase with increasing temperature, eg. p-PDA, 2,7-DAF, 1,5-DAN. This effect may be explained by the poor interchain attraction available in the asymmetric groups, leading to relatively unrestricted disentanglement and flow of polymer chains. With increased temperature, essentially no 'tie points' are available and materials fail at low extension. On the other hand, symmetrical groups give rise to strong interchain attractive forces which provide strong 'tie points' through hard segment aggregation, thus leading to restricted chain disentanglement and poor slippage of polymer chains past each other. As the temperature is increased towards 150°C, the effectiveness of these 'tie points' decreases, and EB increases.

The effect of variations of catalyst level on EB is illustrated in Graph 6.17. Increased catalyst concentration gives a similar effect to increased asymmetry in the hard segment. This is thought to be due to the formation of covalent crosslink sites in highly catalysed materials, and hence the disruption of intermolecular attractive forces. The proportion of effective 'tie points' is thus reduced as catalyst concentration increases.
A similar effect is illustrated by Graph 6.18. The extent of covalent crosslinking would be anticipated to be in the order \( p\text{-PDA (90)} > p\text{-PDA (95)} > p\text{-PDA (100)} \). Results indicate that EB also follows this order, with \( p\text{-PDA (90)} \) falling off at approximately 100\(^\circ\)C.

Graph 6.19 illustrates the effect of hard segment content variation on EB. Over the entire temperature range, EB increases with decreasing hard segment content. This may be explained by the higher proportion of intermolecular attractive forces available at higher NCO levels, thus giving rise to strong 'tie points' which remain effective, even at 150\(^\circ\)C.

6.3.2 Tension Set

Values of tension set are recorded as a percentage of the original specimen length in Table 6.1. At 100\% extension, it may be assumed that crystallisation of the soft segment is minimal and that most of the set is attributed to plastic deformation of hard segment domains.

Results indicate that tension set increases with increased hard segment content. This is shown by comparing \( p\text{-PDA, p-PDA (10 NCO) and p-PDA (15 NCO)} \). 1,5-DAN and 1,5-DAN (10 NCO) also illustrate this effect. It would appear therefore that plastic deformation of hard segment domains increases as the size and proportion of hard segments increases.
It is suggested that disruption of domain structure followed by the formation of new hydrogen bonded sites on extension of the elastomer, is responsible for high set in these materials.

Elastomers incorporating asymmetrical groups are generally seen to give low set values. Poor domain structure and mixed soft and hard segments are two factors which would be anticipated to give low set by minimising plastic domain deformation and soft segment crystallisation. This effect is particularly apparent in o-PDA and 2,3-DAF. It may be anticipated that higher set would be promoted by more symmetrical structures. However, this is not found for p-PDA, 1,5-DAN and 2,7-DAF. It is suggested that the hard segment content in these materials is too low to form domain structures of sufficient size to undergo permanent deformation, through the formation of new hydrogen bonded sites.

Increased catalyst level appears to give a slight increase in tension set, as shown in the series p-PDA, p-PDA (0.1), p-PDA (0.5) and p-PDA (1.0). This is also evident in the catalysed MOCA and 2,4-DPT materials. It is possible that free stannous octoate catalyst is acting as an internal lubricant, allowing easier polymer chain slippage and flow throughout the elastomer network.
6.3.3 Tear

The tear Propagation Strength, \(T_p\) (i.e. the force per unit thickness required to propagate a tear through the material) and the total Tear Energy, \(T_e\) (i.e. the work per unit thickness required to propagate a tear through the material) are shown in Tables 6.2 and 6.3. Materials were found to fall into two distinct types:

a) **Low extensibility** (Table 6.2)

Elastomers of this type yielded Load/Extension curves of the type shown in Fig 6.2. The force required to propagate a tear through the material remains essentially constant and extension of the polymer network is minimal.

b) **High extensibility** (Table 6.3)

Fig 6.3 illustrates a typical Load/Extension curve for this type of material. In this case, the polymer network is subject to increasing extension throughout the test period. The tear propagation force therefore increases, and it is convenient to record a minimum \((T_p\text{ min})\) and a maximum \((T_p\text{ max})\) value of Tear Strength.

Values of \(T_p\) and \(T_e\) were calculated for all materials as shown in Appendix 4. Generally it is found that symmetrical groups in the hard segment give rise to low extensibility materials (Table 6.2) eg. p-PDA, 1,5-DAN, 2,7-DAF. Materials with higher hard segment content also fall into this class, ie. p-PDA (10 NCO), 1,5-DAN (10 NCO) and 3,6-DAA (10 NCO).
Asymmetrical groups tend to give high extensibility tear, as shown by p-PDA, 2,3-DAF, 2,4-DPT. These general trends are supported by the previous results reported for EB at room temperature. Values of $T_p$ and particularly $T_e$, are greater for highly extensible materials due to the additional force and work required to extend the complete polymer network. A comparison of tear values between materials of low and high extensibility is therefore meaningless. However, it is worthwhile comparing values of $T_p$ and $T_e$ within each class.

In general, the more bulky symmetrical groups appear to give lower tear strength and tearing energy than less bulky groups in low extensibility tear. This is illustrated by p-PDA (10 NCO), 1,5-DAN (10 NCO) and 3,6-DAA (10 NCO). p-PDA also gives higher values of $T_p$ and $T_e$ than 1,5-DAN and 2,7-DAF. High tear strength and energy depend primarily on the presence of strong tie points throughout the polymer matrix. These tie points hinder the progress of crack growth and in polyurethanes may take the form of hard segment domains. It would appear that although the extent of physical crosslinking between hard segments should be similar for the symmetrical groups investigated, the more bulky groups yield a less closely packed domain structure with weaker resistance to crack growth.
p-PDA (90) and p-PDA (100) have lower values of $T_p$ and $T_e$ than p-PDA. This result may be explained by the optimum balance of physical and covalent crosslinking in p-PDA; a factor which was thought responsible for the high tensile strength of p-PDA compared with p-PDA (90) and p-PDA (100).

Materials having higher hard segment content are found to give higher values of $T_p$ and $T_e$. This is demonstrated by comparing p-PDA and 1,5-DAN with p-PDA (10 NCO) and 1,5-DAN (10 NCO). Presumably this is due to the presence of larger and more perfectly developed domains which are more effective as crack growth inhibitors.

From Table 6.3, there appears to be little correlation between structure of the chain extender and values of Tear strength or Tear energy in high extensibility tear. However, the effect of catalyst concentration on p-PDA materials is illustrated. While $T_p$ remains essentially constant with increasing catalyst concentration, $T_e$ increases significantly. This is thought to be due to the higher extensibility imparted to p-PDA by catalysis with stannous octoate (Graph 6.17). It would appear that easy slippage and flow of polymer chains resulting in high extension but little increase in tearing load, account for the high tear energy of catalysed p-PDA.
6.3.4 **Hardness**

Values of Hardness (IRHD) are given in Table 6.4. Symmetrical, bulky groups give rise to materials of hardness in the 90° region, with only a minor increase being found in three ring systems (3,6-DAA, 2,7-DAF) compared with the single ring system of p-PDA. Bulky, asymmetrical groups eg. o-PDA, 2,3-DAF and 2,4-DPT, give much softer materials, indicative of relatively poor packing of hard segments. 1,4-B.D. also gives softer materials, presumably due to the flexible nature of the -O(CH₉)₄O- unit and the lower interchain attraction afforded by urethane groups compared with urea groups. The low hardness of MOCA is thought to be a result of low molecular weight and the high catalyst level used. These factors would be expected to similarly affect 2,4-DPT.

As the level of catalyst is increased in p-PDA, the hardness decreases slightly. This may be due to poorer domain formation as a result of increased covalent crosslinking promoted by catalysis. Increased hard segment content gives a marked increase in hardness, as shown by p-PDA (10 NCO), 1,5-DAN (10 NCO), 3,6-DAA (10 NCO) and p-PDA (15 NCO). A higher extent of hard segment attraction accompanied by a higher concentration of bulky, rigid groups are two factors which would contribute greatly to this effect.
<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Tension Set %</th>
<th>Relaxation Time (Minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>p-PDA</td>
<td>7.50</td>
<td>5.00</td>
</tr>
<tr>
<td>o-PDA</td>
<td>10.00</td>
<td>6.25</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>7.50</td>
<td>6.25</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>15.00</td>
<td>10.00</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>8.75</td>
<td>6.25</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>10.00</td>
<td>7.50</td>
</tr>
<tr>
<td>1,4-B.D.</td>
<td>6.25</td>
<td>5.00</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>6.25</td>
<td>3.75</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>8.75</td>
<td>6.25</td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>11.25</td>
<td>7.50</td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>15.00</td>
<td>10.00</td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>18.75</td>
<td>11.25</td>
</tr>
<tr>
<td>p-PDA (10 NCO)</td>
<td>52.50</td>
<td>47.50</td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)</td>
<td>56.25</td>
<td>50.00</td>
</tr>
<tr>
<td>p-PDA (15 NCO)</td>
<td>77.50</td>
<td>75.00</td>
</tr>
<tr>
<td>MOCA</td>
<td>32.50</td>
<td>18.75</td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>38.75</td>
<td>23.75</td>
</tr>
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</table>
TABLE 6.2
TEAR PROPERTIES OF LOW EXTENSIBILITY POLYURETHANE ELASTOMERS

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Tear Strength (Propagation) $T_p$ (kN.m$^{-1}$)</th>
<th>Tear Energy $T_e$ (J.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PDA</td>
<td>12.4</td>
<td>398</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>5.8</td>
<td>165</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>10.2</td>
<td>306</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>8.6</td>
<td>284</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>9.1</td>
<td>278</td>
</tr>
<tr>
<td>p-PDA (10 NCO)</td>
<td>28.4</td>
<td>825</td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)</td>
<td>18.8</td>
<td>498</td>
</tr>
<tr>
<td>3,6-DAA (10 NCO)</td>
<td>8.2</td>
<td>220</td>
</tr>
<tr>
<td>1,4-B.D.</td>
<td>9.0</td>
<td>348</td>
</tr>
</tbody>
</table>
TABLE 6.3

TEAR PROPERTIES OF HIGH EXTENSIBILITY POLYURETHANE ELASTOMERS

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Tear Strength (Propagation) (kN.m⁻¹)</th>
<th>Tear Energy (J.m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp min</td>
<td>Tp max</td>
</tr>
<tr>
<td>3,5-DAA</td>
<td>24.7</td>
<td>39.8</td>
</tr>
<tr>
<td>o-PDA</td>
<td>14.7</td>
<td>20.0</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>22.6</td>
<td>24.5</td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>22.2</td>
<td>30.8</td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>21.1</td>
<td>30.2</td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>21.3</td>
<td>24.9</td>
</tr>
<tr>
<td>MOCA</td>
<td>11.5</td>
<td>13.3</td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>7.0</td>
<td>10.1</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Hardness IRHD</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>p-PDA</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>o-PDA</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>77</td>
<td></td>
</tr>
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<td>1,4-B&amp;D</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>93</td>
<td></td>
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<tr>
<td>p-PDA (100)</td>
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<td></td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>p-PDA (10 NCO)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>3,6-DAA (10 NCO)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>MOCA</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>2,4-DPT</td>
<td>69</td>
<td></td>
</tr>
</tbody>
</table>
FIG 6.1
TEAR TEST SAMPLE AND TEARING MODE

Sample thickness
0.5mm

25mm
37.5mm
12.5mm
**FIG 6.2**

LOW EXTENSIBILITY TEAR PROPAGATION CURVE

**FIG 6.3**

HIGH EXTENSIBILITY TEAR PROPAGATION CURVE

*Note:* Te = Area under curves.
GRAPH 6.1 - Ultimate Tensile Strength of Polyurethane Elastomers
-25°C to +150°C

