Synthesis and Molecular Modelling studies of Polyarylene ether sulphone dicyanates

A Thesis presented to the University of Surrey for the degree of Doctor of Philosophy in the Faculty of Science

By

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"Science is nothing but trained and organised common sense....."

Abstract

In this thesis, two major topics are discussed, namely the synthesis and characterisation of a cyanate ester polymer system based on the poly(arylene ether sulphone) backbone, together with the molecular modelling of this and similar polymeric systems.

The molecular modelling studies involve the general modelling of a poly(arylene ether sulphone) oligomer in a vacuum, which has the same repeat unit as UDEL poly(sulphone), originally produced by Union Carbide. The oligomer was characterised by atomistic models of the system using molecular mechanics and molecular dynamics techniques in which the flexibility of the backbone torsional angles were examined. The sulphone torsional angle was identified as the most flexible, followed by the ether torsional angle, with the isopropylidene angle being the most inflexible. Their energy barriers were 1, 4 and 6 kcal/mol respectively. The complexity of the polymeric system was then increased to model the above thermoplastic polymer under the influence of bulk conditions. Finally, the thermoset polymer with a poly(arylene ether sulphone) backbone, linked together by cross-linking cyanurate rings was modelled. Conformational properties were obtained of the various linking groups together with the calculation of various mechanical and physical properties, e.g., the Young's moduli and the glass transition temperatures of the simulated polymers. The results obtained from this work were generally in good agreement with experimental calculations.

The synthetic work involved making the oligomeric repeat unit which constituted the repeat unit used in the thermoset modelling studies. A poly(arylene ether sulphone) dicyanate ester oligomer was synthesised, which when cured, formed a cyanurate ringed thermoset network via the reaction of three cyanate ester groups to form an s-triazine ring. This polymer was then characterised by classical techniques to obtain various mechanical and physical properties of the networked thermoset polymer. These were then compared with the properties calculated in the modelling studies. Fairly good agreement between the experimental and simulated results were observed, e.g., the simulated Young's modulus and Poisson's ratio were 3.64 GPa and 0.35 respectively, whilst the experimental results were 2.50 GPa and 0.33 respectively.
In essence, the objective of this thesis was to synthesise and simulate via molecular simulation some poly(arylene ether sulphone) based thermoplastic and thermoset polymers and then to compare the various properties obtained from both techniques. The results show that molecular modelling techniques can be used to obtain accurate values of various properties of polymeric systems. This indicates that in the future, molecular modelling in conjunction with synthetic techniques may be used to predict trends and values of various properties of polymeric systems.
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Chapter 1: Introduction to polymers

1.1 History of polymers

Polymers have existed since the beginning of time. We only have to look at the constituents of deoxy ribonucleic acid (DNA), proteins and polysaccharides as evidence of this. However, it was not until the 19th century, that semi-synthetic polymers were identified, and the early 20th century, when the first synthesised polymer appeared. It was Charles Goodyear in 1839 who discovered that the elastic properties of natural rubber i.e., poly(isoprene) could be improved by heating with sulphur. This process, known as vulcanisation, produced crosslinks to yield a useful material in the production of automobile tyres. Bakelite became the first fully synthetic commercial polymer to be produced in 1910. This was originally synthesised by Leo Bakeland. He made use of the co-reaction between phenol and formaldehyde to form cross-links. The first synthetic rubber was made from 2,3-dimethylbutadiene during the first world war, but proved to be a poor substitute for natural rubber.

Hermann Staudinger was the first scientist to suggest that the structure of a polymer was composed of very large molecules, which contained long sequences of simple chemical units, linked together by covalent bonds. Staudinger introduced the word *macromolecules* to describe polymers and performed pioneering work on the synthesis, structure and properties of poly(oxyethylene) and poly(styrene). As the science of polymers grew, the number of synthetic polymers in production increased rapidly. These included poly(styrene), nylon, poly(ethylene), poly(vinylchloride), silicone rubbers and poly(tetrafluoroethylene).

Polymers now form an integral part of modern life. One only has to look at everyday commodities such as plastics, packaging and clothing to realise how heavily we rely upon polymeric materials. Polymers can be produced in many forms, as liquids, fibres, films, composites and mouldings and in recent times have been used to replace metals and other materials in numerous applications. Their excellent thermal, electrical and mechanical properties, in addition to their lightweight quality make them ideal substitutes in these areas. Currently, polymers can be 'tailor made' to exhibit these required properties.
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1.2 Definition of polymers

The composition of a polymer consists of molecules which have long sequences of one or more species of atom or groups of atoms, which are linked to each other by covalent bonds. Polymers are formed by reactions of their smallest constitutional part, namely a monomer (repeat unit). This reactive process is called *polymerisation*.

\[
\text{nM} \xrightarrow{\text{Polymerisation}} (M)_n \quad \text{M = monomer}
\]

\[ n = \text{large number} \]

In essence, a small molecule must possess two or more bonding sites to qualify as a monomer, in order that these can be linked to other monomers to form a polymer. The number of bond sites a monomer possesses is referred to as its *functionality*. For polymerisation to occur, monomers must be either bi- or multifunctional. The degree of functionality affects the type of polymer formed, so that bifunctional monomers form linear polymers (*thermoplastics*), whilst those which are polyfunctional (i.e., have three or more bonding sites), can develop into large three-dimensional networks (*thermosets*), containing both branches and crosslinks (see figure 1.1).

![Linear Branched Cross-linked](image)

**Figure 1.1.** The different types of polymer formed: linear, branched and cross-linked polymers.

1.2.1 Types of polymer

When a single species of monomer is used to build a polymer chain, the product is called an *homopolymer*. If two types of monomer are used to form a polymer chain, this produces
what is known as a copolymer, whilst three different monomers create a terpolymer etc. Copolymers produced from bifunctional monomers can be further subdivided as follows:

- **Random copolymers**: occur where the distribution of the monomers in the chain is random, although this will often depend entirely on the reactivities of the individual monomer.
- **Alternating copolymers**: form when there is regular alternation of two different monomers along the chain.
- **Block copolymers**: occur where each individual monomer exists in substantial blocks.
- **Graft copolymers**: where one monomer is grafted onto the backbone of the other to form branches.

### 1.2.2 Configuration of polymers

When a polymer chain contains asymmetric carbon atoms, it is possible to manipulate its configuration by altering the polymerisation conditions. For example, the discovery of the Ziegler-Natta catalyst in 1953 achieved the stereochemical control of polymers. Tacticity may take one of three forms.

- **Isotactic polymers**: If a chain of asymmetric carbon atoms has its constituents in the same steric arrangement, this will become apparent when the polymer, in the all trans zig-zag conformation is viewed along the length of the bonds, which comprise its backbone. In this state the polymer is said to be isotactic. As a result of their regular conformation, isotactic polymers may be crystalline.

![Figure 1.2. An isotactic polymer.](image)

- **Syndiotactic polymers**: A polymer is termed syndiotactic when its main chain supports exact alternation of its substituents, around each asymmetric centre.
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Atactic polymers: When random stereochemistry occurs along the polymer chain, the polymer becomes atactic and is said to be in an amorphous state, i.e., displaying no crystallinity.

The polymers which form the basis of the current work are largely amorphous, e.g., poly(ether sulphones).

1.2.3 Polymer morphology

Varying arrangements of atoms alter the physical state of polymers and consequently, their properties vary considerably. Therefore, the morphology of a polymer, i.e., the three dimensional arrangement of the polymer, is of primary importance. For example, amorphous polymers differ in their properties from semi-crystalline or crystalline polymers. Polymer properties are also effected as they pass through the glass transition temperature ($T_g$).

1.2.3.1 Amorphous polymers

Since the distribution of chains in an amorphous polymer is completely random, the polymer does not then have a specific melting point. Rather, as it is heated and motion of the polymer chains begins, it passes through a number of physical states. Its original glassy state is superceded by a rubbery condition as it passes through its $T_g$ value and finally it becomes viscous at high temperatures. Standard diffraction techniques can not easily be applied in the analysis of amorphous polymers because their conformation displays little...
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Predefined order. Consequently, little information exists about their absolute structural configuration.

The physical nature of an amorphous polymer is dependant on the amount of molecular motion it possesses, which itself is governed by chain flexibility and the temperature of the system in which it operates. A linear amorphous polymer can exist in five distinct states. The graph of the five states will vary in accordance with other determinants such as the molar mass and whether or not the sample is cross-linked or slightly crystalline.

In figure 1.5, the glassy state (A-B) occurs where large scale molecular motion along the chains has ceased. As more heat is applied, the motion of the polymer chains increases and the polymer occupies a greater volume and conformational space. Its physical state moves through the elastic (B-C) where the \( T_g \) is situated, to the rubbery condition (C-D) and on to the rubbery flow (D-E) until it becomes viscous (E-F). Further heating to much higher temperatures results in degradation.

![Figure 1.5. The five states in the heating of an amorphous polymer.](image)

### 1.2.3.2 Semi-crystalline polymers

Semi-crystalline polymers have regions of both amorphous and crystalline behaviour. Therefore, they have two transition points; the \( T_g \) and the melting temperature (\( T_m \)). Characteristic X-ray powder patterns can be obtained from the crystalline region, showing long-range order. The very nature of the polymerisation process, makes fully crystalline
polymers very rare, but as a result of crystal packing, three dimensional order occurs. Consequently, they have a characteristic melting temperature \( (T_m^0) \), but do not exhibit a \( T_g \).

1.2.3.3 The glass transition temperature

Since passing through the \( T_g \) enables the polymer to explore a region of free volume, the properties of a polymer change dramatically having passed through this point. Consequently, only polymers with an amorphous region possess a \( T_g \). By determining their thermodynamic properties, \( i.e. \), heat capacity \( (C_p) \), loss modulus \( (E') \) and volume expansion coefficient \( (\alpha) \), the \( T_g \) can be measured. These values can be measured respectively by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermomechanical analysis (TMA).

It is the poor packing of the chains in an amorphous polymer which creates its capacity for free volume. At low temperatures, chain motion ceases and so the polymer is unable to explore its volume potential. However, as the temperature is increased, it is able to explore this region. This process is represented in figure 1.6 as seen in an amorphous, semi-crystalline and crystalline polymer.

![Figure 1.6. Graph of specific volume of a polymer vs. increasing temperature.](image)

The \( T_g \) itself is affected in a polymer by various factors concerning the chemical nature and structure of the molecules:

- **Effect of chain flexibility**: the greater flexibility of the rotational bonds the lower the \( T_g \). \( i.e. \), polymers containing \( \text{CH}_2 \) linkages have low \( T_g \)s, whereas polymers containing the inflexible linkage \( p \)-phenylene have higher \( T_g \)s.
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- **Effect of molecular structure**: bulky side groups increase the observed $T_g$ due to more steric hindrance making chain rotation more difficult. Also the tacticity of polymers and *cis-trans* isomerism alters the $T_g$.

- **Effect of molecular weight**: as the polymer grows or increases its molecular weight ($M_w$), the chains need more thermal energy to increase their motion as they become more tangled, resulting in higher $T_g$.

- **Effect of cross links**: as they are introduced, so the density of the polymer is increased and the motion of the sample is reduced, increasing $T_g$.

1.2.4 Classification of polymers by molecular weight

Since the polymerisation process itself is dependant on factors such as viscosity and temperature, it is not surprising that polymers rarely have a well defined $M_w$, but rather this is distributed over a wide area. There are three main ways to express the average molecular weight of a polymer:

\[
\langle M \rangle_n = \frac{\sum N_i M_i}{\sum N_i} \quad \langle M \rangle_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \langle M \rangle_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}
\]

where $N_i$ is the number of molecules of species $i$ of molar mass $M_i$, $\langle M \rangle_n$ is the number average molecular weight, $\langle M \rangle_w$ is the weight average molecular weight and $\langle M \rangle_z$ is the $z$-average molecular weight. This is shown in figure 1.7\(^2\), where a typical mass distribution of a polymer sample is shown.

A variety of methods are employed to measure the $\langle M \rangle_w$, the $\langle M \rangle_w$ and the $\langle M \rangle_z$ of which the most widely used is *gel permeation chromatography* (GPC) or *size exclusion chromatography* (SEC). GPC is capable of separating polymers of very high molecular weight up to a $M_w$ of $10^6$. GPC can also separate *oligomers*, i.e., polymers in which only a few of the monomer units are joined together.
1.2.5 Thermoplastic polymers

Thermoplastic polymers are formed when the functionality of the constituent monomers has a value of two. These are linear or branched polymers which will soften when heated. Below their $T_g$ value, movement of the polymer chains is limited, so they are effectively frozen in position. Above their $T_g$ value however, they undergo main chain rotation about their bonds and generally move with ease. They can be moulded and remoulded into virtually any shape, using processing techniques such as injection moulding and extrusion. They are soluble in solvents and exhibit good flexural toughness and moulding characteristics, but are limited in their use at high temperatures and often have unacceptable solvent resistance. They constitute the largest proportion of polymers currently in industrial use. Examples include poly(tetrafluoroethylene) (PTFE), high and low density poly(ethylene) (HDPE, LDPE), poly(vinylchloride) (PVC) and poly(styrene).

1.2.6 Thermoset polymers

Thermoset polymers are formed when the functionality of the constituent monomers has a value of three or greater. Once cured, a thermoset polymer will exhibit an huge three-dimensional network structure. They are rigid materials in which chain motion is greatly restricted by a high degree of crosslinking. Thermosets are intractable once formed and although they will degrade at certain high temperatures, they will not soften when heated. Owing to their inherent rigidity, they generally have high $T_g$ and consequently can be used at elevated temperatures. They are not soluble in solvents and are often brittle and
susceptible to moisture permeation. Examples of thermoset polymers include phenolic resins (e.g., bakelite) and epoxy resins.

Owing to the varying properties thermoplastic and thermoset polymers possess, they are often blended with one another, especially in high temperature applications. The most amenable properties from both kinds of polymers can be utilised, so that polymers can have good processibility, thermal and toughness properties.

1.3 Polymerisation Mechanisms

There are two primary routes by which polymerisation may occur. Condensation polymerisations are classified as those which yield polymers whose repeat units have fewer atoms present than in the monomers. This state usually arises from chemical reactions which involve the elimination of a small molecule (e.g., \( \text{H}_2\text{O}, \text{HCl} \)). Addition polymerisations are those which yield polymers whose repeat units have identical molecular formulae to their component monomers.

On some occasions however, these classifications were found to be unsatisfactory for a number of systems, e.g., the formation of poly(urethanes). This is because they grow by a step-mechanism, but without the elimination of a small molecule. Therefore, a different type of classification, better defined by the underlying mechanism of the polymerisation is used. Polymerisations in which the polymer chains grow step-wise by reactions that can occur between any two molecular species, are known as step-growth polymerisations. Those in which the polymer chain grows only by the reaction of the monomer, with a reactive end-group on the growing chain, are known as chain-growth polymerisation. This process usually requires an initial reaction between the monomer and an initiator in order to start the growth of the chain.

1.3.1 Step-growth (condensation) polymerisation

Step-growth polymerisations which involve reactions in which small molecules are eliminated are called polycondensations. The formation of a linear, semi-crystalline poly(ketone) with the elimination of potassium fluoride is a typical example (see figure 1.8). This type of reaction is often referred to as an \( \text{RA}_2 + \text{RB}_2 \) step polymerisation.
1.3.2 Chain-growth (addition) polymerisation

There are many different ways in which monomers undergo chain-growth polymerisation and an example is given as follows.

*Free radical polymerisations* are chain processes in which each polymer molecule grows because a monomer is added to each terminal free-radical reactive site. This reaction can be divided into three distinct stages: *initiation*, *propagation* and *termination*, which each have associated kinetic parameters and activation energies.

### 1.4 Poly(ether sulphones)

Poly(ether sulphones)$^{3,4,5,6,7,8,9}$ are a family of engineering thermoplastics, that can be used consistently to temperatures greater than 190°C. They are tough, rigid materials of high thermal stability which show good mechanical properties, particularly their creep resistance. Poly(ether sulphones) are resistant to attack by dilute acids and alkalis, and can easily be converted for use in product manufacture making them particularly suited to the process of injection moulding. These amorphous materials have a $T_g$ in the range of 180°C to 230°C$^3$ depending on the nature of the polymer backbone. Chemically, they are related to poly(ether ketones)$^{10}$, an analogous semi-crystalline family of materials which possess a $T_g$ in the region of 150°C and a $T_m$ of approximately 330°C$^3$.

---

Figure 1.8. Synthesis of a poly(ketone), a polycondensation reaction.
1.4.1 Discovery of poly(ether sulphones)

Routes to aromatic poly(sulphones) were discovered independently but almost simultaneously in the early 1960's by a number of companies: 3M Corporation, Union Carbide and ICI plastics division. The search for materials of this type led to the discovery of polymers composed of linked aromatic rings, which exhibited high thermal and oxidative stability, to which various linking groups could be incorporated, as shown in figure 1.9.

![Figure 1.9. Schematic of the poly(sulphone) monomer unit where X = SO₂ and Y = SO₂, O, C(CH₃)₂.](image)

Such linking groups play a crucial part in determining the properties of the polymer, since they control the flexibility of the chain and determine its overall polarity. Links can be selected so that good stability is retained and the polymer is sufficiently flexible to show thermoplasticity at temperatures much greater than 150°C. The sulphone linkage was investigated as its degree of stability was already well known. However, chains consisting of solely sulphone linkages i.e., poly(phenylene sulphone), displayed rigid thermoplasticity. Therefore, other linking groups were added to the chain, typically that of ether, and attention became concentrated on poly(arylene ether sulphones). Poly(arylene ether sulphones) are prepared as shown in figure 1.10 to produce the 'Udel' poly(sulphone) (made by Union Carbide, Tₘ = 195°C). Other poly(sulphones) commercially prepared include Astrel 360 (made by 3M, Tₘ = 285°C), poly(ether sulphone) 720P and 200P (made by ICI, Tₘ = 250°C and 230°C respectively) and these are shown in table 1.1.

\[
\begin{align*}
nMO-\text{Ar} & -\text{OM} & + & n\text{Hal}-\text{Ar}'-\text{Hal} \\
\text{Dimethylsulphoxide} & \quad \text{(DMSO)} \downarrow \\
\left[\text{O}-\text{Ar}-\text{O}-\text{Ar}'\right]_n & + & 2n\text{MHal}
\end{align*}
\]

where M = alkali metal; Ar and Ar' are arylenes residues
Polymers produced by condensation \textit{i.e.}, chain growth reaction, are synthesised by a process known as \textit{polyetherification}\textsuperscript{3,12}. Solvents such as dimethyl sulphoxide or sulpholane can be used in the process. The use of such dipolar aprotic solvents is an important feature of the
process and one which enhances the rate of the substitution reaction\textsuperscript{14}. Ether bonds are formed \textit{via} displacement of the halogen atoms by phenoxide anions. The sulphone group is an essential part of the dihalide. The sulphone group play a vital part in the reaction, since they activate the halogens to be attacked, by the phenoxide anions. Aromatic halides which do not contain powerful electron withdrawing groups, like the sulphones, are unreactive and not suitable for the synthesis of high polymers. Another important route to poly(sulphones) is \textit{via} the polysulphonylation process\textsuperscript{4}.

1.4.2 Properties of poly(ether sulphones)

Poly(sulphones) are almost exclusively amorphous materials, with only a few reported examples becoming crystalline\textsuperscript{15} and these are generally specifically made with rigid biphenyl groups in the backbone\textsuperscript{16}. Variations in their behaviour at high temperature are determined by their $T_g$ values which cover a wide range, depending on the repeat unit; the greater the number of sulphone linkages per unit, the greater the $T_g$ value. The $T_g$ for Udel poly(sulphone) is 195°C\textsuperscript{12} which can be increased by about 15°C in this type of poly(sulphone) by increasing the bulk of the substituents on the central carbon atom. Amoco\textsuperscript{17} commercially produce Radel poly(sulphone) in which the bisphenol-A unit is replaced with a biphenyl unit which increases the $T_g$ by 25°C. Therefore, by altering the linking groups, or by making $o$-phenylene derivatives rather than $p$-phenylene derivatives, the $T_g$ can be greatly altered with a consequent effect on the properties of the materials. Unlike other reinforced thermoplastics, they exhibit good qualities of toughness and rigidity\textsuperscript{18}. They have good electrical and thermal properties\textsuperscript{3,5,19} which are maximised in their commercial applications, and are highly resistant to attack by acids and bases. However, they have relatively low chemical, solvent and stress-crack resistance.

1.4.3 Poly(ether ketones)

As mentioned in section 1.4, poly(ether ketones)\textsuperscript{10} belong to a similar class of polymer family. In this case however, the difference is made by replacing the sulphone linkage with a ketone linkage. These polymers are semi-crystalline and have a lower $T_g$ than poly(sulphones). Initially, they were produced in the same way as poly(sulphones), but as their crystallinity makes them almost entirely insoluble in most solvents, they precipitate out of solution and growth stops\textsuperscript{10}. It was not until the use of dichloromethane\textsuperscript{20}, liquid
hydrogen fluoride\(^21\) and phenyl sulphone\(^22\) as solvents, or the use of Friedel-Crafts acylation\(^23\), that high polymers were produced. Poly(ketones) have exceptional qualities of strength, rigidity and toughness in addition to excellent chemical and radiation resistance. However, they have a number of disadvantages; they are not soluble in any commercial solvents, their \(T_g\) values are fairly low, synthesis is difficult due to processing conditions and consequently they are manufactured in relatively small quantities, which raises production costs\(^24\). This is reflected in the price differential; poly(ketones) can retail for approximately $22/per pound, whereas poly(sulphones) sell for approximately $4.25/per pound\(^25\).

1.4.4 Application of these polymers

It is possible to maximise the individual strengths of both systems by making block copolymers\(^26,27,28\) which utilise areas of poly(sulphone) and poly(ketone) in the backbone of the polymer. These copolymers are made to utilise the best properties from both types of polymer, i.e., have high \(T_g\) and tensile strength. These copolymers are amorphous at poly(ketone) content below 65% and crystalline if greater than 80% of poly(ketone) is present. The \(T_g\) varies from 225°C for 100% poly(sulphone) content to 170°C at 80% poly(ketone) content, whereas the tensile strength increases from 11400psi to 14800psi (78.3 to 101.6 MPa) for the same copolymers. This increase in tensile strength is due mainly to the contribution of the crystalline phase\(^29\). Cao et al.\(^30\) discovered that as the amount of poly(sulphone) in the copolymer increased or the segment length decreased, the melting points and the crystallinity of the copolymers decreases. Poly(sulphone)/poly(ketone)\(^24,31\) blends involve another procedure which utilises the repeat unit from both sulphone and ketone linkages\(^32\), by mixing the two components at various temperatures. There is only one \(T_g\) temperature which varies with the amount of poly(sulphone) and poly(ketone) present. Recently, Pandya et al.\(^33\) and Staniland et al.\(^32\) have produced semi-crystalline poly(arylene ketone sulphones), which have ketone and sulphone linkages present in the repeat unit of the polymer. These polymers have \(T_g\)'s which are higher than for normal poly(ketones) (approximately 160-180°C), whilst the \(T_m\)'s are high at approximately 440°C, but they have fairly low \(M_{ci}\) and \(M_{cw}\) values. Combining the polymers with a fibrous material to produce a composite\(^34,35,36,37,38,39,40\) or lastly by introducing cross links\(^41\) are other ways of improving the properties of the two polymers.
Poly(sulphones) are currently being used to replace metals as they can be used in injection moulding, which is more economical than the costly operation of machining metals. Good electrical properties mean poly(sulphones) can be used in a variety of electronic applications; in printed circuitry boards where solder is used, as coil formers in output transformers, as a dielectric for miniature capacitors and as electrical connectors. Good thermal stability enables them to be used in ovens and as a structural adhesive to upgrade the temperature performance of epoxy resins. Owing to their ability to resist acids and heat, they are currently being evaluated for possible use in gear boxes and in medical equipment which needs to withstand repeated steam, dry heat or chemical sterilisation. Finally, they are used as ultrafiltration membranes. Poly(ether ketones) are used in a variety of specialised electronic and electrical products such as printed circuit boards, in addition to high temperature mono-filaments, valves and seals produced in fluid handling.

1.5 Cyanate esters

Cyanate esters represent a major family of thermosetting resins. They demonstrate a wide range of properties including high fracture toughness, low dielectric loss, dimensional stability at high temperatures with Tg's around 250°C, and overall versatile processing qualities. Their applications include use in the electronic, aerospace and adhesive industries. Commercial cyanate esters are bisphenol derivatives produced by reacting the bisphenol units with cyanogen halides, e.g., cyanogen chloride. They are characterised by the O-C=N functional group and the general form of a cyanate ester is shown in figure 1.11.

![Figure 1.11. A schematic of a typical cyanate monomer, where X= O, C(CH₃)₂, S, C(CF₃)₂ or longer chain aromatics.](image)

1.5.1 Cure of cyanate esters

The cyanate ester monomers polycyclotrimerise when heated in the presence of a catalyst to form substituted s-triazine rings. The curing process results in a three dimensional network which is commonly termed a polycyanurate (see figure 1.12). This is a step-growth process, where three cyanate moieties are needed, to form the produced s-triazine ring.
This is a classic example of where the terms condensation or addition polymerisation terms are outdated in this context. The formation of the \( s \)-triazine rings can easily be followed by infra red (IR) measurements where the C\(=\)N stretches at \( \sim 2200\text{cm}^{-1} \) gradually disappear as the cyanate ester oligomers react. They form bands at approximately 1560 and 1380\text{cm}^{-1} \) for the formation of the \( s \)-triazine ring and the C-O-C cyanurate link. An important feature of the curing process, is that under certain conditions, the cyclotrimerisation of the O-C\(=\)N group, proceeds with virtually quantitative conversion.

\[
3 \quad \text{N} = \text{C} - \text{O} - \text{X} - \text{O} - \text{C} = \text{N}
\]

![Figure 1.12. Schematic diagram of the polycyclotrimerisation of cyanate ester monomers forming \( s \)-triazine rings.](image)

Typical catalysts used are transition metal complexes (chelates or carboxylates) such as copper, cobalt and manganese acetylacetonate or copper and zinc naphthenate. As these
complexes are of low solubility, nonyl phenol (a co-catalyst) is added to act as a diluent. A typical concentration per 100g of a cyanate oligomer would be 4g of nonyl phenol and 0.2g of metal complex (300ppm Cu$^{2+}$). It has been found that the amount of catalyst and co-catalyst has an important effect on the $T_g$ and the thermal stability of the produced polycyanurate network$^{30,51}$. The cure schedule generally falls into two parts. The resin may first be cured at approximately 170°C for 3 hours, and is then post-cured at e.g., approximately 250°C for an hour$^{52}$.

The curing process is known to take place with or without the presence of catalyst for certain monomers$^{45}$ and will also occur in either solution or bulk conditions. Although the reactions of model systems have been studied and IR investigations made to identify some of the intermediates produced during curing$^{53}$, there is little information to determine the species, nature or efficiency of the curing process itself. Fyfe et al.$^{54}$ using $^{13}$C and $^{15}$N enriched cyanates, stated that there was no NMR evidence to suggest that the formation of dimeric or other intermediate species occurs prior to $s$-triazine ring formation. This finding was supported by Barton et al.$^{55}$, using FTIR and $^{13}$C/$^{15}$N NMR, although recent work by Fang et al.$^{56}$ using mass spectroscopy has suggested the presence of a dimeric intermediate.

Polycyanurate resins may be easily toughened, by co-reaction with other materials, normally thermoplastics to form semi-interpenetrating networks (semi-IPNs). Materials containing two polymers, one of which is crosslinked, are defined as semi-IPNs$^{57}$. Woo et al.$^{44}$ have modified bisphenol-A dicyanate using a poly(sulphone) (Udel P1700) and a poly(ether imide) (GE Ultem 1000). With a 20% thermoplastic content, the fracture toughness ($K_{IC}$) has improved from 0.80MPa.m$^{1/2}$ for the neat resin, to 1.10 and 1.45MPa.m$^{1/2}$ respectively for the modified systems, whilst maintaining the high $T_g$ of the thermoset polymer.

Srinivasan et al.$^{58}$ have modified bisphenol-A dicyanate networks with Udel and either the hydroxy or cyanato functional 16K amorphous poly(arylene ether sulphones) or poly(arylene ether ketones). The best results to be produced, occurred when a 25% blend of 90% poly(ether sulphone)/10% Udel was used, giving a fracture toughness of 1.4MPa.m$^{1/2}$, whilst the $T_g$ was preserved at 275°C. If modified with 30% 15K hydroxy or cyanato terminated poly(arylene ether ketone) the fracture toughness increased to 2.1MPa.m$^{1/2}$, but with a corresponding loss in $T_g$ to 150°C (in the same range as the $T_g$ of the semi-crystalline modifier). Wang et al.$^{59,60}$ co-reacted bisphenol-A dicyanate, poly(arylene ether sulphone) and a bis-maleimide in varying concentrations, to give polymers of slightly different
properties. These also have high \( T_g \) values (200-250°C) and have varying fracture toughness. The results show that increasing the molecular weight and the percentage of the poly(arylene ether sulphone) oligomer increases the fracture toughness substantially from 0.8 to 1.5MPa.m\(^{1/2}\), but with a corresponding drop in the \( T_g \) of the material.

Other studies carried out have improved physical and mechanical properties by forming networked composites. This is achieved either via a neat cyanate or by using various thermoplastic modifiers\(^{57,61}\). Composites improve the properties of cyanate esters as the material is normally made from carbon fibre which increases the strength and modulus of the polymer.

### 1.5.2 Specific uses of cyanate ester polymers

In the light of their excellent thermal, dielectric and mechanical properties, cyanate esters have a wide range of applications. They are primarily used in the electronic industry, specifically because their high purity, high thermal stability and low dielectric losses meet the stringent insulation resistance conditions which are required\(^{62,63}\). They are also used as electronic encapsulants. Their high fracture toughness and high service temperature, means they conform to the majority of the high temperature composite applications requirements\(^{64,65,66}\). In addition to their use in the adhesive industry\(^{45}\), cyanate esters are in demand as flame retardant materials\(^{65,67}\).

### 1.6 Organisation of work

The basis of this thesis falls into two categories: synthesis and modelling. Firstly, the synthesis and characterisation of a new polymer, namely a 6-ringed poly(arylene ether sulphone) dicyanate which was cured to form a cyanurate ringed thermoset network. Studies in molecular modelling are then discussed, with specific reference to two simulations: the simulation of a linear amorphous poly(arylene ether sulphone) in the form of a thermoplastic and the modelling of a poly(arylene ether sulphone) dicyanate, in the form of a thermoset.

After the introductory discussion of polymers and their synthesis and properties in chapter 1, chapter 2 details the synthesis and characterisation of a short oligomer of a poly(arylene
ether sulphone) dicyanate. This was formed in a number of reaction stages and was consequently cured into a thermoset polymer. The oligomer was produced by the synthesis of dichlorodiphenylsulphone and bisphenol-A, in which the bisphenol-A moiety was protected, so that the production of high oligomers did not occur. This oligomer was subsequently cyanated to produce the cyanate ester oligomer, which was then cured to form a polymeric resin slab, *via* the reaction of three cyanate groups to form cross-linking cyanurate groups. A parallel study also took place using the commercial prepolymer 2,2'-bis(4-cyanatophenyl) isopropylidene AroCy® B30\(^{52}\), which was also cured to form a thermoset polymer. Testing of the produced resin slabs from both systems, illustrated various physical and mechanical properties of the cured polymers.

Chapter 3 provides a general introduction and background to molecular and polymer modelling with some discussion of the theoretical background behind the techniques. The chapter concludes with a brief modelling study of difluorodiphenylsulphone, 2,2'-bis (4-cyanatophenyl) isopropylidene and a cyanurate ring. In this section, various parameters were modified to give computational molecular structures which were more closely related to the physical 'ideal' structures of the real systems.