KEY:
- □ 2,7-DAF
- ○ p-PDA
- Δ 1,5-DAN
- ♦ 3,6-DAA
- ¶ 2,3-DAF
- ▼ o-PDA
- ▽ MOCA
- □ 1,4-B.D.
- ▼ 2,4-DPT
GRAPH 6.2 - Ultimate Tensile Strength of p-PDA polyurethanes - Effect of Catalysis -25°C to +150°C

KEY:
- ○ p-PDA
- ○ p-PDA (0.1C)
- ○ p-PDA (0.5C)
- ○ p-PDA (1.0C)
GRAPH 6.3 - Ultimate Tensile Strength of p-PDA polyurethanes - Effect of Stoichiometry, -25°C to +150°C
GRAPH 6.4 - Ultimate Tensile Strength of p-PDA Polyurethanes - Effect of Prepolymer NCO content, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (15 NCO)
- p-PDA (10 NCO)
GRAPH 6.5 - Modulus (10%) of Polyurethane Elastomers, -25°C to +150°C

KEY:
- 2,7-DAF
- 3,6-DAA
- p-PDA
- 1,5-DAN
- MOCA
- 1,4-B.D.
- o-PDA
- 2,3-DAF
- 2,4-DPT
GRAPH 6.6 - Modulus (10%) of p-PDA Polyurethanes - Effect of Catalysis, -25°C to +150°C

KEY:
- o p-PDA (0.1C)
- o p-PDA (0.5C)
- o p-PDA (1.0C)
GRAPH 6.7 - Modulus (10%) of p-PDA Polyurethanes - Effect of Stoichiometry, -25°C to +150°C

KEY:
- O p-PDA
- O p-PDA (90)
- O p-PDA (100)
GRAPH 6.8 - Modulus (10%) of p-PDA Polyurethanes - Effect of Prepolymer NCO content, -25°C to +150°C

KEY:
- ○ p-PDA
- φ p-PDA (10 NCO)
- ◦ p-PDA (15 NCO)
Modulus (100%) of Polyurethane Elastomers, -25°C to +150°C

KEY:
- 1,5-DAN
- 2,7-DAF
- p-PDA
- 3,6-DAA
- o-PDA
- 1,4-B.D.
- 2,3-DAF
- MOCA
- 2,4-DPT
Graph 6.10 - Modulus (100%) of p-PDA Polyurethanes - Effect of Catalysis, 
-25°C to +150°C

Key:
- ○ p-PDA
- ○ p-PDA (0.1C)
- ● p-PDA (0.5C)
- ● p-PDA (1.0C)
GRAPH 6.11 - Modulus (100%) of p-PDA (MPa) Polyurethanes - Effect of Stoichiometry -25°C to +150°C

KEY:
- ○ p-PDA
- □ p-PDA (90)
- ◇ p-PDA (100)
GRAPH 6.12 - Modulus (100%) of p-PDA Polyurethanes - Effect of Prepolymer NCO content, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (10 NCO)
- p-PDA (15 NCO)
GRAPH 6.13 - Modulus (300%) of Polyurethane Elastomers, -25°C to +150°C

KEY:

- ▲ 1,5-DAN
- □ 2,7-DAF
- ○ p-PDA
- ● 3,6-DAA
- ▽ 1,4-B.D.
- ● 2,3-DAF
- ▽ MOCA
- ▽ 2,4-DPT
- ▽ o-PDA
GRAPH 6.14 - Modulus (300%) of p-PDA Polyurethanes - Effect of Catalysis, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (0.1C)
- p-PDA (0.5C)
- p-PDA (1.0C)
Modulus (300%) of p-PDA Polyurethanes - Effect of Stoichiometry -25°C to +150°C

GRAPH 6.15 - Modulus (300%) of p-PDA Polyurethanes - Effect of Stoichiometry -25°C to +150°C

KEY:
- ○ p-PDA
- ○ p-PDA (90)
- ○ p-PDA (100)
GRAPH 6.16
Elongation at Break % of Polyurethane Elastomers, -25°C to +150°C

KEY:
- △ 1,5-DAN
- □ 2,7-DAF
- ○ p-PDA
- ▽ 3,6-DAA
- ● 1,4-B.D.
- ★ 2,3-DAF
- MOCA
- ◇ 2,4-DPT
- ▼ α-PDA

EB (%)
GRAPH 6.17 - Elongation at Break % of p-PDA Polyurethanes - Effect of Catalysis, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (0.1°C)
- p-PDA (0.5°C)
- p-PDA (1.0°C)
GRAPH 6.18 - Elongation at Break % of p-PDA Polyurethanes - Effect of Stoichiometry, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (90)
- p-PDA (100)
GRAPH 9.19 - Elongation at break % of p-PDA Polyurethanes - Effect of Prepolymer NCO content, -25°C to +150°C

KEY:
- p-PDA
- p-PDA (10 NCO)
- p-PDA (15 NCO)
PLATE 11: Ring Sample Cutting Tool

PLATE 12: Ring Sample Tensile Grips

PLATE 14: Ring Sample in Place over Tensile Grips.
CHAPTER 7

STRESS RELAXATION & CREEP

7.1 Introduction & Literature Review

Although general mechanical properties serve to characterise an engineering material, they often give only a restricted indication of the properties of the material in actual service conditions. Two properties which extend this characterisation to a further understanding of 'in service' performance are Stress Relaxation and Creep. Stress relaxation relates to the decrease in stress with time for a material held under constant strain. Creep is very closely related to stress relaxation and represents the gradual increase in strain with time under constant load.

Stress relaxation was originally developed as a means of investigating the cleavage of crosslink sites in an elastomeric material. For a material maintained at constant strain, bond scission at crosslink sites may occur to relieve localised internal stresses. The resulting effect would be a gradual decrease in stress with time. By allowing materials to relax at regular intervals, a certain proportion of broken bonds may reform. Thus, a measure of the reversible and irreversible components of bond scission may be obtained.
Stress relaxation and creep have been extensively reviewed\textsuperscript{109,110} although little data has been published in the literature relating to segmented polyurethane elastomers. The present work investigates the effect of variation of hard segment structure on stress relaxation and creep over the temperature range, 23°C to 150°C.

Singh\textsuperscript{111} (et al) investigated stress relaxation in 2,4-TDI based polyether and polyester urethane elastomer networks. Controlled crosslinking was introduced in both systems by using trimethylolpropane. Results of measurements at 130°C demonstrated stress relaxation to be considerably greater for the polyether system than for the polyester system. It was also pointed out that stress relaxation curves approached linearity after a brief initial relaxation period. The initial non-linear portion of the curves was thought to be associated with cleavage of random weak linkages such as allophonate and biuret. The linear portion was identified with urethane group cleavage.

Singh (et al) also measured stress relaxation under intermittent conditions, i.e. samples were extended for only a brief period at regular intervals. By subjecting samples to this type of test, the resulting stress relaxation monitored is a measure of the net effect of chain scission and recombination, i.e. a measure of the irreversible chain scission.
Results indicated that the stress relaxation process is essentially irreversible in a polyether based system at 130°C, whereas a reversible process predominates in the polyester system.

By carrying out stress relaxation studies in both air and nitrogen, Singh (et al) showed good agreement in each case for the polyester network, indicating a non-oxidative process. The polyether network however showed a considerably higher rate of stress relaxation in air, indicative of an oxidative chain scission process. Measurements made over a series of temperatures from 50°C to 150°C, gave further evidence to support these conclusions.

The effect of structure on creep in segmented polyurethanes has received very little attention in the literature. Treloar¹⁰⁹ has outlined the principle processes involved during a typical creep experiment performed on a visco-elastic material (see Graph 7.22). On application of a static load, an almost instantaneous deformation takes place. This portion of the 'deformation-time' profile is essentially elastic, i.e. on removal of the load, the material immediately returns to its original state with no energy loss. The elastic portion is followed by a visco-elastic (time dependent) deformation in which the rate of deformation gradually decreases. Eventually, deformation rate becomes constant reflecting a purely viscous flow process.
Removal of the load results in an immediate recovery followed by a gradual reduction of deformation. Finally, a state of constant deformation is attained and this represents the irreversible or viscous component.

7.2 Experimental

7.2.1 Stress Relaxation

Stress relaxation in polyurethanes was investigated using a Wallace Extension Stress Relaxometer. (See Plate 15). Essentially, the equipment consists of a thermostatically controlled cast aluminium block heating unit having a series of circular chambers. Each chamber may be used in conjunction with a single stress relaxation unit. Samples, in the form of strips 4mm wide, were die cut from cast sheets approximately 0.5mm thick.

Operation of the stress relaxation unit depends on the balancing of a metal cantilever beam (see Fig 7.1). A sample held at constant elongation is connected to one end of this beam and located in a heating chamber. The beam is pivoted at the other extreme, and the downward movement applied by the sample under stress is balanced by a spring arranged centrally above the beam. Any change in stress of the sample is automatically compensated by a change in the extension of the spring. A marker pencil attached directly to the spring is placed in contact with a drum chart rotating at a constant rate of one revolution every 12 hours.
The stress relaxometer may be operated in 'Continuous' mode or 'Intermittent' mode. In the first case, the sample is maintained at the desired elongation and the decrease in stress with time is monitored. In the 'Intermittent' mode, the sample is extended to the desired elongation for only a brief fixed period during each 30 minutes. Operation of the 'Intermittent' mode is controlled by a time switch connected to a pneumatic piston arrangement on each sample grip. Decrease in stress with time is once again monitored, but in this case, only the irreversible contribution to stress relaxation is recorded.

Under normal operating conditions, air is circulated at a constant rate through each sample chamber. A flowmeter monitors this circulation. By connection of a nitrogen supply to the gas inlet valve, measurements may be made in an inert atmosphere.

In the present work, stress relaxation was studied in a series of polyurethanes based on chain extenders having from one to three molecular ring units, namely; p-PDA, o-PDA, 1,5-DAN, 2,7-DAF, 2,3-DAF and 3,6-DAA. In this series, o-PDA and 2,3-DAF represent relatively asymmetric groups. All samples were extended 50% and measurements were made in air over the temperature range 50°C to 150°C. Oxidative effects on stress relaxation were evaluated by comparative measurements in an nitrogen atmosphere.
The extent of reversible stress relaxation was determined for p-PDA, 1,5-DAN and 2,7-DAF by 'Intermittent' mode measurements, in which the samples were extended for a period of 30 seconds in each 30 minute interval.

7.2.2 Creep Measurements

Creep extension was determined using samples in the form of standard dumbbells (ASTM 'D') punched from cast polymer films of thickness approximately 0.5mm. The thickness of each sample was measured accurately to 0.01mm by means of a thickness gauge, and the load required to give a constant stress of 0.9 MPa* was calculated. Benchmarks, 15mm apart were made centrally on the narrow portion of each dumbbell using a chinagraph marker pencil.

A creep rig was constructed, consisting essentially of two parallel series of adjustable jaw grips (Plate 16). The rig was mounted in an accurately controlled air circulating oven having a double glass window in the door section. A clamp, in the form of two triangular aluminium plates, was attached to a tab of each dumbbell and the free tab was securely gripped in a jaw of the creep rig, having allowed the oven to reach the required temperature. After 10 minutes, the distance between the benchmarks on each sample was accurately determined (to 0.1mm) by means of a vertically travelling cathetometer mounted outside the oven window.
This reading was taken as the original length (ie. Time = 0). With the oven door open for the minimum time practical, preweighed loads were suspended from each sample clamp to give the required stress of 0.9 MPa on each sample. (The weight of each clamp was taken into account). Cathetometer readings were taken over a period of approximately fourteen days, each measurement being timed from the point at which the load was applied. Creep extension was studied over a wide temperature range for each polymer, measurements being made at room temperature, 50°C, 75°C, 100°C, 125°C and 150°C.

* Constant stress value of 0.9 MPa was used for comparison with previous work undertaken by G. Mountain (University of Loughborough; Thesis in preparation).