Chapter 4 discusses the application of techniques such as minimisation, conformational analysis and molecular dynamics simulations to the characterisation of a linear model of a poly(arylene ether sulphone) oligomer as an isolated chain, *i.e.*, it was modelled in a vacuum. The movement and flexibility of the linkages involved were evaluated from the conformational analysis and molecular dynamics simulations and compared to crystal data. In addition, a comparative study took place which dealt with a linear chain of the analogous material, namely a poly(arylene ether ketone) oligomer. Also, a study of the cyanurate ring linkage was performed, again using the techniques described above.

Chapter 5 describes the modelling of the polymer poly(arylene ether sulphone) under the influence of periodic boundary conditions, in which various different simulation conditions were applied. Constant volume and constant pressure molecular dynamics simulations were performed, in which factors such as bulk density, intermolecular and intramolecular interactions, solvent and temperature were considered. From these molecular simulation studies, various physical and mechanical properties such as the \(T_g\) and the elastic constants of the system were calculated.
Chapter 6 discusses the modelling of two thermoset polymers, namely bisphenol-A dicyanate and a 6-ringed poly(arylene ether sulphone) dicyanate. Various physical and mechanical properties were obtained from the molecular dynamics simulations, in which the theory behind these techniques is discussed at the beginning of the chapter. These results are then compared to those obtained from the synthetically produced polycyanurate networks, discussed in chapter 2 and to the values obtained for these various properties from other modelled polymers present in the literature.

In conclusion, this thesis seeks to illustrate that polymer modelling and polymer synthesis can be used in tandem to obtain polymer properties. Similar results describing various aspects of the polymer, e.g., polymer conformation and physical and mechanical properties can be obtained from either molecular simulation or polymer characterisation techniques. This shows that molecular modelling can be used in the prediction of accurate polymer properties.

1.7 References

36 J. C. Seferis, Polymer Composites, 7, 158-169 (1986).
49 V. A. Pankratov, S. V. Vinogradova and V. V. Korshak, Russian Chemical Reviews, 46(3) 278-295 (1977) (and references cited therein).
52 Interez Inc. AroCy® B30 Cyanate Ester Resin, data sheet.


Chapter 2

Synthesis and characterisation of Poly (arylene ether sulphone) dicyanates

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2.1 Introduction

In this chapter, the production of a short oligomeric unit of a poly(arylene ether sulphone), with the same nominal repeat unit as Udel® is described. Normally, when poly(arylene ether sulphones) are made, they form a thermoplastic polymer containing many repeat units, but for this system, only a one monomer repeat unit was required. Consequently, a suitable synthesis was needed to produce this kind of monomer. Cyanate end groups were then added to this monomer to form the cyanate ester to enable the newly produced oligomer to co-react and cross-link via the cyanate groups. In this process, which is called cyclotrimerisation, the cyanate groups are converted into cyanurate rings to form a three-dimensional network structure, which is called a thermoset.

Once the cyanate groups had been cyclotrimerised, the properties of the polymer were tested. In this work a model compound, namely AroCy® B30, the ~30% converted prepolymer form of bisphenol-A dicyanate was also tested and used as a comparison (hereafter referred to as B30). Then the synthesised system under investigation was tested. The polymers obtained in this work were characterised using a variety of techniques including differential scanning calorimetry, dynamic mechanical thermal analysis and thermogravimetric analysis, together with other classical analytical techniques. These techniques are discussed briefly in the next section, followed by the synthesis section and finally the polymer processing and properties determination, which is discussed towards the end of the chapter.

2.2 Characterisation techniques

Many different techniques, both classical and specific to polymer characterisation were used in the identification of the oligomer and the newly formed polymer. These techniques are discussed below.

2.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is a widely used and important characterisation technique used in chemistry for small and large compounds and is used extensively in polymer characterisation. NMR was used throughout the synthetic process, to check the reactions to show how far they had proceeded.
and to characterise the synthesised cyanate ester oligomer. Finally, solid state NMR was used to characterise the obtained thermoset polymer. This was used instead of solvent based NMR experiments, because when the oligomer polymerises into a thermoset, it is insoluble and consequently not amenable to solution NMR characterisation.

The observation of NMR signals is possible, because nuclei have angular momenta, which are characterised from quantum mechanics by the spin quantum number, I. In a magnetic field, the spin states become non-degenerate and transitions between these two levels are observed. The observed frequencies depend on the strength of the magnetic field and the magnitude of the nuclear magnetic moment. Important nuclei observed in NMR are $^1$H and $^{13}$C and consequently these nuclei have been used to characterise the oligomer and the polymer more fully. In $^{13}$C NMR, distortionless enhancement by polarisation transfer (DEPT) experiments have been performed to characterise the methyl (-CH$_3$), the methylene (-CH$_2$), the methyne (-CH-) and the quaternary (-C-) groups respectively. In this work a Bruker AC-300 spectrometer was used, operating at 300MHz for proton studies and 68.2MHz for carbon studies. Normal Bruker software was used to acquire and obtain the produced spectra. In the $^1$H NMR determinations the following abbreviations were used: s = singlet, d = doublet, t = triplet and m = multiplet.

2.2.2 Fourier Transform Infra Red (FTIR) Spectroscopy

FTIR is used to define certain atom arrangements within a structure, and although in some instances it may not give a definite picture of a molecule, it can indicate which functional groups are present in a molecule. This occurs because an isolated molecule containing N atoms has (3N - 6) normal modes of vibration, consisting of a complex mixture of bond stretches and deformations. The frequencies and intensities of the modes are sensitive to chemical structure and are often localised into discrete chemical groupings, in which observations of bands in well-defined ranges can indicate the presence of particular groups. The IR spectrum arises from the absorption of radiation, the frequency of which is resonant with the vibrational transition.

FTIR spectroscopy was used to characterise the oligomer and to analyse the synthesised polymer. The instrument which was used was a Perkin Elmer System 2000 interfaced to a
personal computer using the software written by Perkin Elmer. The samples were analysed using either a KBr disk or a liquid film.

### 2.2.3 Chromatography

Chromatographic techniques were used to purify the oligomers for use in micro analysis. Column chromatography was used for this purpose using silica gel of size 0.035-0.07mm with a pore diameter of approximately 6nm. Other techniques used included analytical high performance liquid chromatography (HPLC) to obtain the purity of the final oligomer. The HPLC method used a flow rate of 2ml/min using CH$_2$Cl$_2$ as solvent, with a UV detector set at a wavelength of 270nm, with the readings taken every second. Thin layer chromatography (TLC) was used to monitor reactions, check for impurities and to obtain mobile phases for column chromatography.

### 2.2.4 Differential Scanning Calorimetry (DSC)

DSC utilises heat capacity as a measure of the changes that can occur in the physical properties of a sample, as the temperature is increased.

DSC works by heating two aluminium pans over the required temperature range, one empty pan is used as a reference, whilst the other contains the sample under test. The system is purged with nitrogen. By monitoring the difference in temperature between the two pans and converting $\Delta T$ to heat flow, the heat capacity of the sample is obtained. This is related to eqn. 2.13.

$$\Delta T = K \Delta m C_p R$$  \hspace{1cm} eqn. 2.1

where $\Delta T$ is the temperature difference between the sample and the reference, $\Delta m C_p$ is the difference in total heat capacity between the sample and the reference, $R$ is the heating rate (K/min) and $K$ is a factor which must be calibrated.

Variations in the graph come from exothermic or endothermic processes. It is possible to monitor processes such as the melting temperature ($T_m$) and the glass transition temperature ($T_g$). The $T_m$ is characterised by a minimum in the plot of heat flow against temperature,
whereas at the \( T_g \), there is merely a discontinuity in the baseline. This is because at the \( T_g \), the polymer is in a continuous state of main chain motion, thus permitting a change in free-volume and hence an inflection in the heat flow versus temperature plot is seen. Consequently, the \( T_g \) can be obtained from DSC plots.

The DSC instrument was a Shimadzu DSC-50 interfaced to a Shimadzu TA-501 thermal analyser, which in turn was interfaced to a personal computer. The results were analysed using software written by Shimadzu. The heating rate was 10K/min, under a steady flow of nitrogen (10ml/min). The DSC machine was calibrated using pure Indium and Zinc metal having melting points at 157°C and 420°C respectively.

### 2.2.5 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measures molecular motion in polymers\(^3\). The technique relies on imparting a small sinusoidally varying stress (at a specific frequency 0.01-200Hz, depending on the modulus and sample type) to the material under test which transduces a stress to \( \log(\text{modulus}) \) vs. temperature response. The corresponding lagged sinusoidal strain of the material is measured over a desired temperature range. In the case of a completely elastic material the strain is in phase with the stress, but for a purely viscous material the strain lags behind the stress by 90° (out of phase). Consequently, the behaviour can be resolved into an in-phase elastic like component (the storage modulus \( E' \) or \( G' \)) and an out-of-phase viscous like component (the loss modulus \( E'' \) or \( G'' \)). Below the \( T_g \), the modulus is at its maximum value, but above the \( T_g \), the modulus falls. The phase angle (lag of strain behind stress) is also clearly defined as the 'loss tangent' - \( \tan \delta \). This is physically the ratio of energy lost to energy stored per frequency cycle\(^3\).

\[
\tan \delta = \frac{G''}{G'} \text{ (in shear)} \quad \text{or} \quad \tan \delta = \frac{E''}{E'} \text{ (for Young's modulus)}
\]

**eqn. 2.2**

Various relaxations can be seen from a DMTA scan. These include the \( T_g \) and the \( T_m \) and the moduli and loss tangent, \( \tan \delta \) described earlier.

The instrument which was used was a Polymer Laboratories Mark II DMTA\(^4\), interfaced to a personal computer, in which Polymer Laboratories software was used to analyse the acquired data. The machine incorporated a dual cantilever bending mode head running at a
frequency of 10Hz. The temperature range varied from 40-300°C, with an heating rate of 4K/min.

2.2.6 Thermomechanical Analysis (TMA)

TMA is a technique to measure the linear expansion of a known thickness of material as a function of temperature. Consequently, TMA is used to measure the thermal expansion coefficients of a polymer, namely $\alpha_g$ and $\alpha_l$, which are the expansivities in the glassy and liquid regions respectively. By extrapolation of the produced graph, the $T_g$ can also be obtained, but the DMTA method is a superior method of determining the $T_g$. A small sample is placed in a cell, below a suspended probe, which is just kept in contact with the sample. A small weight is placed on the probe to ensure that it touches the sample. An heating jacket is placed around the sample and the expansion is measured from the formulae given as equation 2.3. The linear expansion of the material is measured electronically via a displacement sensor, whilst the initial thickness of the material is measured by an electronic micrometer.

\[
L = L_0(1 + \int_T^{T_0} \alpha dT) \quad \text{or} \quad \alpha = \frac{\Delta L}{\Delta T} \cdot \frac{K}{L_0}
\]

eqn. 2.3

where $L_0$ is the thickness at temperature $T_0$, $L$ is the thickness at temperature $T$, $\Delta L$ is the change in thickness of the sample, $\Delta T$ is the change in temperature over the simulation run, $\alpha$ is the linear expansion coefficient and $K$ is a calibration constant. As the material is heated, it expands linearly until there is a transition, e.g., the $T_g$, where there is a change in the gradient of the slope which allows the expansion coefficients to be measured.

A DuPont instrument - a 943 Thermomechanical Analyser was used and interfaced to a Thermal Analyst 2100 which also analysed the data via internal software packages. The heating rate in all the experiments was 10K/min. The instrument was calibrated using aluminium, which gave an expansion coefficient of $22.2 \times 10^{-6} \text{K}^{-1}$ (literature value = $25.4 \times 10^{-6} \text{K}^{-1}$). This gave a value of 1.32 for the calibration constant.
2.2.7 Thermogravimetric Analysis (TGA)

TGA consists of measuring the weight change of a known mass of sample, as a function of temperature. Consequently, TGA is used to measure the thermal-oxidative stability of a polymer. As the thermal-oxidative stability increases, there is less decomposition of the polymer. A Shimadzu TGA-50 was used for the analyses which was again interfaced via the thermal analyser to a personal computer. The data was analysed using software written by Shimadzu. The heating rate was 30K/min, under a steady flow of nitrogen (50ml/min). The machine was calibrated using Indium and Zinc, where significant weight loss was measured at their respective melting points.

2.2.8 The Instron Universal Testing Apparatus

An Instron universal testing apparatus (model 1175) was used to obtain the Young's modulus (E) and the Poisson's ratio (v) of the polymers. Polymer strips of approximate size 80mm x 10mm x 3mm were placed between the grips of the machine. A strain of up to 0.4% was applied, and the sample was pulled apart at a rate of 0.5mm/min. The apparatus incorporated an highly sensitive electronic force measuring system and had load cell strain gauges to detect the load applied to the specimen under expansion or compression. Using the Young's modulus and Poisson's ratio calculated from the measurements, the other values of the elastic constants (see section 6.2) were calculated.

2.3 Synthesis of a six-ringed poly(arylene ether sulphone) dicyanate

This synthesis was performed in four stages. First, bisphenol-A was protected by 3,4-dihydro[2H]pyran. Second, this was made to react with dichlorodiphenylsulphone to form a protected 6-ringed poly(arylene ether sulphone). Third, this was deprotected and finally, the resulting structure was made to react with cyanogen bromide (CNBr) to form the 6-ringed poly(arylene ether sulphone) dicyanate ester oligomer.

2.3.1 Step 1 - Synthesis of protected bisphenol-A

A 250ml beaker, equipped with a magnetic stirrer bar was charged with bisphenol-A (30.96g, 0.136mol), diethylether (100ml) and para-toluenesulphonic acid (TsOH) as
catalyst. 3,4-dihydro[2H]pyran (11.41g, 0.136mol) was added dropwise to the solution over an hour. The solution was stirred continuously at room temperature for 12 hours, which formed a pale yellow/brown solution, as shown in figure 2.1.

NaOH (20g, 200ml water) was added to the solution, making sure the solution was alkaline, to form the dihydropyran sodium salt of bisphenol-A. The resulting white compound was vacuum filtered and washed with diethylether (200ml). Then the compound was washed twice with NaOH (20g in 200ml water) and finally with water (200ml) under vacuum to remove any impurities. After drying the product for two days in a vacuum dessicator, the product turned a light brown/white colour. The crude material was used in the next stage without further purification.

Yield = 20.45g (45.1%).
TLC in 1:1 ether/hexane shows one spot at an rf = 0.6.
Melting point = 185-187°C

Elemental analysis:
Expect for C_{20}H_{23}O_3Na: C 71.85%, H 6.88%, N 0.0%.
Found C 66.87%, H 6.77%, N 0.0%.

This carbon value was low due to the amount of solvent and water in the product which was very difficult to remove. If a mole of water is assumed to be in the product (this is assumed as approximately 5ml of water is removed in the next stage of the synthesis), then the
expected percentage amounts change to: C 68.18%, H 7.10%, N 0.0%, which shows the percentage of carbon approaching the theoretical value.

$^1$H NMR (CD$_3$OD) $\delta$: 1.55 (s, 6H), 1.63 - 2.01 (m, 6H), 3.55 (m, 1H), 3.90 (m, 1H), 5.35 (t, J=3.4Hz, 1H), 6.55 (d, J=6.5Hz, 2H), 6.84-6.90 (m, 4H), 7.1-7.2(d, J=8.7Hz, 2H).

$^{13}$C NMR and DEPT (CD$_3$OD) $\delta$: 20.10 (-CH$_2$-), 26.37 (-CH$_2$-), 31.59 (-CH$_2$-), 31.71 (-CH$_3$), 42.46 (-C-), 63.22 (-CH$_2$-), 97.96 (-CH-), 116.82 (-CH-), 117.41 (-CH-), 128.44 (-CH-), 128.66 (-CH-), 140.05 (-C-), 146.33 (-C-), 155.98 (-C-), 160.83 (-C-).

FTIR (KBr disks) $\nu$ cm$^{-1}$: 831 (1,4-disubstituted benzene), 1035 (-C=O-), 1075 (-C=O-), 1147 (-SO$_2$-), 1241 (-C=O-), 1360 (-C(CH$_3$)$_2$-), 1384 (-C(CH$_3$)$_2$-), 1442 (-CH$_3$-CH$_2$-), 1453 (-CH$_3$-CH$_2$-), 1509 (Ar C=C), 1582 (Ar C=C), 1602 (Ar C=C), 2869 (-CH$_3$), 2942 (-CH$_3$), 3015 (Ar-H).

2.3.2 Step 2 - Synthesis of a protected 6-ringed poly(arylene ether sulphone)

A 500ml round bottomed flask equipped with a Dean-Stark trap, a reflux condenser, a thermometer and a magnetic stirrer bar was charged with protected bisphenol-A (45.0g, 0.136mol), dichlorodiphenylsulphone (DCDPS) (19.33g, 0.068mol), potassium carbonate (18.59g, 0.136mol), N,N-dimethylacetamide (DMAC) (200ml) and toluene (100ml). The mixture was heated to reflux temperature, and water was removed as an azeotrope with toluene in the Dean-Stark trap. 5ml of water was removed, and more protected bisphenol-A (5g) was added to keep the molar ratios constant between the protected bisphenol-A and the DCDPS molecules. The reflux temperature gradually increased as more toluene was removed from the reaction, until the reflux temperature reached 160°C. At this point the Dean-Stark trap was removed and an air condenser was added. The reaction mixture was boiled under reflux (160°C) for a further 2 days, as shown in figure 2.2, then allowed to cool to room temperature.

The product was poured into water (150ml) and extracted with CH$_2$Cl$_2$ (4x50ml) to remove any inorganic salts. The CH$_2$Cl$_2$ extract was then washed with water (4x50ml) to remove any residual DMAC which is soluble in both water and CH$_2$Cl$_2$. The solution was dried over MgSO$_4$ and the solvent was removed by rotary evaporation.
Yield = 55.45g (98.2%)

TLC in 1:1 ether/hexane gave two spots (rf = 0.6 (major spot) and rf = 0.7). Therefore column chromatography on a small amount of the product was performed using the identical conditions, to enable microanalysis and NMR to be performed on a cleaner material.

Melting point = 66-68°C

Elemental analysis:
Expect for C_{52}H_{54}SO_8: C 74.44%, H 6.43%, N 0.0%,
Found C 74.16%, H 6.68%, N 0.0%.

^1H NMR (CDCl_3) δ: 1.66 (s, 12H), 1.81-2.03 (m, 12H), 3.57 (m, 2H), 3.93 (m, 2H), 5.38 (t, J=3.2Hz, 2H), 6.89 - 7.48 (m, 20H), 7.83 (d, J=8.52Hz, 4H).

^13C NMR and DEPT (CDCl_3) δ: 18.81 (-CH_2-), 25.22 (-CH_2-), 30.42 (-CH_2-), 30.94 (-CH_3), 42.07 (-C-), 62.13 (-CH_2-), 96.45 (-CH-), 115.87 (-CH-), 117.57 (-CH-), 119.68 (-CH-), 127.62 (-CH-), 128.45 (-CH-), 129.63 (-CH-), 135.27 (-C-), 143.28 (-C-), 147.66 (-C-), 152.58 (-C-), 155.05 (-C-), 162.09 (-C-).

FTIR (KBr plates) v cm^{-1}: 834 (1,4-disubstituted benzene), 1036 (-C-O-), 1074 (-C-O-), 1151 (-SO_2-), 1244 (-C-O-), 1362 (-C(CH_3)_2-), 1386 (-C(CH_3)_2-), 1442 (-CH_3,-CH_2-), 1488
(-CH₂-), 1505 (Ar C-C), 1587 (Ar C-C), 1614 (Ar C-C), 2872 (-CH₃), 2944 (-CH₃), 3036 (Ar-H).

2.3.3 Step 3 - Synthesis of a 6-ringed poly(arylene ether sulphone)

A 500ml round bottom flask equipped with a reflux condenser, a thermometer and a magnetic stirrer bar was charged with protected 6-ringed poly(arylene ether sulphone) (55.45g, 0.066mol), methanol (150ml) and TsOH as catalyst. The solution was heated under reflux for a day at 70°C, (see figure 2.3) and then allowed to cool to room temperature.

The methanol was removed in a rotary evaporator and the product was dissolved in CH₂Cl₂ (100ml). The organic layer was washed with water (6x50ml) to remove any residual salts formed. The solution was dried over MgSO₄ and the solvent removed by rotary evaporation.

![Figure 2.3. Schematic diagram showing the preparation of 6-ringed poly(arylene ether sulphone).](image)

Yield=44.1g (99.5%).

TLC in 3:1 ether/hexane gave three spots (rf = 0.5 (major spot) and rf = 0.6 and 0.4 (minor spots)). Column chromatography was performed on a small amount of the product using the same conditions, to enable the sample to be analysed by microanalysis and NMR.

Melting point = 115-117°C
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Elemental analysis:
Expect for C_{42}H_{38}SO_{6}: C 75.22%, H 5.67%, N 0.0%,
Found C 74.38%, H 5.87%, N 0.0%.

^{1}H NMR (CDCl\textsubscript{3}) $\delta$: 1.65 (s, 12H), 6.74 (d, J=8.63Hz, 4H), 6.90 (d, J=8.67Hz, 4H), 6.98 (d, J=8.86Hz, 4H), 7.09 (d, J=8.65Hz, 4H), 7.21 (d, J=8.69Hz, 4H), 7.83 (d, J=8.85Hz, 4H).

^{13}C NMR and DEPT $\delta$: 30.97 (-CH\textsubscript{3}), 42.02 (-C-), 114.82 (-CH-), 117.60 (-CH-), 119.70 (-CH-), 127.90 (-CH-), 128.42 (-CH-), 129.63 (-CH-), 135.18 (-C-), 142.55 (-C-), 147.67 (-C-), 152.57 (-C-), 153.47 (-C-), 162.09 (-C-).

FTIR (KBr plates) $\nu$ cm\textsuperscript{-1}: 834 (1,4-disubstituted benzene), 1035 (-C-0-), 1075 (-C-0-), 1151 (-SO\textsubscript{2}-), 1245 (-C-O-), 1363 (-C(CH\textsubscript{3})\textsubscript{2}-), 1385 (-C(CH\textsubscript{3})\textsubscript{2}-), 1446 (-CH\textsubscript{3}), 1505 (Ar C-C), 1587 (Ar C-C), 1614 (Ar C-C), 2872 (-CH\textsubscript{3}), 2943 (-CH\textsubscript{3}), 3035 (Ar-H).

2.3.4 Step 4 - Synthesis of a 6-ringed poly(arylene ether sulphone) dicyanate

The reaction described below was based on the work of Grigat and Pütter\textsuperscript{6}, with a few modifications. A 250ml round bottom flask equipped with a thermometer (-10°C to 80°C), a magnetic stirrer bar and a dropping funnel was cooled to -5°C using ice and NaCl. 6-ringed poly(arylene ether sulphone) (44.1g, 0.066mol) was dissolved in freshly distilled analar acetone (100ml). Cyanogen bromide (CNBr) (14.00g, 0.132mol) was added carefully to the solution. Triethylamine (13.31g, 0.132mol) (freshly distilled and dried over activated 4Å beads), was added dropwise over a period of an hour maintaining the temperature between -5°C and 5°C for the duration of the experiment (see figure 2.4), to minimise side reactions (e.g., the Von Braun reaction\textsuperscript{7}). Immediate formation of the triethylamine hydrogenbromide salt showed that the reaction had been initiated. The reaction mixture was then left for 1 hour to warm to room temperature. All apparatus which had been in contact with CNBr was placed in a bleach/NaOH/water bath to neutralise any residual CNBr on the apparatus.

Water (100ml) was added to dissolve the organic salt which was formed and the solution was extracted into CH\textsubscript{2}Cl\textsubscript{2} (3x50ml) and then washed with water (3x50ml). The solution was dried over MgSO\textsubscript{4} and the solvent removed by rotary evaporation.
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Figure 2.4. Schematic diagram showing the preparation of the 6-ringed poly(arylene ether sulphone) dicyanate oligomer.

Yield = 42.90g (90.5%).
TLC in ether/CH$_2$Cl$_2$/petroleum ether (40-60°C fraction) (1:3:4) gave one major spot at $r_f$ = 0.6. Column chromatography was performed, using the same conditions, so a small amount of material could be used for microanalysis, NMR and DSC analysis.
Analytical HPLC using CH$_2$Cl$_2$ as solvent gives one major peak at a retention time of 30mins and a few other peaks which are clearly impurities (see figure 2.5).
Melting point = 75.96°C (by DSC)

Elemental analysis:
Expect for C$_{44}$H$_{36}$SO$_6$N$_2$: C 73.33%, H 5.00%, N 3.88%,
Found C 73.02%, H 4.98%, N 3.87%.

$^1$H NMR (CDCl$_3$) 6; 1.69 (s, 12H), 6.97 (d, $J$=8.67Hz, 4H), 7.21 (m, 16H), 7.85 (d, $J$=8.84Hz, 4H).

$^{13}$C NMR and DEPT 6; 30.84 (-CH$_3$), 42.51 (-C-), 109.56 (-C=N), 114.91 (-CH-), 117.70 (-CH-), 119.89 (-CH-), 128.36 (-CH-), 128.74 (-CH-), 129.70 (-CH-), 135.47 (-C-), 146.53 (-C-), 149.39 (-C-), 150.89 (-C-), 153.02 (-C-), 161.86 (-C-).
FTIR (KBr plates) ν cm⁻¹; 835 (1,4-disubstituted benzene), 1035 (-C=O-), 1078 (-C=O-), 1152 (-SO₂⁻), 1245 (-C=O-), 1365 (-C(CH₃)₂-), 1387 (-C(CH₃)₂-), 1489 (-CH₃), 1505 (Ar-C-C), 1586 (Ar-C-C), 2237 (-C≡N), 2271 (-C≡N), 2875 (-CH₃), 2939 (-CH₃), 3039 (Ar-H).

2.3.5 Discussion

In this present work, a short, predefined oligomeric length of a poly(arylene ether sulphone) was prepared, which was then reacted to form the cyanate ester. In previous work¹, high polymers of at least a molecular number (<M>ₙ) of 4500 were produced using a slight excess of bisphenol-A and DCDPS, but with different conditions, much higher polymers can be produced. Ganguly et al.⁹ produced the 6-ringed poly(arylene ether sulphone) oligomer, but needed to use a 2.5 times, molar excess of bisphenol-A, and stringent work up procedures to remove the excess bisphenol-A. In the synthetic scheme presented here for the preparation of the 6-ringed poly(arylene ether sulphone) (6-ringed PIES), and ultimately the 6-ringed poly(arylene ether sulphone) dicyanate (6-ringed PIES dicyanate), only small amounts of impurities were observed (see figure 2.5).

At the end of the first stage of the reaction the product was always a brown solid. The cyanate ester was glassy at room temperature when all the solvent was removed, but it flowed when heated. Purification by column chromatography of a small amount of the cyanated product formed white flakes. The final product was also characterised by analytical HPLC using CH₂Cl₂ as solvent to establish the purity of the polymer. The trace of the HPLC plot is given in figure 2.5. This shows one major peak, with a retention time of 30 minutes, together with a few minor peaks showing the slight impurity of the oligomer.

However, despite the HPLC analysis which shows the presence of a few impurities, NMR, FTIR and the micro analysis data are all consistent with the proposed synthesised oligomer in figure 2.4. The reaction scheme can be followed stringently, by examining either the ¹H or the ¹³C NMR spectra, which show the build-up of the proposed oligomer from the initial starting material to the final structure. Subtle changes in the spectra, indicate the presence of various groups, e.g., in the ¹H spectra, the aromatic protons of the cyanated product are in a multiplet, whereas in the precursor, the aromatic protons are in a series of doublets, whilst in the ¹³C spectra, there is a C≡N singlet at 109.5 ppm in the cyanated product which is absent in the un-cyanated precursor.
The above syntheses were repeated a number of times, in order to produce sufficient 6-ringed PIES dicyanate. In these syntheses, the quantities of reactants varied slightly, depending on the quantity of the dihydropyran salt of bisphenol-A obtained in stage 1 of the synthesis. Approximately 100g of the 6-ringed PIES dicyanate oligomer was produced, which was later cured into resin plaques (see section 2.5.1). The yields of all the reactions were greater than 90%, with the exception of the first reaction, because some of the bisphenol-A became protected on both sides. However, this was minimised by adding the dihydropyran dropwise. In this case, the unreacted bisphenol-A was removed by washing the product on a filter with NaOH, and the di-protected bisphenol-A was removed with diethylether.

The 6-ringed PIES and the 6-ringed PIES dicyanate were easily distinguished by a variety of techniques. First, they were distinguished by \(^1\)H NMR in the aromatic region. In each spectra the protons nearest the sulphone group were deshielded and consequently shifted further downfield to approximately 7.9ppm, whereas the arrangement of the other protons was completely different. In the case of the 6-ringed PIES oligomer, the remaining aromatic region of the spectrum was arranged as five doublets, corresponding to the other five different types of phenyl protons present. However, with the 6-ringed PIES dicyanate
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Oligomer, the vast majority of the aromatic protons were centred together in a multiplet. Second, $^{13}$C NMR and FTIR spectra easily distinguish between the two oligomers. There was a NMR shift at 109.5 ppm corresponding to the C of the cyanate group, whereas from FTIR there were cyanate stretches at approximately 2240 and 2270 cm$^{-1}$. These were both absent in the uncyanated hydroxy-terminated 6-ringed PIES oligomer.

2.4 Mechanical and physical property determination of AroCy® B30

In the following sections, various mechanical and physical properties of the synthesised polymer are calculated. However, because of the complexity of the cyclotrimerisation process, which produces a three-dimensional thermoset network, another system, namely the commercial B30 oligomer was also tested.

2.4.1 Cure of bisphenol-A dicyanate prepolymer (B30)

B30 is a bisphenol-A dicyanate prepolymer (see figure 2.6) which has been partially converted to a nominal percentage of 30%. B30 was supplied by Hi-Tek Polymers and used as received. Before any physical or mechanical testing was possible, B30 had to be fully cured, i.e., the process that converts the oligomer into a polymer. The following procedure was used to cure the B30 oligomer.

![Figure 2.6. Schematic of the monomer structure of B30 (bisphenol-A dicyanate).](image)

i) A mould consisting of two glass plates and two sheets of pink melonex were attached to the glass sheets by a thin but even layer of silicone grease. Pink melonex was used because it has a fine coating of silicone, which prevents adhesion of the resin on to the melonex surface. Any air bubbles were smoothed out and it was determined that there was about a 3 cm lip at the top of the glass plates to assist with the pouring in of the resin. In addition 3 mm spacers made from aluminium and a strand of silicone rubber (2 mm bore, 4 mm total diameter) were placed between the glass plates. The purpose of the silicone rubber was to contain the poured resin in the mould. The plates were clamped together tightly as shown in
fig 2.7. These plates were then placed in an oven at 80°C to keep the glass plates warm, to enable the heated B30 resin to be poured between the warm glass plates more easily.

ii) The B30 oligomer (50g) was removed from its container by heating with an hair dryer and poured into an 500ml beaker. Copper (II) naphthenate (300ppm, Cu^{2+}) and nonyl phenol were added as catalyst (100 parts of resin and 4 parts of nonylphenol, 2g) to the warm oligomer and thoroughly mixed.

![Figure 2.7. Schematic of the mould used to cure B30 and the 6-ringed PIIES dicyanate oligomer.](image)

iii) The resulting mixture was 'degassed' in an oven at 85°C under high vacuum for 10 minutes. This removed any trapped air or solvent from the oligomer. The oligomer foamed as trapped air or solvent expanded and escaped into the oven. Clearly this would be detrimental in the curing of the system, as air pockets weaken any slab of resin produced.

iv) The resulting 'degassed' oligomer was quickly poured between the two glass plates using the two melonex sheets as guides, being careful to ensure that no large air traps were formed. When the mould was full, it was placed upright in a fan assisted oven with time and temperature controls and the cure of the oligomer commenced. The system was cured in the upright position so that the resin would not pour out when molten, to maintain the shape and size of the mould.

v) The oven was heated from room temperature to 175°C in 45 minutes, at which temperature the oligomer was cured for 3 hours, to form the 3-dimensional network
thermoset polymer (figure 2.8). In this process, the polar O-C=N functional groups were converted to less polar cyanurate ring moieties\(^9\). The oven was then slowly cooled down over a period of hours to prevent any stressing or cracking of the system.

vi) The resulting resin slab was removed from the mould and a 'post-cure' was performed on the produced resin. The 'post-cure' was for one hour at 225°C. The resin slab was placed between two glass and melonex sheets with a large weight on top, to retain the shape of the resin plaque. This 'post-cure' was performed to ensure that the percentage conversion rate of cyanate groups to cyanurate rings was greater than 85%. The oven was again allowed to cool down slowly, to minimise any stressing of the system.