7.3 Results and Discussion

7.3.1 Stress Relaxation

Stress relaxation was recorded graphically on the Wallace Stress Relaxometer as a decrease in Force with Time. For comparison of data for a series of samples it is more meaningful to consider the variation in Relative Force (ie. \(f(t)\)/\(f(0)\)) with Time. In this case \(f(t)\) and \(f(0)\) represent the force applied by the sample at time 't' and at the start of the relaxation (ie. Immediately after extension to 50%) respectively. Results are presented here graphically as \(\log(f(t)\times10)/f(0)\) versus Time.
Graphs 7.1 - 7.5 show a comparison of Stress Relaxation for different chain extension agents at fixed temperatures over the range 50°C - 150°C. Graphs 7.6 - 7.11 illustrate the effect of temperature on Stress Relaxation for each polyurethane. Results of measurements made in air are compared with Stress Relaxation under a nitrogen atmosphere in Graphs 7.12 - 7.16. 'Intermittent' mode stress relaxation data are presented in comparison with 'Continuous' data for p-PDA, 1,5-DAN and 2,7-DAF in Graphs 7.17 - 7.21.

From graphs 7.1 - 7.5 it can be seen that bulky symmetrical groups contribute significantly to low stress relaxation at elevated temperatures. Between 50°C and 100°C, 1,5-DAN and 2,7-DAF show relatively little relaxation. Above 100°C, both these materials show a rapid increase in stress relaxation, although the more bulky 2,7-DAF shows retention of some stress at 150°C after approximately 17 hours. Results also indicate a pronounced effect of highly asymmetric groupings in polyurethane materials. At 50°C, 2,3-DAF and 3,6-DAA show relatively high stress relaxation. This effect is enhanced at higher temperatures.

Graphs 7.12 - 7.16 illustrate the effect of an inert atmosphere on stress relaxation. It is seen that only a slight increase in relaxation rate is found in an atmosphere of air compared with a nitrogen atmosphere.
This effect was found in each case investigated, suggesting only a limited extent of oxidative cleavage. Unlike the materials investigated by Singh¹¹¹ (et al), which consisted of highly crosslinked networks, the only covalent crosslinking present in these materials would be a small proportion of allophonate and biuret sites. This difference in structure would account for the apparent contradiction between the present data and that recorded by Singh (et al) for polyether based urethanes. Assuming oxidative cleavage to predominate at crosslink sites, this would account for the minimal extent of oxidative cleavage observed in the materials investigated here.

A comparison of 'Intermittent' and 'Continuous' Stress Relaxation data (Graphs 7.17 - 7.21) indicates an essentially reversible relaxation process in the materials investigated. Once again, results appear to contradict the data of Singh¹¹¹ (et al) who demonstrated irreversible relaxation in polyether networks. It is suggested that fundamental structural differences are again responsible for this apparent contradiction. The materials investigated in this instance show only a very low extent of relaxation under 'Intermittent' conditions, indicating minimal irreversible relaxation. This irreversible portion of stress relaxation is most probably due to chain scission at weak allophonate and biuret crosslink sites.
It is suggested that reversible stress relaxation in segmented linear polyurethanes may be explained by physical relaxation processes which depend greatly on the reorganisation of hard segment interactions. Physical relaxation processes associated with unrestrained flexible linear soft segments would also be expected to contribute to the total relaxation. These latter processes may include simple chain uncoiling in the direction of applied stress and disentanglement of chains to relieve stress. However, it would be anticipated that such processes are generally considerably restrained by the presence of Hard Segment 'Tie Points' throughout the soft segment matrix. It can be seen therefore that physical relaxation processes are controlled by the degree of organisation of hard segments. This would explain the observed decrease in stress relaxation with increased symmetry in hard segment structure. The effect of temperature is also explained. With increasing temperature hard segment interactions are progressively reduced and dissociation of hard segment domain structures become more pronounced.

Fig 7.2 illustrates three possible relaxation processes which involve dissociation of hard segment interactions such as hydrogen bond breakdown. In each case, it can be seen that the effective chain length in the direction of stress is increased, thus reducing the overall internal stress at constant elongation.
On relief of localised stress at a particular site, it may be possible for new hard segment interactions to form, as illustrated in process (3), Fig 7.2. Here, interaction between hard segments A & B has dissociated due to stress at elevated temperature and a new interaction between A & C has formed allowing a disentanglement of polymer chains and hence a relief of localised stress.

7.3.2 Creep

Graphs 7.24 - 7.32 illustrate the results of creep determination on the polyurethanes investigated. Results are presented as Creep Extension (%) vs. log (Time). Graph 7.23 shows a typical Creep curve (p-PDA at 100°C) obtained by plotting creep extension (%) vs. Time. Comparison with Graph 7.22 illustrates the viscoelastic nature of these materials.

Graphs 7.24 - 7.29 show the effect of temperature on creep for each polyurethane. p-PDA, 1,5-DAN and 2,7-DAF give very little creep at temperatures up to 100°C. Above 100°C, creep increases rapidly and results in a high rate of viscous flow leading to material failure. This effect is illustrated in Graphs 7.24, 7.26 and 7.27. o-PDA and 2,3-DAF show significant creep at relatively low temperatures, while creep in 3,6-DAF increases rapidly above 50°C (see Graphs 7.25, 7.28 and 7.29).
Creep at elevated temperatures, associated with the bulky symmetrical chain extension agents is illustrated in Graphs 7.30 - 7.32. At 100°C, 1,5-DAN is found to give very little creep relative to p-PDA and 2,7-DAF. At higher temperatures, creep increases rapidly in all cases.

It is suggested that mechanisms very similar to those described for stress relaxation, play a major part in creep behaviour of segmented polyurethane elastomers, ie. Physical structure based on the association of hard segments undergoes reorganisation particularly at elevated temperatures. The initial rapid creep extension is thought to be associated with an essentially elastic chain disentanglement process, whereas the final steady creep process depends on the dissociation of hard segment interactions resulting in chain slippage and molecular flow. These processes would account for the relatively low creep extension found in the symmetrical types (ie. p-PDA, 1,5-DAN, 2,7-DAF) at temperatures up to 100°C. At higher temperatures, softening of hard segment domain structures becomes significant and molecular flow is promoted. Poorer domain structure in the asymmetric types allows chain slippage and flow at lower temperatures.
KEY:
A = Sample under elongation
B = Thermostatted cast aluminium block heating unit
C = Cantilever beam
D = Compensating spring
E = Rotating drum chart
F = Cantilever beam electronic balancing unit
G = Pneumatic piston
FIG 7.2

PHYSICAL RELAXATION PHENOMENA IN A LINEAR SEGMENTED POLYURETHANE NETWORK

(1) Dissociation of hard segment interactions under stress at elevated temperature.

\[ \text{stress} \]

(2) Intramolecular hydrogen bond disruption.

\[ \text{stress} \]

(3) Promotion of chain disentanglement as a result of dissociation of hard segment 'tie points'.

\[ \text{stress} \]

Where, \( \overline{\text{Hard Segment}} \) and \( \overline{\text{Soft Segment}} \)
CONTINUOUS STRESS RELAXATION OF POLYURETHANE ELASTOMERS IN AIR AT 50°C

Graph 7.1

KEY:
- □ 2,7-DAF
- △ 1,5-DAN
- ▽ o-PDA
- ○ p-PDA
- ● 2,3-DAF
- ♦ 3,6-DAA

Time (Hours)
Graph 7.2

Continuous Stress Relaxation of Polyurethane Elastomers in Air at 75°C

KEY:
- △ 1,5-DAN
- □ 2,7-DAF
- ○ p-PDA
- ● 2,3-DAF
- ▼ α-PDA
CONTINUOUS STRESS RELAXATION OF POLYURETHANE ELASTOMERS IN AIR AT 100°C

KEY:
- △ 1,5-DAN
- □ 2,7-DAF
- ○ p-PDA
- ◊ 2,3-DAF

GRAPH 7.3

log \left( \frac{f(t) \times 10}{f(0)} \right)
GRAPH 7.4

CONTINUOUS STRESS RELAXATION OF POLYURETHANE ELASTOMERS IN AIR AT 125°C

KEY:

- 2,7-DAF
- p-PDA
- 1,5-DAN

\[
\log \left( \frac{f(t) \times 10}{f(0)} \right)
\]

Time (Hours)

0.0 0.2 0.4 0.6 0.8 1.0

0 10 20 30
CONTINUOUS STRESS RELAXATION OF POLYURETHANE ELASTOMERS IN AIR AT 150°C

GRAPH 7.5

KEY:

- □ 2,7-DAF
- ○ p-PDA
- △ 1,5-DAN
\[
\log \left( \frac{f(t) \times 10}{f(0)} \right)
\]

**GRAPH 7.6**

CONTINUOUS STRESS RELAXATION OF p-PDA ELASTOMER IN AIR AT DIFFERENT TEMPERATURES

- 50°C
- 75°C
- 100°C
- 125°C
- 150°C

Time (Hours)
GRAPH 7.7
CONTINUOUS STRESS RELAXATION OF α-PDA ELASTOMER IN AIR AT DIFFERENT TEMPERATURES

\[ \log \left( \frac{f(t) \times 10}{f(0)} \right) \]

- 50°C
- 75°C (Failed)
log \left( \frac{f(t)}{f(0)} \times 10 \right) 

**GRAPH 7.8**

CONTINUOUS STRESS RELAXATION OF 1,5-DAN ELASTOMER IN AIR AT DIFFERENT TEMPERATURES

- **50°C, 75°C**
- **100°C**
- **125°C**
- **150°C**

**Time (Hours)**
GRAPH 7.9

CONTINUOUS STRESS RELAXATION OF 2,7-DAF ELASTOMER IN AIR AT DIFFERENT TEMPERATURES

\[ \log \left( \frac{f(t)}{f(0)} \times 10 \right) \]

- 50°C
- 75°C
- 100°C
- 125°C
- 150°C

Time (Hours)
GRAPH 7.10
CONTINUOUS STRESS RELAXATION OF 2,3-DAF ELASTOMER IN AIR AT DIFFERENT TEMPERATURE

\[ \log \left( \frac{f(t) \times 10}{f(0)} \right) \]
Graph 7.11

Continuous Stress Relaxation of 3,6-DAA Elastomer in Air at Different Temperatures

\[ \frac{\log(f(t) \times 100)}{f(0)} \]

Time (Hours)

- 50°C
- 75°C
- 100°C
- 125°C
GRAPH 7.12
CONTINUOUS STRESS RELAXATION OF p-PDA ELASTOMER AT 125°C; AIR VS. NITROGEN ATMOSPHERE

\[ \log \left( \frac{f(t) \times 10}{f(\sigma)} \right) \]

Time (Hours)

\( N_2 \)

\( \text{Air} \)
CONTINUOUS STRESS RELAXATION OF 1,5-DAN ELASTOMER AT 125°C; AIR VS. NITROGEN ATMOSPHERE
GRAPH 7.14
CONTINUOUS STRESS RELAXATION OF 2,7-DAF ELASTOMER AT 125°C; AIR VS. NITROGEN ATMOSPHERE
\[
\log \left( \frac{f(t)}{f(0)} \times 10 \right)
\]

GRAPH 7.15

CONTINUOUS STRESS RELAXATION OF 2,3-DAF ELASTOMER AT 75°C; AIR VS. NITROGEN ATMOSPHERE

Time (Hours)
GRAPH 7.16
CONTINUOUS STRESS RELAXATION OF 3,6-DAA ELASTOMER AT 50°C; AIR VS. NITROGEN ATMOSPHERE
GRAPH 7.17
STRESS RELAXATION OF p-PDA ELASTOMER IN AIR AT 100°C; CONTINUOUS VS. INTERMITTENT

\[ \log \left( \frac{f(t)}{f(0)} \times 10 \right) \]

Time (Hours)

0 10 20 30
GRAPH 7.18

STRESS RELAXATION OF 1,5-DAN ELASTOMER IN AIR AT 100°C: CONTINUOUS VS. INTERMITTENT

\[ \log \left( \frac{f(t) \times 10}{f(0)} \right) \]

Intermittent

Continuous
Graph 7.19

Stress relaxation of 1,5-DAN elastomer in air at 125°C; continuous vs. intermittent.

\[
\log \left( \frac{f(t) \times 10}{f(0)} \right)
\]

Time (Hours)
GRAPH 7.20

STRESS RELAXATION OF 1,5-DAN ELASTOMER IN AIR AT 150°C; CONTINUOUS VS. INTERMITTENT

\[
\log \left( \frac{f(t)}{f(0)} \times 10 \right)
\]

Time (Hours)

Continuous

Intermittent
GRAPH 7.21

STRESS RELAXATION OF 2,7-DAF ELASTOMER IN AIR AT 100°C; CONTINUOUS VS. INTERMITTENT

\[ \log \left( \frac{f(t) \times 10}{f(0)} \right) \]

Intermittent

Continuous

Time (Hours)

0 10 20 30
GRAPH 7.22

CREASE IN A VISCOELASTIC MATERIAL

- Visco-elastic Region
- Elastic Region
- Viscous component of deformation
- Load applied at \( T = 0 \)
- Immediate recovery

Deformation vs. Time

Load applied

Load removed
Graph 7.23

Extension creep of p-PDA elastomer at 100°C.
GRAPH 7.24

EXTENSION CREEP OF p-PDA ELASTOMER AT DIFFERENT TEMPERATURES

Elongation (%)
GRAPH 7.25

EXTENSION CREEP OF o-PDA ELASTOMER AT DIFFERENT TEMPERATURES

Elongation (%) vs Time (mins)

- 50°C
- 23°C

Note: The graph shows the extension creep of o-PDA elastomer at different temperatures. The x-axis represents time in minutes, and the y-axis represents elongation in percent.
Graph 7.26

EXTENSION CREEP OF 1,5-DAN ELASTOMER AT DIFFERENT TEMPERATURES

Elongation (%) vs. Time (min)
GRAPH 7.27

EXTENSION CREEP OF 2,7-DAF ELASTOMER AT DIFFERENT TEMPERATURES

Elongation (%)
Elongation (%)  

GRAPH 7.28
EXTENSION CREEP OF 2,3-DAF ELASTOMER
AT DIFFERENT TEMPERATURES

- Fail
- 75°C
- 50°C
- 23°C

Time (mins)

0 1 10 10^2 10^3 10^4
GRAPH 7.29

EXTENSION CREEP OF 3,6-DAA ELASTOMER AT DIFFERENT TEMPERATURES

Elongation (%) vs. Time (Min)

- 100°C
- 75°C
- 50°C
- 23°C

Fail
Elongation (%)  

**GRAPH 7.30**

EXTENSION CREEP OF POLYURETHANE ELASTOMERS AT 100°C

**KEY:**
- o p-PDA
- □ 2,7-DAF
- △ 1,5-DAN

Time (mins)
Graph 7.31

Extension creep of polyurethane elastomers at 125°C

Elongation (%)

KEY:
- ○ p-PDA
- □ 2,7-DAF
- △ 1,5-DAN

Fail
GRAPH 7.32
EXTENSION CREEP OF POLYURETHANE ELASTOMERS AT 150°C

KEY:
- p-PDA
- 2,7-DAF
- 1,5-DAN

Elongation (%) vs. Time (mins)
PLATE 15: Stress Relaxation Equipment.

PLATE 16: Creep Rig with Samples in Position.
8.1 Introduction

An elastomeric material in use under actual service conditions, may be required to withstand repeated deformation without significant loss in performance. A typical example is to be found in wheel and tyre applications of elastomers, where material is subjected to a cyclic compressive deformation. Polyurethanes, whilst having outstanding strength properties and wear resistance, have been found to give poor performance in many dynamic applications. This has been attributed to the relatively high heat build-up in polyurethanes compared with other types of elastomers. The use of polyurethanes in applications where a high frequency of deformation is maintained, is very much restricted by internal heat build-up leading to softening of the bulk material and subsequent deterioration of properties. Where this condition is combined with severe surface abrasion of the type experienced by surface to surface slipping, then melting of the urethane polymer surface can occur. This usually results in a failure situation. For this reason, polyurethane tyres are suitable for use on slow moving vehicles but are unsuitable as conventional automobile tyres.
When an elastomeric material is deformed and then allowed to regain its original state, a net amount of work is performed on the material. This is illustrated in Fig 8.1 for an extension-retraction cycle. On extending the material (AB), an amount of work equal to the area ABD is performed on the system. On retraction of the material (BC), an amount of work equal to the area CBD is done by the system. The net work performed on the system is therefore given by the area of the closed hysteresis loop ABCA and this represents the energy dissipated as heat during the complete cycle. The residual extension AC represents a certain amount of set in the material.

The present section aims to investigate the effect of the hard segment structure as influenced by the chain extension agent, on the hysteresis behaviour of polyurethane elastomers. Hysteresis Loss, i.e. the energy dissipated expressed as a percentage of the energy expended on the system, was determined over the temperature range 0°C to 100°C.

Very little has been published in the literature on hysteresis in segmented polyurethane elastomers. Gianatasio and Ferrari\textsuperscript{113} investigated the effect of isocyanate structure on hysteresis in a polyester based system using MOCA as chain extension agent. Three isocyanates were evaluated, namely TDI (100\% 2,4), TDI (80\% 2,4 + 20\% 2,6) and TDDI (3,3'-bitoluene diisocyanate).
Results showed a higher hysteresis loss in the case of TDDI, a trend which was shown to be related to hardness and modulus. It was suggested that the comparatively rigid and regular structure of TDDI has an important effect. Hysteresis loss was also shown to increase with increasing isocyanate level, again in relation to hardness and modulus. Polyurethanes based on a polyether polyol were found to have lower hysteresis loss than equivalent polyester materials, a factor attributed to the less polar character of the polyether segment. Introduction of a significantly high level of covalent crosslinking by using a low chain extension ratio and high curing temperature gave rise to lower hysteresis losses. This was thought to be due to the lower cohesive energy resulting in the non linear structure produced. A similar result was found using a polyol-amine curative system.

On repeated deformation, segmented polyurethane elastomers show a progressive reduction in modulus. This behaviour closely resembles the phenomenon observed in filler-reinforced vulcanised rubbers, known as 'Stress Softening' or the 'Mullins Effect'. This effect has been explained in terms of the orientation and restructuring of the structural entities present initially. During extension of a polyurethane elastomer on the first cycle, stress induced crystallisation of soft segments may take place.
With increasing extension, hard segments may then slip from domain structures due to stress acting on hydrogen bonded sites. Continuation of this process results in the formation of new hard segment arrangements. On relaxation of the material, soft segments retract into random coils while hard segments maintain their new arrangements under the restraint of newly formed hydrogen bonds. A second cycle of extension and contraction will lead to a further increase in hard segment organisation and this process will continue in subsequent cycles until an optimal internal restructuring is attained.

Gianatasio and Ferrari\textsuperscript{113} demonstrated that over a series of ten consecutive extension/retraction cycles in each polyurethane investigated, 89 to 93 percent of the total hysteresis loss occurred in the first cycle. The mechanism described above provides a plausible explanation of this effect. During the first cycle, a relatively high stress is required for a given elongation and almost all the energy expended is retained in the restructured system. Subsequent cycles undergo only minor restructuring of hard segments and therefore the stress required for a given elongation is reduced and the hysteresis loss is considerably lower.
8.2 Experimental

Hysteresis loss was determined by subjecting polyurethane samples to multiple stress-strain cycles and measuring the area of the conditioned hysteresis loop. Measurements were made over the temperature range, 0°C to 100°C.

Samples in the form of rings were prepared for testing as described in Section 6.2. A floor-standing Instron machine equipped with variable temperature facilities was used throughout (see Section 6.2). For meaningful comparison of the hysteresis behaviour of different polyurethanes, all samples were subjected to a series of preconditioning cycles prior to measurement of the final cycle. Preliminary experiments showed the third and fourth cycles to follow almost identical paths. On this basis, all samples were preconditioned at test temperature by cycling three times to 80% of the previously calculated extension at break. Preconditioned samples were then allowed to relax for 30 minutes at test temperature, before measuring their new dimensions, i.e. Mean Circumference, thickness and radial width. Finally, samples were cycled to 100% extension, having calculated the elongation required using the new ring dimensions. Equations relating the vertical grip separation with sample elongation are given in Appendix 5.
Hysteresis loss was determined from the load extension loops recorded on the Instron. A computer programme (Appendix 5) was used to calculate values of hysteresis loss. Input data for each closed loop was recorded on paper tape in the form of X-Y coordinates, using a 'd-mac' X-Y plotter and pencil follower connected to a 'Creed' tape punch machine. Conversion factors in units of load and extension, corresponding to the X-Y coordinates, were included on each set of input data.

8.3 Results and Discussion

Fig. 8.2 illustrates the first four elongation/retraction cycles for p-PDA at ambient conditions. Elongation in each cycle was to 80% of the elongation at break. It can be seen from Fig. 8.2 that the greatest proportion of hysteresis loss occurs in the first cycle, and that the third and fourth cycles show very little difference in hysteresis loss. p-PDA was found to be typical of all the polyurethanes investigated here and illustrates the stress softening effect in these materials.

Computed hysteresis results are tabulated for all samples over the temperature range 0°C to 100°C in Tables 8.1 - 8.5. Here, cycle (1) refers to the initial cycle to 80% of the elongation at break, and 'Conditioned Cycle' refers to the final cycle to 100% based on the sample dimensions after three conditioning cycles.
Graphs 8.1 - 8.6 illustrate the effect of temperature on hysteresis loss for both cycles.

Polyurethanes of high hard segment content were found to give very high set in the first cycle. As a result, extension of conditioned samples to 100% caused tensile failure. Therefore, under the test conditions applied, no useful results were obtainable for these materials. However, the effect of hard segment content is indicated by the results shown in Table 8.2 for p-PDA (10 NCO) and 1,5-DAN (10 NCO). Here, hysteresis losses in the conditioned cycles were determined for 40% extension. Comparison with p-PDA and 1,5-DAN show significantly greater hysteresis losses in both the first cycles and the conditioned cycles of the higher hard segment materials. This effect can be explained by the presence of larger domain structures associated with the longer hard segments. Dissociation of these domains and subsequent formation of reorganised arrangements of hard segments, would account for the higher net energy absorption observed.

From graphs 8.1 and 8.4 it can be seen that hysteresis loss generally decreases with increasing temperature, over the temperature range investigated. This effect is explained by the increased heat energy absorption by the material resulting in enhanced dissociation of hydrogen bonded structures present initially.
Reorganisation of the initial structure is therefore promoted by increase in temperature, and heat build up due to applied stress is reduced.

As illustrated in graph 8.1, all materials exhibited high hysteresis loss in the first cycle, particularly at ambient conditions. This is primarily associated with the high degree of structural reorganisation which takes place in the first cycle. o-PDA, 2,3-DAF and 1,4-B.D. each failed on cycling at 50°C and higher temperatures.