![Figure 2.8. Schematic of the bisphenol-A dicyanate network.](image)

When the system was cured, FTIR and solid state NMR was performed on the polymer network to ascertain how many of the cyanate groups have been converted to cyanurate rings. In B30, the cyanate stretches at 2236 and 2271 cm\(^{-1}\) of the part cured resin have almost disappeared, whilst the C=N aromatic stretch of the cyanurate ring and the C-O stretch from the cyanurate ring have increased in intensity at 1563 and 1364 cm\(^{-1}\) respectively. Finally, there is a broad O-H stretch at 3200-3500 cm\(^{-1}\) due to the co-catalyst which was added to the system. Solid state NMR shows an aromatic carbon singlet at 173.9 ppm indicating a carbon atom in a cyanurate ring, whilst the C=N peak at 109.5 ppm
has virtually disappeared. These two results clearly indicate that almost 100% cure of the resin has been achieved, although unreacted oligomer still remained in the system.

### 2.4.2 Mechanical property testing

Before the mechanical testing was possible, it was necessary to machine the cured B30 resin plates into strips (approximately 10mm wide, 80mm long and 3mm thick) using a water cooled diamond wheel. Aluminium tabs (approximately 10mm wide, 14mm long and 1mm thick) were cut and lightly abraded on one side. A similar abrasion was also made on the B30 strips approximately 60mm apart. A coating of a toughened acrylic adhesive (F241) and Initiator No. 1 (both produced by Permabond) were applied to the abraded side of the resin strips and the tabs respectively, which were then immediately stuck to the resin strips. Four aluminium tabs were glued to each strip (two on the top; two on the bottom), so that it was easier for the grips of the mechanical testing apparatus to hold the B30 strips. All strips were left for at least 24 hours, under a load to enable the glue to harden. Any residual glue or silicone coating from the melonex was removed by wiping with a cloth soaked in methanol.

Young's modulus and Poisson's ratio were chosen as the elastic constants to be measured. Using these results, the remaining elastic constants were determined (see section 6.2 for explanation). Two 5mm strain gauges (Techni Measure, FLA-5-11, with a resistance of 2.14Ω) were placed on the B30 strip. First, a light abrasion was made on the sample, to make it easier to attach the strain gauges and the connecting terminals to the sample. Any residual particles were removed from the strip using a slightly alkaline solution. One strain gauge was placed slightly above centre and parallel to the strip, \( i.e., \) parallel to the applied force, to measure Young's modulus. The other strain gauge was placed in the centre of the strip but perpendicular to the applied force, to measure Poisson's ratio. The strain gauges were attached to the B30 resin using cyanoacrylate adhesive (\( 'CN' \), Techni Measure), along with connecting terminals (Techni Measure, TF 25), which were then soldered to the strain gauges. These connecting terminals attach the strain gauges and the sample undertest to the strain meters of the mechanical testing apparatus. The six strips were placed in the Instron apparatus, ensuring that each test piece was lined up exactly parallel to the machine to obtain the 'correct' Young's modulus and Poisson's ratio. A typical stress/strain curve for Young's modulus and Poisson's ratio are given in figure 2.9 and the results are given in table...
2.1. As the transverse strain ($\varepsilon_t$) gave a negative value, the polarity of the transverse strain was inverted, to plot the strain in a positive direction. The other elastic constants were obtained from these results (see section 6.2). These results together with their standard deviations are given in table 2.2.

![Figure 2.9](image)

**Figure 2.9.** A typical stress/strain curve for B30, giving both the Young's modulus and Poisson's ratio for the sample, up to a strain of 0.3%. The stress ($\sigma$) is shown in Pascals (N/m$^2$), whilst the longitudinal and the transverse strains ($\varepsilon_l$ and $\varepsilon_t$) are shown as micro-strains.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Area (mm$^2$)</th>
<th>Young's Modulus (GPa)</th>
<th>Poisson's Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.86</td>
<td>3.13</td>
<td>0.355</td>
</tr>
<tr>
<td>2</td>
<td>28.89</td>
<td>3.36</td>
<td>0.355</td>
</tr>
<tr>
<td>3</td>
<td>32.14</td>
<td>3.59</td>
<td>0.350</td>
</tr>
<tr>
<td>4</td>
<td>31.95</td>
<td>3.48</td>
<td>0.350</td>
</tr>
<tr>
<td>5</td>
<td>31.19</td>
<td>3.33</td>
<td>0.340</td>
</tr>
<tr>
<td>6</td>
<td>30.37</td>
<td>3.42</td>
<td>0.355</td>
</tr>
</tbody>
</table>

**Table 2.1.** Results of the Young's moduli and Poisson's ratio from the six test pieces for the B30 thermoset polymer.

The results in table 2.1 show the accuracy in the Young's moduli and Poisson's ratio results, where in the six samples tested the result varies only by a small amount, in which the average Young's modulus value is $3.39\pm0.16$GPa, whilst the average Poisson's ratio is $0.351\pm0.01$. 
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<table>
<thead>
<tr>
<th>Elastic property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus - E (GPa)</td>
<td>3.39 ± 0.16</td>
</tr>
<tr>
<td>Poisson's Ratio - ν</td>
<td>0.35 ± 0.01</td>
</tr>
<tr>
<td>Bulk Modulus - B (GPa)</td>
<td>3.79 ± 0.28</td>
</tr>
<tr>
<td>Shear Modulus - G (GPa)</td>
<td>1.25 ± 0.05</td>
</tr>
<tr>
<td>Lambda - λ (GPa)</td>
<td>2.95 ± 0.25</td>
</tr>
</tbody>
</table>

Table 2.2. Table of the five elastic constants as derived from Young's modulus and Poisson's ratio for the B30 thermoset polymer.

Inspection of the Young's modulus result in table 2.2, showed that this was close to its value in the literature of 3.17 GPa\(^*\), which was to be expected. Other dicyanates based on the bisphenol-A derivative in which the central linking atom has been changed, have similar values. These are in the range of 2.76-3.35 GPa\(^*\), whereas a meta disubstituted phenyl ring has a much higher Young's modulus of 4.76 GPa\(^*\). The Poisson's ratio of 0.35 was slightly lower than the literature value of 0.40\(^*\), but the brittleness expected from the supposed high cross-link density of the B30 network is offset by the ease of rotation around the -O- linkages connecting the benzene and cyanurate rings. It is also believed that some degree of bonding occurs between rings to form intramolecular cycles which interpenetrate\(^*\).

2.4.3 Physical property testing

DSC measurements were performed on some B30 prepolymers, which had been catalysed with copper (II) naphthenate, whilst other physical tests were performed on the cured B30 resin plaque. A portion of the cured resin was ground up and used in TGA analysis, and some 40x10x3 mm and 9x9x3 mm pieces were prepared for use in DMTA and TMA analyses respectively.

DSC measurements were made on 9.3 mg of the B30 prepolymers, which gave a trace shown in figure 2.10. This shows an exothermic transition with a maximum exothermic temperature at 203°C, with onset and completion temperatures of 161° and 239°C respectively. Consequently, the cure temperature of 175°C was ideal for the curing of this polymeric system. The heat given out in the exothermic reaction during the formation of the...
cyanurate rings was 0.47kJ/g (31.2kcal/mol) for the oligomer (i.e., per two cyanate groups). A second DSC scan on the same sample gave a $T_g$ of 262°C.

![DSC trace of catalysed B30 prepolymer, showing the exothermic reaction peaking at 203°C.](image)

The DMTA trace (figure 2.11) shows a $T_g$ of 278°C, (literature value = 289°C), which indicated an high degree of cure, although as the FTIR and NMR data also show, there was not 100% conversion to cyanurate rings. Other values of the $T_g$ for similar bisphenol-A moieties were in the range 252 to 273°C, as measured by DMTA.

![DMTA trace of the B30 cured resin, showing a $T_g$ of 278°C.](image)
TMA was also performed on the sample, to obtain the thermal expansivities of the polymer. This gave a $T_g$ of 212°C (literature value = 257°C\textsuperscript{12}) and the linear thermal expansion coefficients (LTEC) of $\alpha_g = 6.51 \times 10^{-5}$K\textsuperscript{-1} and $\alpha_l = 2.76 \times 10^{-4}$K\textsuperscript{-1} in the glassy and liquid states respectively. Other values of the $T_g$ for similar bisphenol-A moieties as measured by TMA are in the range 244 to 270°C\textsuperscript{12}. The $T_g$ values of polymers are generally lower when measured by TMA or DSC. In TMA the data recorded was the sum of a number of effects\textsuperscript{3}. These include the thermal expansion and time-dependent creep which vary in an unknown way with heating rate. DSC measures heat changes, using two different methods, namely the \textit{half-height} and \textit{onset} methods to find the $T_g$. This is a quick but not necessarily an accurate way of measuring $T_g$. DMTA, however measures molecular motion in polymers, which describes the $T_g$ far more accurately. Consequently, DMTA is the preferred technique to measure the $T_g$.

TGA was the final technique used to characterise the polymer (see figure 2.12). A sample of ground up polymer was heated to a temperature of 1000°C to obtain the thermo-oxidative stability of the B30 thermoset polymer. The initial onset of degradation occurred at 340°C (literature value = 411°C\textsuperscript{12} for onset of rapid degradation in air), whilst at 1000°C the char % was 38 (literature value = 41%\textsuperscript{12} for degradation in nitrogen). Other similar bisphenol-A derivatives have onset temperatures in the range of 400 to 431°C, where after heating in nitrogen the amount of residual char remaining varied from 43 to 52%\textsuperscript{12}.

![Figure 2.12. TGA trace of the B30 thermoset polymer, showing the initial weight loss at 340°C.](image-url)
2.5 Mechanical and physical property determination of a 6-ringed poly(arylene ether sulphone) dicyanate network

Having synthesised the 6-ringed PIES dicyanate in section 2.3, the oligomer was cured at 125°C, using copper (II) naphthenate as catalyst to form the network polymer. Various mechanical and physical properties of the networked polymer system were then found. A schematic of the formed 3-D thermoset network is shown in figure 2.13.

2.5.1 Cure of a 6-ringed poly(arylene ether sulphone) dicyanate oligomer

Apart from a few adjustments, the 6-ringed PIES dicyanate was cured in a similar way to B30. The major difference was that the cure temperature was reduced from 175°C to 125°C, because of the exothermic reaction which occurs between the cyanate groups, but the 3 hour cure time remained the same. The temperature was lowered to stop the formation of major voids or air bubbles in the system and also because the onset of cure was ascertained to be approximately 125°C by DSC measurement (see figure 2.14). Since the cure temperature was lowered, the post-cure temperature was reduced to 160°C, but again the time remained at one hour. Again, this temperature was reduced to prevent the formation of large air bubbles in the structure, which would clearly effect the mechanical properties of the system. Despite the reduction of the cure and post-cure temperatures, a large number of small air bubbles remained in the resin slab, which unfortunately could not be removed. The amount of catalyst - copper (II) naphthenate was reduced from 4phr to 2phr of oligomer, as there were fewer cyanate groups in the 6-ringed PIES dicyanate oligomer, compared with the B30 prepolymer. The preparation of the moulds and the melonex sheets etc., remained the same as in the previous description.

After curing the 6-ringed PIES dicyanate system, FTIR and solid state NMR were performed on the network polymer to find the percentage of the cyanate groups which have been converted to cyanurate rings. The cyanate stretches at 2237 and 2271cm⁻¹ of the 6-ringed PIES dicyanate have disappeared, whilst a C=N aromatic stretch of the cyanurate ring and a C-O stretch from the cyanurate ring have appeared at 1562 and 1368cm⁻¹ respectively. The C-O cyanurate stretch at 1368cm⁻¹, swamped the fairly weak C(CH₃)₂ bends at 1365 and 1387cm⁻¹ respectively, which almost disappeared from the spectrum.
Finally there was a broad O-H stretch at 3200-3600 cm\(^{-1}\) due to the co-catalyst - nonyl phenol which was added to the system. Solid state NMR shows a weak aromatic carbon singlet at 173.7 ppm indicating a carbon atom in a cyanurate ring, whilst the C=N peak at 109.56 ppm has been swamped by other signals, due to the small amount of sample which was used in the experiment. Hence, it can not be ascertained fully whether the peak has disappeared or is simply hidden by other peaks. However both results show that a large degree of conversion has taken place.

\[
3 \text{NCO} - R - \text{OCN} \\
\text{Catalyst} \\
\text{Heat - 125}^\circ\text{C i.e. Cure}
\]

where \( R = \)

\[
\begin{array}{c}
\text{O} \\
\text{R} \\
\text{O} \\
\text{R} \\
\text{O} \\
\text{R} \\
\text{O} \\
\text{R} \\
\end{array}
\]

Figure 2.13. Schematic showing the thermoset polymer network formed from the 6-ringed PIES dicyanate oligomer.
2.5.2 Mechanical property testing

Young's modulus and Poisson's ratio were obtained from the 6-ringed PIES cyanurate resin plaque. This was performed by cutting up the resin plaque into strips and using the Instron apparatus and the conditions which were used for the B30 network. These results are given in table 2.3, whilst the averaged results and the standard deviations for the five elastic constants are given in table 2.4.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Area (mm²)</th>
<th>Young's Modulus (GPa)</th>
<th>Poisson's Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.55</td>
<td>2.53</td>
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</tr>
<tr>
<td>2</td>
<td>33.55</td>
<td>2.50</td>
<td>0.350</td>
</tr>
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<td>3</td>
<td>31.66</td>
<td>2.53</td>
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<tr>
<td>4</td>
<td>31.66</td>
<td>2.45</td>
<td>0.335</td>
</tr>
</tbody>
</table>

Table 2.3. Results of the Young's moduli and Poisson's ratio from the four test pieces, for the 6-ringed PIES dicyanate thermoset polymer.

<table>
<thead>
<tr>
<th>Elastic property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus - E (GPa)</td>
<td>2.50 ± 0.04</td>
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<tr>
<td>Poisson's Ratio - (\nu)</td>
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<td>Bulk Modulus - B (GPa)</td>
<td>2.53 ± 0.28</td>
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<tr>
<td>Shear Modulus - G (GPa)</td>
<td>0.89 ± 0.10</td>
</tr>
<tr>
<td>Lambda - (\lambda) (GPa)</td>
<td>1.91 ± 0.29</td>
</tr>
</tbody>
</table>

Table 2.4. Table of the five elastic constants as derived from Young's modulus and Poisson's ratio for the 6-ringed PIES dicyanate polymer.

Examination of the elastic constants showed that the B30 results are approximately 33% greater than those of the 6-ringed PIES dicyanate. This was due to the longer oligomeric length in the latter case, which has more degrees of rotational freedom and a lower cross-link density. However, there were a few voids and air bubbles in the prepared sample of 6-ringed PIES cyanurate resin plaque which would lower the values of the elastic constants.
2.5.3 Physical property testing

Using the cured 6-ringed PIES cyanurate resin plaque, TGA measurements were made on a sample of ground resin, whilst DMTA and TMA measurements were made on several smaller prepared resin plaque pieces of the cyanurate polymer. DSC measurements were made on the columned sample, to obtain the melting temperature and the onset temperature for the cure of the system, whilst on the second scan the T\textsubscript{g} was obtained.

DSC was performed on 6.7mg of the chromatographically purified 6-ringed PIES dicyanate oligomer as shown in figure 2.14. The sample had a melting temperature of 76°C, whilst the onset reaction temperature was 129°C. This gave a maximum exothermic peak of 170°C, with an energy of 0.12kJ/g (20.7kcal/mol). On reheating the sample, the T\textsubscript{g} was 155°C. As the onset cure temperature was much lower in this case, the cure temperature was lowered to 125°C. At this lower temperature, the oligomer had time to react because the temperature was isothermally controlled for 3 hours, but reaction at much higher temperatures produced heterogeneous samples, which were very difficult to test.

![Figure 2.14](image_url)  
**Figure 2.14.** DSC trace of the uncatalysed columned 6-ringed PIES dicyanate, showing a melting temperature of 76°C for the oligomer and a maximum exothermic reaction peak of 170°C, whilst the T\textsubscript{g} was shown on run 2 to be 155°C.

DMTA was performed on the sample to give a T\textsubscript{g} of 140°C as shown in figure 2.15. This is known as the $\alpha$ relaxation. There was also a relaxation at approximately 175°C, which is
known as the $\alpha_c'$ relaxation. The upper temperature limit of the experiment was
approximately 210°C, where the $\log(\tan(\delta))$ value became fairly erratic due to the initial
degradation of the sample (see figure 2.17). However, because of the weight loss shown
from the TGA trace (figure 2.17) in the 100-200°C range, greater care is necessary when
assigning these peaks, especially the 2nd peak, i.e., the $\alpha_c'$ transition where weight loss in
the sample could be a major influence in the peak. This is shown at approximately 175°C on
the DMTA graph (figure 2.15).

![Figure 2.15. DMTA trace of the 6-ringed PIES dicyanate resin showing a $T_g$ of 140°C.](image)

A TMA trace of the 6-ringed PIES dicyanate is shown in figure 2.16. This shows a $T_g$ of
131°C for the polymer, whilst the linear thermal expansion coefficient (LTEC) in the glassy
region ($\alpha_g$) was $7.52 \times 10^{-5} \text{K}^{-1}$ and in the liquid region ($\alpha_l$) was $1.92 \times 10^{-4} \text{K}^{-1}$. This slightly
lower value of the $T_g$ was in accordance with the values obtained for other dicyanate
polymers from TMA experiments.\textsuperscript{12}.
Chapter 2: Synthesis and characterisation of networked polymers

A TMA trace of the 6-ringed PIES dicyanate is shown in figure 2.16, which shows the initial decomposition of the polymer starting at approximately 100°C. This is most likely due to the removal of water or solvent in the polymeric system or to the removal of impurities in the system, e.g., an iminocarbamate which can be formed as a side product in the cyanation reaction. However, the major decomposition of the sample occurs at approximately 380°C and finishes at approximately 600°C. Running the TGA experiment under nitrogen, to a temperature of 1000°C, the residual char was 28%.

Figure 2.16. TMA trace of a 6-ringed PIES dicyanate resin, showing a $T_g$ of 131°C, whilst $\alpha_g$ and $\alpha_t$ were $7.52 \times 10^{-5} \text{K}^{-1}$ and $1.92 \times 10^{-4} \text{K}^{-1}$ respectively.

A TGA trace of the 6-ringed PIES dicyanate is shown in figure 2.17, which shows the initial decomposition of the polymer starting at approximately 100°C. This is most likely due to the removal of water or solvent in the polymeric system or to the removal of impurities in the system, e.g., an iminocarbamate which can be formed as a side product in the cyanation reaction. However, the major decomposition of the sample occurs at approximately 380°C and finishes at approximately 600°C. Running the TGA experiment under nitrogen, to a temperature of 1000°C, the residual char was 28%.

Figure 2.17. TGA trace of some ground 6-ringed PIES dicyanate resin heated to a temperature of 1000°C.
2.6 Discussion

An high degree of cure is shown for both samples by solid state NMR and FTIR, where either a C=\(\text{N}\) cyanate peak or stretch has virtually disappeared and a C=\(\text{N}\) cyanurate peak or stretch has appeared. These results and the high \(T_g\) value for B30, indicate that the cure cycles for both B30 and the one ascertained for the 6-ringed PIES dicyanate were correct for each individual sample. However the \(T_g\) value of the 6-ringed PIES dicyanate network does appear to be low at 140°C as ascertained by DMTA analysis, especially when a \(T_g\) of 220°C was found for a different poly(ether sulphone) dicyanate oligomer which contained 26 repeat units per oligomer\(^{13}\). This low \(T_g\) could be partially explained by a few voids in the sample, which would cause a weakness and lower the \(T_g\).

The anomaly of the \(T_g\), having a lower value at smaller oligomeric lengths was also shown by the bisphenol-A poly(carbonate) dicyanates. Huang \textit{et al.}\(^{14}\) have shown that when the number of repeat units of bisphenol-A poly(carbonate) was seven in a bisphenol-A poly(carbonate) cyanate ester oligomer, the \(T_g\) was 104°C. However, when the seven repeat unit bisphenol-A poly(carbonate) cyanate ester oligomer was cured with hydroxy terminated bisphenol-A poly(carbonate), to form a semi-interpenetrating network, the \(T_g\) increased dramatically to 169°C, which was far nearer the \(T_g\) of the neat poly(carbonate) of 150°C\(^{15}\). Parker \textit{et al.}\(^{13}\) produced an high oligomeric poly(ether sulphone) dicyanate of approximate molecular weight of 6000 (26 repeat units), which they found difficult to characterise by classical techniques (IR, NMR) due to the small amount of cyanate in the oligomer in relation to the rest of the oligomer. However, on a second reheating using DSC, a well-defined \(T_g\) of 221°C was obtained. Hergenrother\(^{16}\) on the other hand, noted in a study of high poly(ether sulphone) dicyanate oligomers, that with molecular weight greater than 6000, the low concentration of reactive end groups prevented complete cross-linking in the reaction which led to partially soluble materials.

Spathis \textit{et al.}\(^{17}\) who formed six thermosetting epoxy resin networks using different cure temperatures, measured the thermal expansion of these polymers using TMA. They found that when the post-cure temperature was low, there was anomalous behaviour in the \(T_g\) region, but at higher cure temperatures, the normal TMA expansion curves were seen. They concluded that there were some volume-contraction effects taking place in the material, or non-expansion effects in that region, when the samples were not fully post-cured at the
higher temperature. Consequently, the free-volume formation of the polymer was incomplete at the lower post-cure temperatures, although at high post-cure temperatures, these effects were not seen. Work by Barlay et al.\textsuperscript{18} on rigid-rod s-triazine linked thermoset polymers, which had a terephthalate linkage, obtained a $T_g$ of 185°C, which had an $\alpha_c$ at approximately 240°C. The TGA plot showed that decomposition commenced at 400°C and the residual char left at 800°C was about 37%, when the sample was run under nitrogen. The sample was totally decomposed by 620°C when the sample was run under oxygen. These results are similar to those presented in this thesis, except that the DMTA results for the rigid-rod thermoset polymer were approximately 40°C higher and that there was no initial decomposition of their sample between approximately 100 to 200°C.

Gaitonde et al.\textsuperscript{19} on their work on the low temperature thermal expansion of poly(ether ether ketone) (PEEK) composites, also obtained the low temperature expansion curve of PEEK resin, where the expansion tailed off gradually as the temperature rose from -150 to 30°C, giving a LTEC in the glassy region ($\alpha_g$) of $5.17 \times 10^{-5} \text{K}^{-1}$, which is very similar in magnitude and value to that of the synthesised 6-ringed PIES dicyanate networked thermoset polymer. Meanwhile, Blundell et al.\textsuperscript{20} obtained the thermal expansion coefficient of an orientated film of PEEK by crystallographic methods. The expansion rate in the 'a' direction was approximately three times that of the 'b' direction because the interchain forces are weaker in this direction. However, around the $T_g$ value of 145°C, there was an increase in the expansion coefficient of 'a', and a reduction in the 'b' expansion coefficient. Over the whole 300°C temperature range, the LTEC ($\alpha_g$) was $5.50 \times 10^{-5} \text{K}^{-1}$, which was unchanged when passing through the $T_g$. This result agreed very well with the result obtained from Gaitonde et al.\textsuperscript{19} who used the dilatometer technique to obtain their values of the thermal expansion coefficients.

In the mechanical testing results, the results obtained for Young's modulus and Poisson's ratio, for both systems were reproducible with every small standard deviation (especially when compared to the simulated results given in chapter 6). However, for the 6-ringed PIES dicyanate polymer, it would have been preferable if more test pieces could had been prepared. Unfortunately, constraints were put on the cured resin slabs by the other physical tests which were performed and the requirement of the resin test pieces to be as homogeneous and void free as possible.
The enthalpy of the reaction cure of B30 was 31.2 kcal/mol, and for 6-ringed PIES dicyanate was 20.7 kcal/mol as ascertained by DSC analysis. Both DSC traces of the oligomers, clearly show the cure temperatures which were required for both systems, i.e., 175°C for B30, whilst a lower cure temperature of 125°C was used for the 6-ringed PIES dicyanate. This temperature of 125°C was modified in an attempt to obtain the best cure for the sample, i.e., a resin plaque which was homogeneous and contained the minimum number possible of voids and air bubbles in the system. This resulted in a resin plaque which contained a few voids as compared to a sample containing many voids and air bubbles, if an higher cure temperature of 175°C was used.

DMTA was used solely to obtain the $T_g$ of these two thermoset polymers, as it is the most reliable method for $T_g$ measurement. TMA on the other hand was used primarily to obtain the thermal expansion coefficients, so that the results could be compared with those from simulation studies (see chapter 6 for further details) and secondarily to obtain the $T_g$, which was significantly lower using this technique. DSC on the other hand was used primarily to obtain the cure temperatures, and secondarily used as a method of calculating the $T_g$. Finally TGA was performed on the samples to obtain their thermo-oxidative stability. Clearly, different results would be obtained if the samples were burnt in air, i.e., oxygen, where the formation of various oxides would significantly reduce the amount of residual char after heating to 1000°C.

2.7 Conclusion

After the synthesis of a 6-ringed PIES dicyanate, it was then cured into a three-dimensional thermoset polymer and characterised. Various mechanical and physical properties were obtained by a variety of techniques. A commercial system was also characterised and the results were correlated where possible with literature values. Agreement was within a few percent. Correlation of some experimental results, indicated that the results obtained for the 6-ringed PIES dicyanate are fairly accurate, after allowing for experimental error.

After the experimental work, the next stage of this thesis describes the modelling of the above thermoset polymers. This enables comparisons to be made between experimental and modelled results and this is shown in chapter six. In earlier work, much simpler structures were modelled. These include modelling the repeat unit of poly(isopropylidene ether
sulphone) in a vacuum in chapter four. Modelling the thermoplastic, polymer poly
(isopropylidene ether sulphone) under the influence of bulk conditions, where various
properties are calculated is given in chapter five. However, before this work is described, an
introduction to molecular modelling is given in chapter three.

2.8 References

3 R. E. Wetton, *Polymer Characterisation*, B. J. Hunt and M. I. James, (Ed.) Blackie,
4 Polymer Laboratories Pamphlet, PL-DMTA Dynamic Mechanical Thermal Analyser
  (1994).
5 Du Pont Instruments 943 Thermomechanical Analyser manual.
7 A. W. Snow, The synthesis, manufacture and characterisation of cyanate ester monomers,
  Chapter 2, *The Chemistry and Technology of Cyanate Ester Resins*, I. Hamerton (Ed.),
  Blackie, Glasgow, 7-57 (1994).
8 A. Noshay, M. Matzner and C. N. Merriam, *Journal of Polymer Science: Part A-1*, 9,
  3147-3159 (1971)
11 T. Fang and D. A. Shimp, Polycyanurate Esters: Science and Applications, *Progress in
12 D. A. Shimp, J. R. Christenson, S. J. Ising, 34th International SAMPE Symposium, May
  8-11th, 34(2) 222-233 (1989).
15 D. W. Van Krevelen. *Properties of polymers: Their estimation and correlation with
16 P. M. Hergenrother, *ACS Organic Coatings and Applied Polymer Science Proceedings,
  46*, 165 (1982).


Chapter 3

Introduction to Molecular and Polymer Modelling

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3.1 Introduction

This chapter is concerned mainly with introducing the terms: molecular and polymer modelling. A brief description of the underlying theory involved in the process is outlined, as well as the various techniques used in applying these theories. A brief molecular modelling study on bis(4-fluorophenyl)sulphone, 2,2'-bis(4-cyanatophenyl) isopropylidene and a cyanurate ring was performed, to give an introduction into the use of these techniques.

3.2 Molecular and polymer modelling

The use of computational chemistry and particularly molecular modelling has increased immensely over the last few years. Recently, it has been used as an aid to our understanding of various chemical phenomena. As a result of this increased interest in modelling, various companies have been set up to exploit this new field commercially. The advent of widely available workstations, combining high computational speeds and superb graphics, greatly aids molecular simulation studies\(^1,2,3\).

Poly(sulphones) are complex, amorphous systems, which unlike the crystalline phase, have many degrees of freedom. To accurately describe the nature and structure of such systems is difficult, as there are few experimental characterisation techniques which can be used to describe the internal structure of amorphous polymers\(^4\). Generally, only global chain dimensions, such as end-to-end distance or density can be obtained, although some localised structure can be obtained from spectroscopic techniques\(^5\). Consequently, molecular modelling is being used, along with some experimental techniques to characterise the structure and properties of amorphous polymers. The use of high speed quality workstations enables the characterisation of polymers to be achieved, by obtaining their geometric parameters, atomic charges, chain flexibility, energy barriers to rotation and various elastic properties etc. Accuracy in property prediction is solely dependent on the force field and the model used to describe the structure. Hence greater accuracy in property prediction is achieved as the accuracy of the force field and the model improves. It is also important to compare calculated data with experimental data, if at all possible.

In this thesis, experimental work is compared with calculated data, for both the thermoplastic poly(isopropylidene ether sulphone) polymer and the cross-linked thermoset
polymers based on the B30 and the 6-ringed poly(arylene ether sulphone) dicyanate oligomer, which were described in chapter 2.

3.3 Molecular modelling techniques

Some of the various techniques used in molecular and polymer modelling are described in the next section.

3.3.1 Molecular mechanics

Molecular mechanics (MM), in its simplest form, treats each atom as an hard sphere of approximate atomic radius depending on the size of the atom, whilst a bond is treated as a spring of a particular strength (weaker for single bonds, stronger for triple bonds) in which the energy of a bond obeys Hooke's law (see figure 3.2). The behaviour of the molecule can be described by a set of mathematical equations, whose form is similar to those of classical mechanics. This set of potential functions is known as a force field. MM is used to search for the minimum energy of a particular molecule as described by the force field. A force field is used to describe the nature, orientation and potential energy of the particular molecule under consideration. Various parameters, e.g., the bond lengths and the bond angles coexist in the force field, together with various potential functions which facilitate description of the nature of the system under investigation. The energy of a structure is divided into two constituent parts, bonded i.e., valence terms and non-bonded terms.

\[ E_{\text{tot}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{nb}} \]  

where \( E_{\text{tot}} \) is the total energy, \( E_{\text{bond}} \) is the energy of stretching or compressing a bond, \( E_{\text{angle}} \) is the energy due to the bending of bond angles, \( E_{\text{tors}} \) is the torsional energy due to rotations about bonds and \( E_{\text{nb}} \) is the energy due to non bonded interactions.

Additional contributions that effect the energy of the structure, such as electrostatic interactions, hydrogen bonded terms and five-bodied cross terms may be added to the force field. However, five bodied terms are generally only included if very accurate models of the structures are needed, e.g., for simulating the infra red spectra of various compounds. There are many MM force fields available. These include Dreiding\(^6\), AMBER\(^8\), CHARMM\(^9\),
MM2\textsuperscript{10}, MMP2\textsuperscript{11}, MM3\textsuperscript{12} and CVFF\textsuperscript{13}. These force fields have different uses and are related to different topics within chemistry, e.g., AMBER is used to describe proteins and amino acids, whilst the MM2 type of force field is used to describe small organic molecules. These parameters are generally obtained from X-ray data for geometric properties, whilst the force constants are obtained from IR and Raman spectroscopy.