A comparison of actual values of cycle (1) hysteresis losses with those observed in the conditioned cycle, would be meaningless, as the nature of the two cycling conditions differs. In the case of cycle (1), all samples were elongated to 80% of their elongation at break, whereas for the conditioned cycle, all samples were extended to 100% of their equilibrated dimensions. However, a significant effect is demonstrated when structural trends within each cycle are compared. Considering cycle (1), it can be seen that hysteresis loss, particularly at ambient conditions, is essentially independent of gross structural changes in the polyurethane hard segment. This is shown by comparing p-PDA with o-PDA and 2,7-DAF with 2,3-DAF. Similar comparisons in the conditioned cycles however demonstrate significantly lower hysteresis losses in the case of the asymmetrical o-PDA and 2,3-DAF structures.
An explanation of this effect may be found in terms of the restructuring of initial molecular arrangements. During the first three cycles (to 80% of elongation at break), polyurethanes having asymmetrical hard segment structures, may readily attain an equilibrium situation of molecular reorganisation. Steric hindrance, allowing only limited initial hard segment association, would be expected to contribute to ease of structural rearrangement. Poor initial structural formation may therefore result in a rapid structural reorganisation during cycling, with the greatest hysteresis loss being shown in the first cycle. Hysteresis loss in the conditioned cycle is therefore greatly reduced compared with cycle (1). In the case of the more symmetrical types, eg. p-PDA and 2,7-DAF, high cycle (1) hysteresis losses are associated with the disruption of relatively ordered initial domain structures. However, subsequent cycling may result in a stepwise restructuring through a series of intermediate molecular organisations. This would result in a gradual decrease in hysteresis loss on cycling, with a high value retained in the conditioned cycle.

1,4-BD was found to exhibit similar hysteresis behaviour to c-PDA and 2,3-DAF. Although cycle (1) hysteresis loss was shown to be rather low compared with other polyurethanes investigated (Graph 8.1), once again a very marked decrease in hysteresis loss was demonstrated in the conditioned cycle (Graph 8.4).
This effect may be explained in terms of relatively poor domain structure as outlined for o-PDA and 2,3-DAF, and also the lower cohesive energy associated with the urethane groups present in 1,4-B.D. compared with the urea groups in all other polyurethanes investigated.

The effect of chain extension stoichiometry on hysteresis is shown in Graphs 8.1 and 8.5 for p-PDA. Over the range investigated, i.e. 90 to 100 percent, there appears to be little effect on hysteresis loss in the conditioned cycle. Although a relatively wide spread of results is found in cycle (1), this may reflect the dependence of cycling extension on the individual elongation at break values.

Catalyst concentration also appears to have only a minor effect of hysteresis loss in the conditioned cycle. At room temperature, hysteresis loss is shown to generally decrease as catalyst concentration increases (Graph 8.6). This would seem reasonable assuming the higher levels of catalyst give improved internal lubrication, thus assisting a restructuring process. Once again, a wider spread of results in cycle (1) (Graph 8.3) may be associated with the variation between samples of the actual conditions of cycling.
<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>CYCLE (1)</th>
<th>CONDITIONED CYCLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ei MJ.m⁻³</td>
<td>Eo MJ.m⁻³</td>
</tr>
<tr>
<td>p-PDA</td>
<td>46.04</td>
<td>9.07</td>
</tr>
<tr>
<td>o-PDA</td>
<td>58.36</td>
<td>9.00</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>33.11</td>
<td>8.65</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>57.55</td>
<td>8.85</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>58.69</td>
<td>10.60</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>59.75</td>
<td>10.13</td>
</tr>
<tr>
<td>1,4-B.D.</td>
<td>18.30</td>
<td>5.32</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>60.04</td>
<td>13.48</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>50.30</td>
<td>10.98</td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>61.73</td>
<td>11.60</td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>72.51</td>
<td>11.34</td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>58.38</td>
<td>9.08</td>
</tr>
</tbody>
</table>

Where:  
- Ei = Energy absorbed on extension  
- Eo = Energy released on retraction  
- Ea = Net energy absorbed on complete cycle  
- (Ea)(100) (Ei) (%) = % energy absorbed in complete cycle, i.e. Hysteresis Loss (%)  
- (Ei)
### TABLE 8.2

**HYSTERESIS PROPERTIES OF POLYURETHANE ELASTOMERS AT 23°C**

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>CYCLE (1)</th>
<th>CONDITIONED CYCLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_i$ MJ.m$^{-3}$</td>
<td>$E_o$ MJ.m$^{-3}$</td>
</tr>
<tr>
<td>p-PDA</td>
<td>41.97</td>
<td>10.00</td>
</tr>
<tr>
<td>o-PDA</td>
<td>30.54</td>
<td>6.26</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>39.65</td>
<td>10.15</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>42.44</td>
<td>8.12</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>49.78</td>
<td>13.58</td>
</tr>
<tr>
<td>2,3-DAF</td>
<td>37.13</td>
<td>7.95</td>
</tr>
<tr>
<td>1,4-B.D.</td>
<td>15.37</td>
<td>5.88</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>48.99</td>
<td>10.40</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>28.70</td>
<td>9.00</td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>48.81</td>
<td>10.15</td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>37.77</td>
<td>7.08</td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>34.41</td>
<td>5.81</td>
</tr>
<tr>
<td>p-PDA (10 NCO)*</td>
<td>56.86</td>
<td>4.63</td>
</tr>
<tr>
<td>1,5-DAN (10 NCO)*</td>
<td>55.97</td>
<td>5.32</td>
</tr>
</tbody>
</table>

* 40% Extension in conditioned cycle.

Note: Key as Table 8.1
<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>CYCLE (1)</th>
<th></th>
<th></th>
<th>CONDITIONED CYCLE</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ei MJ.m⁻³</td>
<td>Eo MJ.m⁻³</td>
<td>Ea MJ.m⁻³</td>
<td>(Ea)100 (Ei) (%)</td>
<td>Ei MJ.m⁻³</td>
<td>Eo MJ.m⁻³</td>
<td>Ea MJ.m⁻³</td>
</tr>
<tr>
<td>p-PDA</td>
<td>41.97</td>
<td>12.15</td>
<td>29.82</td>
<td>71.05</td>
<td>3.49</td>
<td>1.55</td>
<td>1.94</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>36.69</td>
<td>9.95</td>
<td>26.74</td>
<td>72.88</td>
<td>3.17</td>
<td>1.44</td>
<td>1.73</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>31.82</td>
<td>6.07</td>
<td>25.75</td>
<td>80.92</td>
<td>2.65</td>
<td>1.02</td>
<td>1.63</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>37.39</td>
<td>12.06</td>
<td>25.33</td>
<td>67.75</td>
<td>2.75</td>
<td>1.13</td>
<td>1.62</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>54.37</td>
<td>12.14</td>
<td>42.23</td>
<td>77.67</td>
<td>3.30</td>
<td>1.36</td>
<td>1.94</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>25.39</td>
<td>9.53</td>
<td>15.86</td>
<td>62.47</td>
<td>3.57</td>
<td>1.53</td>
<td>2.04</td>
</tr>
<tr>
<td>p-PDA (0.1)</td>
<td>45.99</td>
<td>10.76</td>
<td>35.23</td>
<td>76.60</td>
<td>3.11</td>
<td>1.33</td>
<td>1.78</td>
</tr>
<tr>
<td>p-PDA (0.5)</td>
<td>35.24</td>
<td>5.51</td>
<td>29.73</td>
<td>84.36</td>
<td>2.23</td>
<td>1.10</td>
<td>1.13</td>
</tr>
<tr>
<td>p-PDA (1.0)</td>
<td>14.80</td>
<td>3.12</td>
<td>11.68</td>
<td>78.92</td>
<td>1.79</td>
<td>0.88</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Note: Key as Table 8.1
**TABLE 8.4**

HYSTERESIS PROPERTIES OF POLYURETHANE ELASTOMERS AT 75°C

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Ei MJ.m⁻³</th>
<th>Eo MJ.m⁻³</th>
<th>Ea MJ.m⁻³</th>
<th>(Ea)₁₀₀ (Ei)(%</th>
<th>Ei MJ.m⁻³</th>
<th>Eo MJ.m⁻³</th>
<th>Ea MJ.m⁻³</th>
<th>(Ea)₁₀₀ (Ei)(%</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PDA</td>
<td>36.89</td>
<td>10.40</td>
<td>26.49</td>
<td>71.01</td>
<td>3.11</td>
<td>1.43</td>
<td>1.68</td>
<td>54.02</td>
</tr>
<tr>
<td>1,5-DAN</td>
<td>34.52</td>
<td>10.27</td>
<td>24.25</td>
<td>70.25</td>
<td>2.81</td>
<td>1.37</td>
<td>1.44</td>
<td>51.25</td>
</tr>
<tr>
<td>3,6-DAA</td>
<td>24.28</td>
<td>5.02</td>
<td>19.26</td>
<td>79.32</td>
<td>2.09</td>
<td>0.90</td>
<td>1.19</td>
<td>56.94</td>
</tr>
<tr>
<td>2,7-DAF</td>
<td>32.46</td>
<td>11.87</td>
<td>20.59</td>
<td>63.43</td>
<td>3.05</td>
<td>1.40</td>
<td>1.65</td>
<td>54.10</td>
</tr>
<tr>
<td>p-PDA (90)</td>
<td>24.41</td>
<td>9.57</td>
<td>14.84</td>
<td>60.79</td>
<td>2.86</td>
<td>1.56</td>
<td>1.30</td>
<td>45.45</td>
</tr>
<tr>
<td>p-PDA (100)</td>
<td>18.51</td>
<td>8.59</td>
<td>9.92</td>
<td>53.59</td>
<td>3.12</td>
<td>1.59</td>
<td>1.53</td>
<td>49.04</td>
</tr>
</tbody>
</table>

Note: Key as Table 8.1
| Polyurethane | CYCLE (1) | | | | CONDITIONED CYCLE | | | |
| | Ei MJ.m⁻³ | Eo MJ.m⁻³ | Ea MJ.m⁻³ | (Ea/100 Ei)(% | Ei MJ.m⁻³ | Eo MJ.m⁻³ | Ea MJ.m⁻³ | (Ea/100 Ei)(% |
| p-PDA | 37.96 | 10.29 | 27.67 | 72.89 | 3.74 | 1.80 | 1.94 | 51.87 |
| 1,5-DAN | 28.77 | 9.24 | 19.53 | 67.88 | 2.50 | 1.30 | 1.20 | 48.00 |
| 3,6-DAA | 11.30 | 2.80 | 8.50 | 75.22 | 1.63 | 0.87 | 0.76 | 46.63 |
| 2,7-DAF | 19.91 | 8.76 | 11.15 | 56.00 | 2.68 | 1.48 | 1.20 | 44.78 |
| p-PDA (90) | 20.82 | 9.09 | 11.73 | 56.34 | 2.55 | 1.55 | 1.00 | 39.22 |
| p-PDA (100) | 13.69 | 7.77 | 5.92 | 43.24 | 2.47 | 1.52 | 0.95 | 38.46 |

Note: Key as Table 8.1
FIG. 8.1

TYPICAL HYSTERESIS CURVE

KEY:

HYSTERESIS LOSS

Load (kgf)

Extension (mm)

A

C

D

B
FIG. 8.2 - HYSTERESIS CURVES OF p-PDA ELASTOMER AT ROOM TEMPERATURE; FIRST FOUR CYCLES TO 80% ELONGATION AT BREAK.
GRAPH 8.1

HYSTERESIS LOSS OF POLYURETHANE
ELASTOMERS; 0°C to 100°C; Cycle (1)

KEY:
- 3,6-DAA
- o-PDA
- 2,3-DAF
- p-PDA
- 1,5-DAN
- 2,7-DAF
- 1,4-B.D.
GRAPH 8.2
HYSTERESIS LOSS OF \( p \)-PDA ELASTOMER
EFFECT OF STOICHIOMETRY; 0°C TO 100°C; Cycle (1)

Hysteresis Loss (%)

KEY:

- \( p \)-PDA
- \( p \)-PDA (50)
- \( p \)-PDA (100)
GRAPH 8.3

HYSTERESIS LOSS OF p-PDA ELASTOMER -
EFFECT OF CATALYSIS; 0°C to 100°C;
Cycle (1)

KEY:
- p-PDA
- p-PDA (0.1°C)
- p-PDA (0.5°C)
- p-PDA (1.0°C)
HYSTERESIS LOSS OF POLYURETHANE ELASTOMERS; 0°C to 100°C; CONDITIONED CYCLE

KEY:
- 3,6-DAA
- 2,7-DAF
- p-PDA
- 1,5-DAN
- 2,3-DAF
- o-PDA
- 1,4-B.D.
HYSTERESIS LOSS OF p-PDA ELASTOMER -
EFFECT OF STOICHIOMETRY; 0°C to 100°C;
CONDITIONED CYCLE.