DreidingII\textsuperscript{6} is a generic force field and was mainly used to describe the molecules under investigation. However, a few changes to the values in the parameter set were made (see section 3.5) in order to describe the produced atomistic models more accurately. The MM2 force field was also used, but only to confirm the geometry of the structures determined by the DreidingII force field. Consequently, the DreidingII force field will be looked at in greater detail in the next section.

### 3.3.2 The DreidingII force field

The DreidingII force field is made up of the following potential functions which describe the total energy of the structure. The bonded terms are shown below in figure 3.1 and show the two-body, three-body and four-bodied terms respectively.

**Figure 3.1.** The bonded parameters as used in the DreidingII force field: a) the bond length, b) the bond angle, c) the torsional angle and d) the inversion angle. Note that the atoms are labeled from 1 to L depending on which interaction is observed.
The potential functions of the representative parts of the bonded energies of the DreidingII force field are given by the following four formulae.

A bond length is observed when two adjacent atoms I and J are joined by a common bond IJ, whilst the bond energy is given as:

$$E_b = \frac{1}{2} \sum k_b (r - r_o)^2$$  \hspace{1cm} \text{eqn. 3.2}$$

where $E_b$ is the bond energy, $k_b$ is the force constant of the bond, $r$ is the actual bond length and $r_o$ is the equilibrium bond length. The energy of a bond length is related to an harmonic oscillator as shown in figure 3.2 below, i.e., it obeys Hooke's law.

![Figure 3.2 - The energy profile of a bond length as related to an harmonic oscillator. $R_o$ is the equilibrium bond distance. If $R=R_o$ then $E_b=0$ so the value of $E_b$ is a measure of strain energy.](image)

Other potentials used to describe bond lengths include the Morse potential, but this potential is generally only used when starting with molecules of good initial geometry. The Morse potential is computationally more expensive than the Harmonic approximation and consequently the Harmonic approximation is the preferred option.

Given any two bonds joined to a common atom (e.g. IJ and JK in figure 3.1(b)), the bond angle interaction is a function of the angle $\theta$ between them.
Chapter 3: Introduction to molecular and polymer modelling

\[ E_0 = \frac{1}{2} \sum k_0 (\theta - \theta_e)^2 \quad \text{eqn. 3.3} \]

where \( E_0 \) is the bond angle energy, \( k_0 \) is the force constant, \( \theta \) is the actual bond angle and \( \theta_e \) is the equilibrium bond angle. Again the energy of a bond angle is related to an harmonic oscillator.

Given any two bonds \( IJ \) and \( KL \), attached to a common bond \( JK \), (figure 3.1(c)), the dihedral angle \( \phi \) is defined as the angle between the \( JKL \) plane and the \( UK \) plane.

\[ E_\phi = \frac{1}{2} V_{jk} \left\{ 1 - \cos \left[ N_{jk} (\phi - \phi_e) \right] \right\} \quad \text{eqn. 3.4} \]

where \( V_{jk} \) is the rotational barrier, \( N_{jk} \) is the periodicity, \( \phi \) is the actual dihedral angle and \( \phi_e \) is the equilibrium dihedral angle.

The Inversion term \( E_\omega \) is defined as the angle between the \( IL \) axis and the \( IJK \) plane (see figure 3.1(d)).

\[ E_\omega = \frac{1}{2} C (\cos \omega - \cos \omega_e)^2 \quad \text{eqn. 3.5} \]

where \( K_\omega = C \sin^2 \omega_e \) and \( K_\omega \) is the force constant, \( \omega \) is the actual angle between the \( IL \) axis and the \( IJK \) plane and \( \omega_e \) is the equilibrium angle between the \( IL \) axis and the \( IJK \) plane.

The potential functions of the representative parts of the non bonded energies are given by the following three formulae.

All atoms exhibit a long range attraction proportional to \( 1/R^6 \). This is generally referred to as the van der Waals (VDW) attraction. At sufficiently short distances, interaction of all atoms are repulsive and for non bonded interactions, this is proportional to \( 1/R^{12} \).

Consequently, the VDW energy is written as a form of the Lennard-Jones 12-6 potential function.

\[ E_{\text{VDW}} (R) = D_0 \left\{ \left[ \frac{R_0}{R} \right]^{12} - 2 \left[ \frac{R_0}{R} \right]^{6} \right\} \quad \text{eqn. 3.6} \]
where $D_o$ is the bond strength (well depth) in kcal/mol, $R_o$ is the bond length and $R$ is the separation between atom pairs.

The molecular modelling program used in this thesis, *i.e.*, POLYGRAF uses a cut-off at 9Å in calculating the non bonded interactions as it assumes any interaction above that value is negligible. The Lennard-Jones 12 - 6 potential function with all its constituent parts is shown below in figure 3.3.

![Figure 3.3. The Lennard-Jones potential showing the 12-6 non bonded VDW potential model between two atoms, together with the constituent parts which make up this potential. For the H-bonding term a 12-10 potential was used.](image)

The hydrogen bonding function uses a modified Lennard-Jones type 12-10 potential function as described below.

$$E_{\text{HA}}(R) = D_o \left\{ 5 \left[ \frac{R_o}{R} \right]^{12} - 6 \left[ \frac{R_o}{R} \right]^{10} \right\}$$  \hspace{1cm} \text{eqn. 3.7}

where $D_o$ is the hydrogen bond strength, $R_o$ is the equilibrium H-bond length and $R$ is the distance between the donor and acceptor atoms.
The final term used describes the electrostatic interaction between two charged bodies separated by a distance $r$.

$$E_{\text{elec}} = \sum_{i \neq j} \frac{q_i q_j}{4\pi \varepsilon r}$$ \hspace{1cm} \text{eqn. 3.8}$$

where $q_i$ is the partial charge on atom $i$, $q_j$ is the partial charge on atom $j$, $r$ is the distance between atoms and $\varepsilon$ is the dielectric constant.

Summation of all the above potential terms gives the final potential energy of the structure.

$$E_{\text{tot}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{inv}} + E_{\text{VDW}} + E_{\text{HB}} + E_{\text{elec}}$$ \hspace{1cm} \text{eqn. 3.9}$$

3.3.3 Minimisation techniques

The aim of an energy minimisation routine is to find a set of coordinates representing a molecular system, such that the energy of the system is at a minimum. The lowest possible energy a molecule can have is described as the \textit{global} minimum, whilst other 'minima' are described as \textit{local} minima. The computational process used to determine this function is called \textit{minimisation} and various routines have been produced to facilitate this function. The general strategy of minimisation involves essentially two steps. First, the description of the energy of a structure as a function of its coordinates is provided by the force field. Second, a minimisation routine is applied which adjusts the molecular structure by lowering the value of the potential energy function. There are a number of minimisation algorithms available, some are based on a first derivative energy method of the potential function ($dE/dr=0$), whilst others are based on the second derivative method ($d^2E/dr^2=0$). Some of the MM routines available will be discussed further.
Chapter 3: Introduction to molecular and polymer modelling

3.3.3.1 Steepest - Descents method\textsuperscript{15}

This is the simplest method used to minimise a structure and is generally used if the starting structure has poor geometry. It uses the first derivative method to obtain its minimised structure. The method adjusts the coordinates of the structure, so if the dE/dr is less than the previous value of dE/dr, it stores these changes. It has however a major problem, in that it has great difficulty in overcoming local minima.

Figure 3.4. Schematic of the minimisation process. In this simple example, the algorithm is able to minimise the molecule's high energy state A, overcome the local minimum (B) and place the structure in its global minimum conformation (C).
3.3.3.2 **Conjugate - Gradients method**

This method is similar to steepest descents, but it also stores the direction in which the minimisation is proceeding. Consequently, it has the ability to overcome local minima and hence find the global minimum. Generally this method is used when the starting geometry of the structure is reasonable, i.e., the unminimised starting material has similar geometric values to that of the minimised structure.

3.3.3.3 **Fletcher - Powell method**

This method uses both first and second derivatives to obtain the minimum energy of the structure. It is a very powerful method which greatly accelerates energy convergence. However, there is a limit to the number of atoms (N) which can be used. It needs to store a $3N \times 3N$ matrix and consequently the computational time required, dramatically increases for large structures by a factor of $N^3$. Therefore, the conjugate gradient method is the default minimisation technique used.

3.3.4 Molecular Dynamics

Molecular dynamics (MD) calculations are used to investigate the dynamical behaviour of molecules as a function of time. In MM, the molecule is simulated at 0K whereas MD simulations are performed at a temperature, over a time period where the molecule is continuously in a state of motion (see figure 3.5). Newton's second law of motion is applied to a molecule and by integrating this equation, so the motion of the molecule, and consequently the movement of its atoms can be observed.

\[ F = ma \] \hspace{1cm} \text{eqn. 3.10}

where $F$ is the force on each atom, $m$ is the mass of each atom and $a$ is the acceleration of each atom. The force can be computed directly from the derivative of the potential energy $E$, with respect to the coordinates.

\[ \frac{\delta E}{\delta r} = m \frac{\delta^2 r}{\delta r^2} \] \hspace{1cm} \text{eqn. 3.11}
where $r$ are the coordinates of each atom.

The energy and the mass are known, therefore the acceleration can be calculated. Using the following equations of motion, the velocity and the position of each atom can be predicted.

\[ v = u + at \quad \text{eqn. 3.12} \]
\[ s = ut + \frac{1}{2}at^2 \quad \text{eqn. 3.13} \]

where $u$ is the initial velocity, $v$ is the new velocity and $s$ is the new position. In order to integrate the equations efficiently, a very small time step ($\delta t$) is required. This time step must be around the value of the period of the highest-frequency molecular vibrations to be simulated which are the bond stretching modes. Consequently $\delta t$ must be in the order of 1 femtosecond ($1 \times 10^{-15}$s). To derive a usable scheme for microscopic systems a Taylor expansion is used.

\[ s(t+\delta t) = s(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + ... \quad \text{eqn. 3.14} \]
\[ s(t-\delta t) = s(t) - v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + ... \quad \text{eqn. 3.15} \]

The addition of these two equations gives the basis of the Verlet algorithm\textsuperscript{19} for integrating the equations of motion.

\[ s(t+\delta t) = 2s(t) - s(t-\delta t) + a(t)\delta t^2 \quad \text{eqn. 3.16} \]

$s$, $v$ and $a$ are now vectors because molecules are composed of atoms with varying positions, velocities and accelerations. The Verlet method is widely used for MD calculations as it is stable, but improved variants, e.g., the summed Verlet\textsuperscript{20} and the leap frog\textsuperscript{21} method are aimed at improving the precision with which the velocities are calculated. The velocities are calculated from the following formula.

\[ v(t) = \frac{\{s(t+\delta t) - s(t-\delta t)\}}{2\delta t} \quad \text{eqn. 3.17} \]

The initial velocities given to the atoms are randomly distributed depending on the temperature of the simulation run and are given by:
3kT = \sum_{i=1}^{N} \frac{mv_i^2}{N}

where $N$ is the number of atoms, $k$ is the Boltzman constant and $T$ is the temperature in Kelvin.

![Figure 3.5](image.png)

**Figure 3.5.** This schematic shows the movement of atoms in a MD simulation at a specific time over a period of a few picoseconds.

Throughout the length of a MD simulation, a check is kept on the positions and velocities of the atoms present. Trajectory information is stored at regular time intervals, *e.g.*, 0.1ps. These trajectory files can be played back at a later date, to watch the movement of the molecule as a 'movie'. By using these produced trajectory files, various properties of the molecule can be obtained. Examples of properties obtained include the self diffusion coefficient, the radial distribution function and correlation functions. These will be explained in greater detail in chapter 5. The data for these properties is usually collected when the system has equilibrated (*i.e.*, when the PE and the KE of the system is relatively constant).

Different types of MD simulations can be performed, depending on the properties required. These include:

- **Quenched dynamics**: where steps of minimisation follow, after a period of MD simulation.
- Isothermal experiments (NVT) \( i.e.\), constant volume, constant temperature experiments.
- Isobaric-isothermal experiments (NPT) \( i.e.\), constant pressure, constant temperature experiments.
- Adiabatic experiments (NPE) \( i.e.\), constant pressure, constant energy experiments.
- Adiabatic experiments (NVE) \( i.e.\), constant volume, constant energy experiments,

where \( N \) equals the number of atoms in the simulation.

In this work, quenched dynamics and the (NVT) and (NPT) ensembles have been used to perform MD simulations on the oligomeric and polymeric systems.

### 3.3.5 Monte Carlo method

The conformational space of a molecule can be searched in many ways. This can be performed sequentially by using a systematic search, \( i.e.\), conformational analysis\(^{22}\) (see section 4.2.2). However, this becomes very time consuming for large molecules. Another method uses the Monte Carlo (MC) algorithm\(^{23}\). By its very name, it suggests a random process.

The Monte Carlo technique is used to generate random conformations of a structure, under fairly stringent conditions. It works by applying random rotations to a molecule's rotatable bonds. Randomly generated conformations with atoms closer than their VDW distance are rejected. This is known as 'bump' checking. If a conformation is accepted, then this is used to generate the next conformation, whereas if a conformation is rejected then the structure returns to its initial state.

### 3.3.6 Periodic Boundary Conditions

Periodic boundary conditions (PBC)\(^{24}\) are used to simulate molecular systems in a periodic lattice of identical subunits. By applying PBC to simulations, the influence of bulk effects can be included, thereby improving the model of the system represented. The molecule is placed in a simulation box, usually a cube, which is replicated in three directions to form a 3x3x3 lattice of identical cubes. Atoms in the simulated box can interact with 'image' atoms within a cutoff distance of 9\( \text{Å} \). If an atom or groups of atoms translate out of a simulated
box, then an equivalent number of atoms enter the box from the opposite side. This is shown in figure 3.6.

![Figure 3.6](image.png)

**Figure 3.6.** This schematic shows a representation of periodic boundary conditions. Note the simulated cell surrounded by 8 identical images and the translational movement of the molecules.

Because of the infinite system shown, the modification of the calculation of forces and energies has to be considered. Generally, molecules in the simulated cell are only allowed to interact with molecules or molecular images which are in close proximity and which are within a distance of half the cell size. All periodic algorithms imply a cutoff to limit the short range interactions which is always less than half the cell size. Long range interactions are accounted for using the Ewald sum technique\(^{25,26,27}\).

### 3.3.7 Tail correction

This concept of joining molecules together, by *tail-correction*, in periodic cells was first suggested by Weber *et al.*,\(^{28}\) as a way of minimising end effects. Basically the head of the polymer is joined to the tail of its image. This process can generally only be applied when the 'head' of the polymer and the 'tail' of the image are in fairly close proximity within the PBC, although the join does not necessarily have to be across periodic boundaries. This process is shown in figure 3.7.
3.3.8 Quantum mechanics

Whereas MM treats molecules as a series of balls and springs, Quantum mechanics (QM)\textsuperscript{29} treats the structure of a molecule by a series of delocalised molecular orbitals based on the simpler ones derived from the hydrogen atom, \textit{i.e.}, Schrödinger's equation.

\[ H\Psi = E\Psi \]  
\text{eqn. 3.19}

where \( H \) is the time-independent Hamiltonian operator, \( \Psi \) is the wavefunction and \( E \) are the energy levels. Solving this equation yields the energy levels (eigenvalues) and orbital directions (eigenvectors). As this method considers electrons, calculations are very expensive in computer time and memory usage. Consequently, levels of approximation are used to cut down on computational time. These methods are called semi-empirical and use parameter sets to derive overlap integrals. One of the methods used was MOPAC V\textsuperscript{30}, which is one of the most popular semi-empirical techniques. MOPAC uses modified neglect of differential overlap (MNDO) and the parameter sets are derived from experimental data to obtain properties such as partial charges on the atoms, ionisation energies and dipole moments. Here MOPAC was used to calculate partial atomic charges on the molecules under test.
3.4 Hardware and software used

The modelling work presented here was mainly performed on two platforms. The work on the linear poly(arylene ether sulphone) and the poly(arylene ether ketone) oligomer together with the cyanurate moiety was performed on a Titan mini-supercomputer running UNIX v2.2 and POLYGRAF v2.2 as supplied from Molecular Simulations Inc. The work on modelling poly(arylene ether sulphone) in the 'bulk' together with the poly(arylene ether sulphone) dicyanate modelling was performed on a Silicon Graphics Indigo RS4000 running IRIX version 5.1.1.2. The software used on this platform was Professional POLYGRAF v3.2.1 again supplied by Molecular Simulations Inc. Finally, the work involving use of the Cambridge Crystallographic Database (v5.06) was performed on a DEC MicrovaxII running VMS v5.5.