KEY:
- p-PDA
- p-PDA (90)
- p-PDA (100)
HYSTERESIS LOSS OF p-PDA ELASTOMER - EFFECT OF CATALYSIS; 0°C to 100°C; CONDITIONED CYCLE

KEY:
- p-PDA
- p-PDA (0.1C)
- p-PDA (0.5C)
- p-PDA (1.0C)
CHAPTER 9

GENERAL DISCUSSION & RECOMMENDATIONS
FOR FURTHER WORK

Preceding sections have dealt with specific aspects of polyurethanes, from synthesis through to structure-property correlations. The present section draws an overall evaluation of the trends observed and their dependence on the chemical and morphological structures involved. This is followed by suggestions for further work.

Essentially linear segmented polyurethanes of molecular weight (Mn) in the region 20,000 - 30,000 have been prepared by chain extension in solution. Diamine chain extension agents generally produced solid elastomeric materials, with the exception of MOCA and 2,4-DPT. Steric hindrance has been suggested as a possible cause of low reaction rate for MOCA and 2,4-DPT in solution.

Catalysed MOCA and 2,4-DPT reactions yielded solid elastomers of relatively low strength. Diol chain extension agents gave very low extents of reaction in solution and catalysis only yielded useful solid products for 1,4-B.D. Polyurethanes of higher hard segment content were prepared by increasing the available isocyanate content of the prepolymer, followed by chain extension to the required stoichiometry.
By following the decrease in available isocyanate during reaction, the relative reactivity of chain extension agents was observed. Results showed that amine groups in close proximity on an aromatic ring structure give rise to rapid reaction with isocyanate in the prepolymer. This was demonstrated by o-PDA and 2,3-DAF. Bulky chain extension agents with well separated amine groups give a much reduced rate of reaction, eg. 1,5-DAN, 2,7-DAF and 3,6-DAA. One possible explanation of this effect is the interaction of DMF solvent with amine groups. Where amine groups are well separated, both can interact with solvent and hence give low reaction rate with isocyanate groups. However, due to steric factors, amine groups in close proximity cannot both readily interact with solvent and hence are more available for reaction with free isocyanate groups.

Structure of polyurethanes was determined by infrared spectrometry, thermal analysis and X-ray studies. Consideration of data obtained from all three techniques shows support for the hard segment domain model suggested by Bonart. This model has been shown to account for the general mechanical properties and time dependent properties exhibited by the polyurethanes investigated. Temperature effect on domain structure has been suggested as responsible for the observed behaviour of polyurethane elastomers over a broad temperature range.
Hysteresis loss has been found to depend on the chemical structure of the hard segment and this has been explained in terms of the reorganisation of hard segment domains.

The most pronounced effects of structural variation have been shown to be due to the symmetry of the chain extension agent. This has been demonstrated throughout by comparison of o-PDA and p-PDA, and also 2,3-DAF and 2,7-DAF. Infra-red spectroscopic analysis indicated (Table 4.3) very similar extents of NH group hydrogen bonding for o-PDA and p-PDA (66% and 68% respectively). However 2,3-DAF showed significantly lower hydrogen bonding than 2,7-DAF (41% and 65% respectively). Similarly 2,4-DPT was found to give only 46% hydrogen bonding. Clearly, the symmetry of the chain extension agent has a marked effect on the ease of NH group hydrogen bond formation. It would appear that increased bulkiness of pendant groups adjacent to the hard segment urea group, gives rise to decreased probability of urea NH group hydrogen bonding, due to the promotion of polymer chain separation. This would explain the anomalous behaviour of o-PDA and 2,3-DAF. Although both groups are asymmetrical, o-PDA cannot impart sufficient polymer chain separation to result in decreased hydrogen bonding.

Thermal analysis results indicate significantly lower T₃ transitions for o-PDA and 2,3-DAF relative to p-PDA and 2,7-DAF (Table 5.1).
As this transition has been associated with the dissociation of hydrogen bonded hard segment domains, it would appear that both o-PDA and 2,3-DAF give poor domain formation relative to their symmetrical counterparts. Considering this evidence together with the infra-red analysis data discussed above, o-PDA and 2,3-DAF would be anticipated to take part in soft/hard segment mixing, with o-PDA allowing a significant proportion of urea NH groups to be hydrogen bonded to the soft segment ether oxygens.

The effects of molecular symmetry on domain formation and phase separation, and subsequently on the properties of the bulk elastomer have been demonstrated. Tensile strength properties are generally much improved in the symmetrical p-PDA and 2,7-DAF compared with o-PDA and 2,3-DAF. The greater degree of hard segment domain formation associated with p-PDA and 2,7-DAF, gives rise to high modulus and tensile strength values and relatively hard materials. Symmetry appears to have little effect on tension set, and this was explained in terms of the low extent of plastic deformation of domains involved. It was suggested that at the 4.75% NCO level in the prepolymer, domains formed were of insufficient size to give marked variation in plastic deformation with changes in the structure of the chain extension agent.
Extensibility, as related to the elongation at break, was shown to increase at room temperature with decreased symmetry. At elevated temperatures, o-PDA and 2,3-DAF were found to lose their extensibility and fail, whereas the symmetrical types exhibited increased extensibility up to 150°C. This effect was explained in terms of the retention of domains acting as 'tie points' at elevated temperatures in symmetrical structures.

Tear strength determined at room temperature was found to be dependent on the extensibility of the polyurethanes investigated. Asymmetry in the hard segment, resulted in high tear strength and tear energy due to increased extensibility of the bulk material.

Molecular symmetry was also shown to have an important effect on stress relaxation and creep. A comparison of p-PDA and 2,7-DAF with o-PDA and 2,3-DAF shows a much greater extent of stress relaxation and creep in the case of the latter asymmetrical types. This has been explained in terms of the effects of domain structure on physical relaxation phenomena. Relaxation processes are promoted with increased asymmetry as a result of poorly defined domain structure 'tie points'.

Hysteresis loss was found to decrease as the symmetry of the chain extension agent decreased. Once again, this effect was explained by the relative ease of physical relaxation in the asymmetric types.
It was suggested that hysteresis loss is dependent on hard segment domain perfection. Where symmetrical hard domains are available leading to well defined domain structures, a high internal heat build up results during a cyclic extension test. This is thought to be due to a high net energy absorption associated with reorganisation of domain structures. A similar process in the asymmetric types requires less energy absorption as only poorly defined domain structures undergo reorganisation.

By comparing p-PDA, 1,5-DAN and 2,7-DAF, the effect of increased 'bulkiness' in the chain extension agent can be seen. In comparison with the symmetry effect discussed above, 'bulkiness' appears to have a less significant effect on the properties of the polyurethane elastomer. Infra-red spectroscopy indicated no marked variation in the extent of hydrogen bond formation and X-ray studies showed all materials to be amorphous in the relaxed state. A slight increase in the $T_g$ transition temperature was found with increasing 'bulkiness', possibly associated with increased thermal stability of the more bulky hard segment domains.

General mechanical properties were not found to be greatly affected by the size of the chain extension agent ring structure and no apparent correlation appeared to exist. All materials (ie. p-PDA, 1,5-DAN and 2,7-DAF) exhibited a high level of physical properties and in contrast with the asymmetrical structures, showed some retention of properties at elevated temperatures (ie. up to 150°C).
Stress relaxation, creep and hysteresis behaviour were also found to be very similar in each case.

The effect of increasing the hard segment:soft segment ratio has been demonstrated in p-PDA, 1,5-DAN and 3,6-DAA. Structural studies showed essentially complete hydrogen bonding for p-PDA (10 NCO and 15 NCO) and 1,5-DAN (10 NCO and 15 NCO) and minimal hard/soft segment mixing as indicated by the loss of $T_2$ thermal transitions. 3,6-DAA (10 NCO and 15 NCO) gave $T_2$ transitions although NH group hydrogen bond formation was complete, suggesting hard/soft segment hydrogen bonding. $T_3$ transitions were found to increase with increasing proportions of hard segment in all three materials. This trend has been explained as due to improved hard segment domain formation. X-ray studies and thermal analysis indicated the formation of truly crystalline entities in p-PDA (10 NCO and 15 NCO) and 1,5-DAN (10 NCO and 15 NCO), although this was not found for 3,6-DAA possibly as a result of the lower molecular symmetry present.

Hard segment:soft segment ratio was found to have a significant effect on polyurethane properties, particularly at elevated temperatures. Increased proportion of hard segment resulted in harder materials, 3,6-DAA (10 NCO and 15 NCO) yielding brittle solids. Modulus was also found to increase over the complete temperature range evaluated (-25°C to 150°C).
The importance of strain induced crystallisation of the poly(oxytetramethylene) soft segment in giving rise to high tensile strength, was demonstrated by comparing the tensile strengths of p-PDA, p-PDA (10 NCO) and p-PDA (15 NCO). p-PDA yielded a higher tensile strength at room temperature although p-PDA (10 NCO) and p-PDA (15 NCO) showed greater retention of tensile strength at temperatures above the melting temperature of crystalline poly(oxytetramethylene). Extensibility of materials was found to decrease as the proportion of hard segment increased. This effect would be anticipated as a result of decreased flexibility associated with the increased proportion of bulky rigid domain structures. Increased tension set with increased hard segment content was explained in terms of plastic deformation of hard segment domain structures. Tear strength and tear energy were also found to increase as the hard segment:soft segment ratio increases. It was suggested that this effect may be due to the increased effectiveness of larger hard segment domains in inhibiting crack growth. Due to the high modulus of the higher hard segment materials evaluated, no useful stress relaxation or creep results were obtained under the experimental conditions used. High set also made precycled hysteresis loss measurements impractical, although limited results indicated an increase in hysteresis loss with increased hard segment content. This effect was explained in terms of the higher energy input required to reorientate the larger domain structures present.
The effect of stannous octoate catalysis on the general mechanical properties of p-PDA has been observed. Tensile strength and modulus were found to decrease with increased level of stannous octoate, whereas extensibility increased. Tearing of catalysed p-PDA was found to be of the extensible type, with the increased tear energy associated with increased extension of the bulk material. Polyurethane hardness decreased and tensile set results indicated higher set with increased level of stannous octoate.

From the trends observed, it would appear that stannous octoate is acting as an internal lubricant in p-PDA elastomers. A comparison of the measured molecular weights of p-PDA and the catalysed materials, indicates a reduction of molecular weight with increased catalyst level. However, this would be partly attributable to the low molecular weight catalyst and does not represent a significant variation in polymer structure. Promotion of biuret crosslink sites would be expected to result in increased molecular weight. It would appear therefore, that stannous octoate is not significantly promoting secondary reactions.

The effects of percent stoichiometry chain extension agent on the general physical properties of p-PDA have also been evaluated. Measurement of molecular weight showed very little variation between p-PDA, p-PDA (90) and p-PDA (100), suggesting all materials to have only limited chemical crosslinking.
However, polyurethane properties appear to reflect some variation in crosslinking, with p-PDA (95% stoichiometry) generally giving the optimum level of physical properties. Tensile strength and tear strength were found to be greatest in the 95% stoichiometry material, whereas modulus values appeared not to be significantly affected. Results were explained in terms of the optimum balance of chemical and physical crosslinking in the 95% stoichiometry material.

3,6-DAA polyurethanes were generally shown to behave as a structure intermediate between the symmetrical and the asymmetrical types. This would seem reasonable, as the 3,6-amino group substitution would allow the three fused ring structure to inhibit good close packing of hard segments. Inhibited hard segment domain formations resulted in a low T$_3$ transition compared with the symmetrical types, and the presence of a T$_2$ transition in materials of higher hard segment content suggests significant hard/soft segment mixing. Also, unlike p-PDA and 1,5-DAN materials of higher hard segment content, X-ray studies showed no evidence of true crystallinity in 3,6-DAA.

General mechanical properties of 3,6-DAA were shown to fall between the symmetric and the asymmetric types. This effect is illustrated in tensile strength, modulus, and elongation at break. Tearing was found to be of the extensible type, giving higher tear strength and tear energy than the asymmetric o-PDA and 2,3-DAF.
MOCA and 2,4-DPT materials were of relatively low strength and modulus. It was suggested that this may be partly attributable to the low molecular weights achieved and also to the effect of the high catalyst level (1.0%) required to yield solid elastomeric materials. Infra-red studies indicated a low extent of urea-NH group hydrogen bonding in 2,4-DPT and this has been explained in terms of the chain separating effect of the bulky pendant group present. This factor in 2,4-DPT would also be anticipated to lead to a relatively low level of physical properties.

1,4-B.D. polyurethanes were also found to have low strength properties and low hardness. Although it was found necessary to catalyse the chain extension reaction, a molecular weight of 20,000 was achieved. The influence of catalyst as demonstrated in p-PDA would be expected to significantly reduce general physical properties, although the regular \(-O-(CH_2)_4-O-\) structure would possibly promote hard segment domain formation. Thermal analysis and WAXS results have been explained by the formation of crystalline entities in mixed soft/hard segments. This is thought to result from the common \(-O-(CH_2)_4-O-\) group in both soft and hard segments. This promotion of soft/hard segment mixing would explain the low level of physical properties in 1,4-B.D. materials.
The dependence of polyurethane properties on temperature has been demonstrated. Tensile properties, namely ultimate tensile strength and modulus, were shown to generally decrease over the temperature range -25°C through 150°C. This effect may be attributed to the effect of temperature on the physical crosslink entities present. Thermal analysis indicated three major thermal transition regions, designated T₁, T₂ and T₃. T₁, thought to be associated with the glass transition of the soft segment, lies outside the temperature range observed in polyurethane property evaluations. T₂ and T₃ transitions associated with soft/hard and hard/hard segment hydrogen bonded interactions, were not found to give rise to well defined transitions in tensile properties. It would appear that in all materials investigated, a continuous reduction in tensile properties with increased temperature results from a gradual reduction in effective 'tie points'. This may be associated with a combined effect of T₂ and T₃ transitions giving a broadly defined reduction in tensile properties.

Although there appears to be no distinct transitions in tensile properties which may be associated with T₂ and T₃, retention of tensile strength and modulus at elevated temperature does appear to correlate with thermal transition data. At 150°C, p-PDA, 1,5-DAN and 2,7-DAF retain significant tensile strength and modulus. All three materials exhibit high T₃ transitions, i.e. 181°C, 188°C and 189°C respectively (see Table 5.1).
These results may be contrasted with the less symmetrical bulky types such as o-PDA and 2,3-DAF, which have markedly lower $T_3$ transitions (137°C and 128°C respectively) and exhibit only minimal retention of strength at 50°C. The relatively low thermal stability of these asymmetrical types would be anticipated to be more dependent on the $T_2$ transitions which are thought to represent a high proportion of urea group hydrogen bonding through hard/soft segment interactions. This would seem reasonable considering the $T_2$ transitions of o-PDA and 2,3-DAF (each 65°C). Similarly, 1,4-B.D., 2,4-DPT and MOCA exhibit no retention of tensile properties above 50°C, a factor associated with the absence of any significant $T_3$ transitions.

Increased hard segment/soft segment ratio in p-PDA was shown to result in greater retention of tensile strength and modulus at elevated temperatures. This may be correlated with an increase in $T_3$ transition which reflects improved hard segment domain formation through hydrogen bonding.

Symmetry of chain extension agents was found to play an important part in the temperature dependence of stress relaxation and creep. Results showed that bulky, symmetrical groups contribute to reduced stress relaxation and creep at elevated temperature. For example p-PDA, 1,5-DAN and 2,7-DAF show very little stress relaxation and creep at temperatures up to 100°C compared with the less symmetrical types investigated.
The bulky 2,7-DAF material was found to retain a small proportion of stress after 17 hours at 150°C. Once again, this effect has been explained in terms of the greater contribution of bulky, symmetrical chain extension agents to improved hard segment domain formation and hence greater thermal stability.

Hysteresis loss in polyurethane elastomers has been shown to generally decrease with increased temperature. This was explained as due to the increased heat absorption resulting in a promotion of molecular rearrangement and hence a lower internal heat build up due to applied stress. The temperature dependence of hysteresis loss was found to be significantly affected by only marked changes in the structure of the chain extension agent. p-PDA, 1,5-DAN, 2,7-DAF and 3,6-DAA showed very similar behaviour in the conditioned cycle at temperatures up to 100°C. The asymmetrical o-PDA and 2,3-DAF exhibited significantly lower hysteresis loss and failed on cycling above ambient temperature. This effect is thought to be associated with poorly defined hard segment 'tie points', having relatively poor thermal stability.
Recommendations for Further Work

In view of the results of investigations carried out in the present work, the following recommendations are made:

1. Evaluate the role of solvent in the chain extension reaction in solution. In particular, further investigation should be made into the possibility of interaction of DMF with diamine chain extension agents.

2. Under the polymerisation conditions employed, reaction rate of diols investigated were too low to yield useful solid products. Stannous octoate catalysis only proved effective in the case of 1,4-B.D. An evaluation of solution polymerisation conditions suitable for diol extension should be made, particularly variation of solids content, solvent and catalyst system.

3. Evaluate the role of stannous octoate catalysis in the polyurethanes investigated, and in particular the apparent "internal lubricant" effect of residual stannous octoate when used at high levels.

4. Investigate the effect of chain extension agent molecular structure on hard segment domain formation as observed by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). Data obtained by these techniques would provide useful information on the size and uniformity of domain structures. This may lead to further correlation with observed physical properties.
5. Investigate the effect of carefully controlled covalent crosslinking on stress relaxation, creep and hysteresis, particularly at elevated temperatures. Polyurethanes prepared by incorporating a trifunctional curing agent, e.g. Trimethylolpropane, would form a suitable series for this study.
APPENDIX 1

DETERMINATION OF AVAILABLE ISOCYANATE CONTENT IN THE PREPOLYMER

Theory

The analytical procedure utilises the reaction of available isocyanate groups with di-n-butylamine:

\[ R-\text{NCO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N-H} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N-C-N-R} \]

Addition of excess di-n-butylamine to the prepolymer and subsequent titration against hydrochloric acid, allows the calculation of isocyanate group concentration.

Experimental

Approximately 2g of prepolymer is weighed accurately (± 0.001g) into a clean, dry 250 ml conical flask fitted with an air condenser. 25 mls dry trichlorobenzene is added and the flask heated until all prepolymer has dissolved. 25 mls of 1N di-n-butylamine (in toluene) is accurately measured into the flask by means of a clean dry pippette, and the solution boiled for 30 seconds. After allowing to cool to room temperature, 25 mls of dry methanol is added followed by four drops of bromophenol blue indicator. The solution is titrated against 1N HCl (in methanol) to a permanent yellow end point.

The above procedure is performed on three samples and one blank.
Calculation

The available isocyanate content of the prepolymer is calculated from the following formula:-

\[
\text{Available NCO, } \% = 4.2 \times \frac{\text{HCl Normality} \times (A-B)}{C}
\]

where:

- \(A\) = mls. HCl solution used in blank titration
- \(B\) = mls. HCl solution used in sample titration
- \(C\) = Weight prepolymer sample (g)

Results reported are the average of three samples varying no more than ± 0.1% NCO.
APPENDIX 2

DETERMINATION OF NUMBER AVERAGE MOLECULAR WEIGHT, $\bar{M}_n$.

a) Vapour Pressure Osmometry

The following relationship was used to obtain the calibration constant, $K$, for chloroform solvent at 37°C.

$$\frac{\Delta R}{C} = \frac{K}{M} \left( 1 + \frac{BC}{M} \right) \quad \text{(1)}$$

Where, $\Delta R$ = Resistance difference recorded between sample thermistor bead and pure solvent thermistor bead.

$C$ = Concentration (g.l$^{-1}$) of calibration standard (Benzil)

$M$ = Molecular weight of pure benzil standard = 210.23

Using benzil solutions of accurately known concentration (in the range 10 - 40g.l$^{-1}$), a graph of $\frac{\Delta R}{C}$ vs. $C$ is plotted and extrapolated to zero concentration to give:

$$\left[ \frac{\Delta R}{C} \right]_{C=0} = \frac{K}{M} \quad \text{(2)}$$

Hence $K$ may be determined.

For a polymer in chloroform solvent at 37°C, relation (1) also applies:

$$\frac{\Delta R}{C} = \frac{K}{\bar{M}_n} \left( 1 + \frac{BC}{\bar{M}_n} \right)$$

Where, $\bar{M}_n$ is the number average molecular weight of the polymer.
By plotting $\frac{\Delta R}{C}$ vs. $C$ for polymer solutions of accurately known concentration and extrapolating to zero concentration, $M_n$ may be obtained. (Using value of $K$ determined above).

b) **Membrane Osmometry**

For a non-ideal solution (eg. polymer solution), the following relationship is obeyed:--

$$\frac{\Pi}{RTC} = \frac{1}{M} + A_2C + A_3C^2 +$$

Where,

$\Pi$ = Osmotic pressure

$R$ = Gas constant

$C$ = Solute concentration (g.l$^{-1}$)

$T$ = Absolute temperature (K)

$M$ = Molecular weight

$A_2, A_3$ = 2nd and 3rd virial coefficients.

For a polymer solution at low concentration:--

$$\frac{\Pi}{RTC} = \frac{1}{M_n} + A_2C$$

$$\therefore M_n = \frac{RT}{\left[ \frac{\Pi}{C} \right]_{C=0}}$$

$\left[ \frac{\Pi}{C} \right]_{C=0}$ may be determined by extrapolation to zero concentration of the graph of $\left[ \frac{\Pi}{C} \right]$ vs. $C$. Hence, $M_n$ may be calculated.
APPENDIX 3

CALCULATION OF TENSILE PROPERTIES DETERMINED USING RING SAMPLE GRIPS

All tensile properties were calculated from the Load (kgf)/Extension (mm) curves obtained from the Instron chart recorder.

a) Ultimate Tensile Strength

Ultimate tensile strength is calculated from the recorded load at break using the following formula:

\[
\text{Ultimate Tensile Strength} = \frac{\text{Load (kgf)} \times \text{sample radial width(cm)} \times 10.2}{2 \times \text{sample thickness(cm)}} \text{ MPa}
\]

Sample radial width = 0.2cm (from dimensions of cutting die)

\[
\text{Ultimate Tensile Strength} = \frac{\text{Load (kgf)}}{4.08 \times \text{sample thickness(cm)}} \text{ MPa}
\]

b) Elongation at break

Sample elongation (%) is calculated from the following:

\[
\text{Sample Elongation, } E\% = \frac{100}{M} \left( 2D + G - M \right) \text{ (1)}
\]

Where, \( M \) = Mean Circumference of sample
\( G \) = Constant of grip geometry (see Fig A.1)
\( D \) = Vertical separation of grip spindle centres.

Note: Tensile properties were determined on three samples from each of three cast polyurethane films. The average value of nine results was reported.
For grips used, \( G = 38.74 \text{ mm} \).

For ring samples used, \( M = 78.55 \text{ mm} \).

\[ \therefore (1) \text{ becomes:} - \text{Elongation, } E\% = 2.55D - 50.69 \text{ --- (2)} \]

\( D = \text{Extension recorded on Instron chart (mm) (ie. vertical displacement of grips)} + 15\text{mm (Initial setting of grip separation)}. \)

'Elongation at Break' is obtained from (2) by inserting value of \( D \) at break.

Note:-- Ring samples 'flip over' on extension and sample thickness is therefore considered negligible in the above calculations.

c) **Modulus at 10\%, 100\% and 300\% Elongation**

From (2):-- \( D = 0.39E + 19.9 \text{ --- (3)} \)

For 10\% Extension, \( D = 23.84\text{mm} \) & Extension recorded = 8.84mm.

For 100\% Extension \( D = 59.18\text{mm} \) & Extension recorded = 44.18mm

For 300\% Extension \( D = 137.73\text{mm} \) & Extension recorded = 122.73mm

Modulus at the above extensions is given by:--

\[ \frac{\text{Load (kgf)}}{4.08 \times \text{sample thickness (cm)}} \times \text{MPa} \]

Where, Load (kgf.) is taken from the Instron Load/Extension curves at the recorded extensions given above.
Sample length = 2D + 2X + 2πR

2X + 2πR = Constant G

∴ Sample length = 2D + G
APPENDIX 4

CALCULATION OF TEAR PROPAGATION STRENGTH AND TEAR ENERGY

a) Tear Propagation Strength, \( T_p \)

Materials exhibiting low extension tear, yielded load (kgf)/Extension (mm) curves as shown in Fig 6.2.

Tear propagation strength, \( T_p = \frac{\text{Load (kgf)} \times 9.81}{\text{Sample thickness (mm)}} \) kN.m\(^{-1}\)

Where, Load (kgf) = Average load during tear
Sample thickness (mm) = Thickness at initial position of tear.

Materials exhibiting high extension tear, yielded load (kgf)/Extension (mm) curves as shown in Fig 6.3. For these materials, two values of tear propagation strength were recorded:

\( T_{p,\text{min}} = \frac{\text{Load (kgf) at initial tear} \times 9.81}{\text{Sample thickness (mm)}} \) kN.m\(^{-1}\)

\( T_{p,\text{max}} = \frac{\text{Load (kgf) at final tear} \times 9.81}{\text{Sample thickness (mm)}} \) kN.m\(^{-1}\)

b) Tear Energy, \( T_e \)

Tear energies for low extension and high extension materials were calculated from the areas under the recorded Load (kgf)/Extension (mm) curves.
Tear curves were traced onto tracing paper and weighed accurately (± 0.0005g). Calibration squares were also traced and the weight of a single calibration square calculated. Hence the number of single calibration squares, C, under each tear curve can be calculated from,

\[ C = \frac{\text{Weight Tear curve (g)}}{\text{Weight of single calibration square (g)}} \]

From the dimensions of the ordinate and abscissa of the Instron chart recorder,

\[
\text{Area of single calibration square} = \frac{\text{F.S.L} \times 9.81 \times 2}{100} \text{ N.mm.}
\]

Where, F.S.L = Full scale load (kgf)

\[ \therefore \text{Tear energy, } T_e = \frac{\text{F.S.L} \times 9.81 \times 2 \times C}{100 \times \text{sample thickness} (\text{mm})} \text{ J.m}^{-1} \]
APPENDIX 5

COMPUTATION OF HYSTERESIS PROPERTIES

a) Sample Grip Separation Limits

Hysteresis properties of polyurethanes were calculated from the Load (kgf)/Extension (mm) closed loops recorded from cyclic tensile tests (Section 8.2).

The following procedure was adopted for setting sample grip separation limits during a complete set of hysteresis cycles (Section 8.2):

Using equation (3) (Appendix 3(c));

\[ D = 0.39E + 19.9 \]

Where \( D \) = Extension recorded on the Instron recorder (mm) (i.e. vertical displacement of grips) + 15mm (Initial grip separation)

\( E \) = Sample elongation (%)

\( D \) is calculated for 80% E.B. (E.B. determined previously - Appendix 3(b)) by inserting \( E = 80\% \) E.B. in the above equation.

The sample grip limits may now be set on the Instron machine, i.e. Initial separation = 15mm

Final separation = \((D-15)\)mm

Samples were cycled three times between these limits and then allowed to relax for 30 minutes at test temperature.
The new mean circumference \(M^1\) of conditioned samples was then measured (+ 0.1mm) and used in equation (1) (Appendix 3(b)):-

\[
E = \frac{100}{M^1} \left(2D + G - M\right)
\]

For the final conditioned cycle, \(E = 100\%\).
\[
\therefore D = \frac{M^1 - G}{2}
\]

For the grips used, \(G = 38.74\text{mm} \) (Fig A1)
\[
\therefore D = M^1 - 19.37
\]

Using this new value of \(D\), the sample grip limits may again be set on the Instron; i.e.

Initial Separation = 15mm  
Final Separation = \((D-15)\text{mm}\)

Samples were cycled once between these limits and the conditioned cycle hysteresis loop recorded.

b) Computation of Hysteresis Properties

Hysteresis property data was determined by converting the Instron Load (kgf)/Extension (mm) parameters for each hysteresis loop into X-Y coordinates of an electronic planimeter coupled to a punch tape machine. Punched tape for each closed loop together with sample dimension input data in the form of cards was used with the following computer programme:-
MASTER GESK
COMMON/TAPE1/XMIN,YMIN,XMAX,YMAX,IXMIN,IYMIN,IXMAX,IYMAX
COMMON/TAPE2/N,IX(1000),IY(1000)
COMMON/TAPE3/M,X(1000),Y(1000)
X,Y ARE CURVE CO-ORDINATES,IX,IY VALUES ARE PLANIMETER CO-ORDINATES
N=0
M=1
M=M+N
CALL READTAPE(&:100)
READ(3,1)CIRCM,CIRCINT,SAMPLECS,B,CURVENO
FORMAT(5F0.0)
G=9.80665
C=G*B
C FACTOR IS 9.80665(G)/CHART MAG*FSD(KG)/MAXFSD(YMAX)
CALL OUTMAX(J)
CALL INMAX(K)
CALL SCALEAI=AREA(1,J)AD=AREA(K,N)
SMAX=Y(J)/SAMPLECS*B*SD
MAXEXT=100/CIRCM*(2*X(J)-CIRCINT+38.736+30-2*X(1))
EI=AI/(CIRCM*SAMPLECS)*C
EO=AO/(CIRCM*SAMPLECS)*C
EA=EI-EO
EAP=(EI-EO)/EI*100
WRITE(2,2)CURVEND,CIRCM,SAMPLECS,C,B,EI,ED,EA,EAP,SMAX,MAXEXT
WRITE(2,6)
FORMAT(T15,16H PERCENT STRAIN, T48,17H STRESS(KGF/CM2), T79 116H STRESS(MN/M2), T110,14H STRESS(PSI) )
DO 3 I=10,700,10
SET I IN DO LOOP TO REQUIRED PERCENT EXTENSION RANGE, EG.5-400 PERCENT
XI=0.5*(I*CIRCM/100+CIRCINT-38.736)-15+X(1)
IF(XI.GT.X(J))GO TO 5
S=AITKEN(X,Y,XI,J,3)
SCGS=S*B*50/SAMPLECS
SSI=SCGS/10.20
SIMP=SSI*145.0
WRITE(2,4)I,SCGS,SSI,SIMP
FORMAT( T21,I4,T49,F10.3,T79,F10.3,T110,F10.3)
CONTINUEM=M+1
GOTO 10
STOP
END
SUBROUTINE READTAPE(*)
TO READ SPACE DELIMITED DATA FROM PAPER TAPE. ERROR 0* IS TRAPPED
COMMON/TAPE1/XMIN,YMIN,XMAX,YMAX,IXMIN,IXMIN,IXMAX,IXMAX
COMMON/TAPE2/N,IX(1000),IY(1000)
COMMON/TAPE3/M,X(1000),Y(1000)
IF(N.NE.0)GOTO 10
READ(1,1,END=10)XMIN,YMIN,XMAX,YMAX,
IXMIN,IYMIN,IXMAX,IYMAX,IXMIN,IXMIN,IXMAX,IXMAX,(IX(I),IY(I),I=1,1000)
FORMAT(6F0.0,6I0,200010)
CONTINUE
WRITE(2,5)XMIN,VMIN,XMAX,YMIN,XMIN,VMAX,
IXMIN,IYMIN,IXMAX,IVMIN,IXMIN,IVMAX
FORMAT(11H1INPUT DATA//
XMIN,6X,4HYMIN,6X,4HXMAX,6X,4HYMIN,6X,4HXMIN,6X,4HYMAX/
6F10.3/6I10//4X,2H I,BX,2HIX,BX,2HIV/)}
N=0
DO 2 I=M,1000
IX(I-M+1)=IX(I)
IY(I-M+1)=IY(I)
IF(IX(I).EQ.9999)GOTO 10
IF(IY(I).EQ.8888)GOTO 6
WRITE 2,4)I,IX(I
TY(I)
FORMAT(1H,I5,2!10)
N=N+1
RETURN
RETURN 2
END

SUBROUTINE OUTMAX(K)
COMMON/TAPE2/N,IX(1000),IY(1000)
DO 1 1=1, N-1
J=I
IF(IY(J).LE.IY(1))GOTO 2
IF(IY(J+1).GT.IY(J))GOTO 2
CONTINUE
CONTINUE
K=J
WRITE(2,4)J
FORMAT(22H MAXIMUM OUTWARD POINT, I10)
RETURN
END

SUBROUTINE INMAX(K)
COMMON/TAPE2/N,IX(1000),IY(1000)
DO 1 I=1, N-2
J=N-I+1
IF(IY(J).LE.IY(N))GOTO 2
IF(IY(J-1).GT.IY(J))GOTO 2
CONTINUE
CONTINUE
K=J
WRITE(2,4)J
FORMAT(22H MAXIMUM INWARD POINT, I10)
RETURN
END
SUBROUTINE SCALE
COMMON/TAPE1/XMIN,YMIN,XMAX,YMAX,IXMIN,IYMIN,IXMAX,IYMAX
COMMON/TAPE2/N,IX(1000),IY(1000)
COMMON/TAPE3/M,X(1000),Y(1000)
DO1 I=1,N
X(I)=(XMAX-XMIN)*(IX(I)-IXMIN)/(IXMAX-IXMIN)
Y(I)=(YMAX-YMIN)*(IY(I)-IYMIN)/(IYMAX-IYMIN)
CONTINUE
RETURN
END

FUNCTION AREA(J,K)
COMMON/TAPE1/XMIN,YMIN,XMAX,YMAX,IXMIN,IYMIN,IXMAX,IYMAX
COMMON/TAPE2/N,IX(1000),IY(1000)
COMMON/TAPE3/M,X(1000),Y(1000)
A=0.0
DO1 I=J, K-1
A=A+(Y(I)+Y(I+1))/2.0*(X(I)-X(I+1))
AREA=ABS(A)
RETURN
END

FUNCTION AITKEN(X,Y,ARG,N,M)
C ***** NOTE THAT THE ARRAYS OF DATA POINTS START AT X(1) AND Y(1)
INTEGER SETMIN
DIMENSION X(100),Y(100)
DIMENSION Z(100),F(100)
EPS=10.**(-60)
IF(M.GE.N) M=N-1
J=SETMIN(ARG,M,N,X)
DO1 I=1,M+1
Z(I)=ARG-X(J)
F(I)+Y(J)
J=J+1
DO2 I=1,M
FI=F(I)
ZI=Z(I)
DO 3 J=I+1,M+2
ZIZJ=ZI-Z(J)
FJFI=F(J)-FI
IF(ZIZJ.LE.EPS,AND,J.EQ.I+1) GO TO 3
IF(ZIZJ.LE.EPS) GO TO 2
F(J)=FI+(ZI/ZIZJ)*FJFI
CONTINUE
CONTINUE
AITKEN=F(M+1)
RETURN
END
INTEGER FUNCTION SETMIN(ARG,M,N,X)
DIMENSION X(100)
DO 1 I=1,N
IF(ARG.LE.X(I)) GO TO 2
CONTINUE
I=N
I=I-M/2-1
IF(I.LT.1) I=1
IF(I=M.GT.N) I=N-M
SETMIN=I
RETURN
END
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