3.5 Modelling of some simple monomer units

Before commencing the modelling of the poly(arylene ether sulphone) and the cyanurate polymers, the modelling of some simple monomer units was performed. This was undertaken, so that general modelling techniques and methodologies could be learnt, together with the determination of an ideal model of each of the constituent parts of the polymers modelled in the remaining three chapters of this thesis.

In this brief study, crystal data of the constituent monomers was used, as this seemed to be the ideal data, from which to start the modelling. The crystal data, the minimised structure and the structure minimised with partial charges, were analysed in terms of their energy and geometric values.

3.5.1 Modelling of bisphenol-A dicyanate

Bisphenol-A dicyanate or 2,2'- bis(4-cyanatophenyl)isopropylidene (BPADC), from the work of Davies et al. was modelled using POLYGRAF, the polymer modelling package from Molecular Simulations Inc. The force field used was DreidingII, the default force field present in the modelling package.
The coordinates, the unit parameters and the space group (P21/c) were read into the crystal builder of POLYGRAF. The unit cell was then extended in all directions and the PBC were connected so that a three-dimensional lattice of BPADC molecules were formed. One of these BPADC crystal structures was extracted for future use.

Minimisation using the conjugate gradient technique\(^{16}\) was performed on the system, until energy convergence of \(<0.01\text{kcal/mol}\) was obtained, using chargeless atoms and with MOPAC\(^{32}\) atomic partial charges on the system. The results were as follows in table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Crystal structure</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (kcal/mol)</td>
<td>215.32</td>
<td>81.00</td>
<td>78.331</td>
</tr>
<tr>
<td>Internal energy</td>
<td>116.88</td>
<td>22.74</td>
<td>22.67</td>
</tr>
<tr>
<td>Bonds</td>
<td>109.44</td>
<td>12.56</td>
<td>12.55</td>
</tr>
<tr>
<td>Angles</td>
<td>5.52</td>
<td>5.78</td>
<td>5.69</td>
</tr>
<tr>
<td>Torsions</td>
<td>1.78</td>
<td>4.36</td>
<td>4.40</td>
</tr>
<tr>
<td>Inversions</td>
<td>0.14</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Non-bonded energy</td>
<td>98.45</td>
<td>58.26</td>
<td>55.65</td>
</tr>
<tr>
<td>VDW</td>
<td>98.45</td>
<td>58.26</td>
<td>58.332</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>-</td>
<td>-</td>
<td>-2.68</td>
</tr>
</tbody>
</table>

Table 3.1. Table showing the energy of the constituent parts of the BPADC monomer.

The geometry of the resulting systems was measured. This consisted of the relevant bond lengths, bond angles and torsional angles of the system.

![Figure 3.8. Schematic showing the geometry of the BPADC monomer.](image)
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<table>
<thead>
<tr>
<th>Geometry</th>
<th>Crystal data</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td>1.553</td>
<td>1.504</td>
<td>1.505</td>
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<td>11</td>
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<td>1.504</td>
<td>1.505</td>
</tr>
<tr>
<td>12</td>
<td>1.423</td>
<td>1.343</td>
<td>1.342</td>
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<tr>
<td>13</td>
<td>1.252</td>
<td>1.267</td>
<td>1.268</td>
</tr>
<tr>
<td>122</td>
<td>1.553</td>
<td>1.504</td>
<td>1.505</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td>110.96</td>
<td>109.84</td>
<td>109.96</td>
</tr>
<tr>
<td>a1</td>
<td>105.50</td>
<td>111.70</td>
<td>111.45</td>
</tr>
<tr>
<td>a2</td>
<td>37.48</td>
<td>56.23</td>
<td>55.48</td>
</tr>
<tr>
<td>Torsional angles (°)</td>
<td>74.35</td>
<td>55.37</td>
<td>55.07</td>
</tr>
<tr>
<td>φ1</td>
<td>0.43</td>
<td>89.69</td>
<td>90.37</td>
</tr>
</tbody>
</table>

Table 3.2. Table showing the geometry of the atoms of interest in the BPADC oligomer.

The minimised geometry of the BPADC monomer in table 3.2, shows that the inclusion of charges for this particular system has little effect. In fact, the parameters in the force field, describe the atoms fairly well, with the exception of torsional angle φ3. This is due to the effect of crystal packing and electronic effects, which are described in more detail in section 4.2.6.

3.5.2 Modelling of difluorodiphenylsulphone

Difluorodiphenylsulphone or bis(4-fluorophenyl)sulphone (DFDPS) was modelled using the internal crystal structure solved at the University of Surrey, Chemistry Department\(^\text{33}\). It was modelled in an identical way to the BPADC monomer above.
Chapter 3: *Introduction to molecular and polymer modelling*

<table>
<thead>
<tr>
<th>Total energy (kcal/mol)</th>
<th>Crystal structure</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>139.29</td>
<td>53.12</td>
<td>65.77</td>
</tr>
<tr>
<td>Internal energy</td>
<td>102.2</td>
<td>32.22</td>
<td>32.44</td>
</tr>
<tr>
<td>Bonds</td>
<td>72.18</td>
<td>2.40</td>
<td>2.63</td>
</tr>
<tr>
<td>Angles</td>
<td>27.96</td>
<td>27.79</td>
<td>27.79</td>
</tr>
<tr>
<td>Torsions</td>
<td>2.06</td>
<td>2.03</td>
<td>2.02</td>
</tr>
<tr>
<td>Inversions</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Non-bonded energy</td>
<td>37.09</td>
<td>20.90</td>
<td>33.33</td>
</tr>
<tr>
<td>VDW</td>
<td>37.09</td>
<td>20.90</td>
<td>20.73</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>-</td>
<td>-</td>
<td>12.60</td>
</tr>
</tbody>
</table>

Table 3.3. Table showing the constituent energy parts of the DFDPS molecule.

The geometry of the resulting systems was measured. This consisted of the relevant bond lengths, bond angles and torsional angles of the system as shown in figure 3.9 and table 3.4.

![Figure 3.9. Schematic showing the geometry of the DFDPS molecule.](image)

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Crystal data</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.721</td>
<td>1.743</td>
<td>1.746</td>
</tr>
<tr>
<td>16</td>
<td>1.721</td>
<td>1.743</td>
<td>1.746</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a3</td>
<td>109.52</td>
<td>108.94</td>
<td>108.76</td>
</tr>
<tr>
<td>Torsional angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>φ5</td>
<td>86.04</td>
<td>85.34</td>
<td>85.65</td>
</tr>
<tr>
<td>φ6</td>
<td>76.03</td>
<td>28.90</td>
<td>35.04</td>
</tr>
</tbody>
</table>

Table 3.4. Table showing the geometry of the DFDPS molecule before changing the parameterisation on the sulphur atom.

The results from the minimisation of the DFDPS molecule in table 3.4 shows that the torsion angles and the torsional angle parameters in the force field describing the sulphone
torsional angles, and in particular $\phi_6$, needed further investigation. In the force field, it was found that the sulphur atom described in figure 3.10a, (where the sulphur atom is connected to two atoms and to two lone pairs of electrons) is clearly incorrect. Instead the parameterisation for the sulphur atom is to four connecting atoms, which describes the sulphone group correctly. Consequently, the parameters describing the sulphur atom were changed, so it could be connected to four atoms and not to the lone pairs, as shown in figure 3.10b.

![Schematic of the different parameterisations of the sulphur atom in the DreidingII force field.](image)

Figure 3.10. Schematic of the different parameterisations of the sulphur atom in the DreidingII force field.

The structure was reminimised, noting particularly the $\phi_5$ and $\phi_6$ result. The results for the DFDPS moiety with the new sulphone parameterisation in the parameter file are given below in table 3.5.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Crystal data</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.721</td>
<td>1.742</td>
<td>1.746</td>
</tr>
<tr>
<td>16</td>
<td>1.721</td>
<td>1.742</td>
<td>1.746</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>109.52</td>
<td>108.56</td>
<td>108.29</td>
</tr>
<tr>
<td>Torsional angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_5$</td>
<td>86.04</td>
<td>85.90</td>
<td>85.89</td>
</tr>
<tr>
<td>$\phi_6$</td>
<td>76.03</td>
<td>76.48</td>
<td>76.27</td>
</tr>
</tbody>
</table>

Table 3.5. Table showing the geometry of the DFDPS molecule after changing the parameterisation on the sulphur atom, to better describe the sulphone linkage parameterisation.

Having changed the sulphone parameterisation in the force field, the $\phi_6$ torsional angle improved significantly, as shown in table 3.5, thus justifying the change of the DreidingII parameter set. Apart from this alteration, the rest of the structure was described well. Again the inclusion of the partial charges had little effect on the geometry of the system.
3.5.3 Modelling of a cyanurate ring

A cyanurate ring is the group of atoms which are formed when three cyanate groups are in close enough proximity to react together. The cyanurate rings are important as they link the polymer chains together and give it the three-dimensional linked thermoset structure. 

$s$-triaizines are aromatic six-membered rings containing alternating carbon and nitrogen atoms. The three chains which emanate from the $s$-triazone ring are connected to the three aromatic carbon atoms.

A cyanurate ring was modelled from the work of Fyfe et al., which describes the synthesis and characterisation of some $^{13}$C and $^{15}$N enriched cyanate esters and cyanurate rings. The cyanurate moiety was modelled in a similar way to the BPADC monomer and the results are shown in tables 3.6 and 3.7 and in figure 3.11.

<table>
<thead>
<tr>
<th>Energy Component</th>
<th>Crystal structure</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (kcal/mol)</td>
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<td>98.21</td>
</tr>
<tr>
<td>Internal energy</td>
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<td>38.70</td>
<td>38.97</td>
</tr>
<tr>
<td>Bonds</td>
<td>88.52</td>
<td>15.78</td>
<td>15.60</td>
</tr>
<tr>
<td>Angles</td>
<td>21.74</td>
<td>13.74</td>
<td>14.83</td>
</tr>
<tr>
<td>Torsions</td>
<td>6.08</td>
<td>9.14</td>
<td>8.49</td>
</tr>
<tr>
<td>Inversions</td>
<td>0.38</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Non-bonded energy</td>
<td>144.33</td>
<td>78.54</td>
<td>59.24</td>
</tr>
<tr>
<td>VDW</td>
<td>144.33</td>
<td>78.54</td>
<td>78.85</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>-</td>
<td>-</td>
<td>-19.61</td>
</tr>
</tbody>
</table>

Table 3.6. Table showing the constituent energy parts of the cyanurate moiety.
Figure 3.11. Schematic showing the geometry of the cyanurate moiety.

![Schematic showing the geometry of the cyanurate moiety.](image)

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Crystal data</th>
<th>Minimised</th>
<th>Minimised with charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1.346</td>
<td>1.365</td>
<td>1.365</td>
</tr>
<tr>
<td>110</td>
<td>1.400</td>
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<tr>
<td>111</td>
<td>1.337</td>
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<td>112</td>
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<td>1.380</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a5</td>
<td>124.34</td>
<td>116.61</td>
<td>116.63</td>
</tr>
<tr>
<td>a6</td>
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<td>a10</td>
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<td>118.79</td>
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<td></td>
</tr>
<tr>
<td>φ9</td>
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<td>-152.27</td>
</tr>
<tr>
<td>φ10</td>
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<td>81.68</td>
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<tr>
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<td>-97.85</td>
<td>-171.05</td>
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<tr>
<td>φ12</td>
<td>-111.10</td>
<td>-87.47</td>
<td>-98.29</td>
</tr>
<tr>
<td>φ13</td>
<td>178.74</td>
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<td>174.67</td>
</tr>
<tr>
<td>φ14</td>
<td>-107.73</td>
<td>-90.08</td>
<td>-89.92</td>
</tr>
</tbody>
</table>

Table 3.7. Table showing some the geometry of the cyanurate moiety, before changing the parameterisation of the s-triazine ring bond angles.
Having obtained the geometry of the modelled cyanurate moiety and having compared the results with the crystal data, it can be seen from table 3.7, that the parameters describing the carbon-nitrogen bond angles were incorrect and needed some slight adjustment. Different force fields were tried, in which both the MM2\textsuperscript{10}, and the MMP2\textsuperscript{11} force fields, which is specifically parameterised for aromatic systems were used. These force fields had no great effect on the results which were obtained, when the cyanurate system was remodelled. Therefore, as these other force fields made little difference to the geometry of the s-triazine ring, and as the Dreiding\textsuperscript{II} force field was the preferred force field, and the one which was used for the majority of the modelling work in the thesis, it was decided to alter the Dreiding\textsuperscript{II} force field accordingly. Therefore the Dreiding\textsuperscript{II} force field was altered, so that it described the C–N aromatic bond more accurately. This was performed by changing slightly two types of bond angle; namely the aromatic C-N-C bond angle from 120° to 113° and the N-C-N bond angle from 120° to 127° in the Dreiding\textsuperscript{II} parameter set. This is shown in figure 3.12.

\begin{figure}[h]
\centering
\begin{tikzpicture}
  \node (n1) at (0,0) {N};
  \node (n2) at (1,0) {N};
  \node (n3) at (2,0) {N};
  \draw (n1) -- (n2) -- (n3) -- (n1);
\end{tikzpicture}
\caption{The original and changed bond angle parameters for an aromatic C-N-C bond angle and an aromatic N-C-N bond angle.}
\end{figure}

With the addition of the new bond angle parameters to the Dreiding\textsuperscript{II} force field, the minimisations were repeated. The results (see table 3.8) show slightly better correlation between the bond angle values for the experimental crystal and modelled minimised data, in addition to an improvement in the other geometric values.
Table 3.8. Table showing some of the geometry of the cyanurate moiety, after changing the parameterisation of the s-triazine ring bond angles.

Changing the bond angle parameters in the force field improved the geometry of the bond angles in the minimised s-triazine ring, so that the structure moved away from the very regular 'benzene-like' configuration. The parameters describing the bonds had to be changed, because none of the force fields which were used, described the s-triazine ring adequately. However, these bond angles are still not as accurate as the crystal bond angle results. Changing the default bond angle parameters in the force field, also altered the torsional angles ($\phi_9$-$\phi_{14}$). This however is not a great problem, because the new values
described these torsional angles, just as adequately as the old values. They are flexible linkages so they can take up many different orientations in space. A more detailed modelling study of this linkage is shown in section 4.5.

3.6 Conclusion

A brief modelling study of the three structures and optimisation of the DreidingII force field, required for the sulphone linkage and the bond angles in the \( \sigma \)-triazine ring was performed to give a better fit between experimental and simulated data. The force field was optimised to improve geometric results between crystal and minimised data. However, the effect of charge on these simple systems had little effect, but this influence becomes more important in larger and more complicated structures. In chapter 4, an in-depth modelling study of an oligomer of poly(arylene ether sulphone) is described using the constituent parts discussed here, as well as the modelling of a poly(arylene ether ketone) oligomer. Furthermore, a more detailed analysis of the cyanurate linkage was performed, using both conformational analysis and MD techniques.

3.7 References

7 Professional POLYGRAF manual (v3.2.1) Molecular Simulations Inc. VB-1 to VB-24 (1993).


13 Biosym Technologies Manual CV3/1, Scranton Road, San Diego, CA 92121-2777.

14 Molecular Simulations Inc. 16 New England Executive Park, Burlington, MA 01803-5297.


30 MOPAC program, version 5.0, QCPE 455, Quantum Chemistry Program Exchange, Indiana University, Indiana, USA.


Chapter 4

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4.1 Introduction

In this chapter, the modelling and characterisation of a single oligomer of a poly(arylene ether sulphone) is described. The polymer chosen was a poly(ether sulphone), namely poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulphone-1,4-phenylene) with a nominal repeat unit similar to Udel™. This is produced by Union Carbide, whose repeat unit is shown in figure 4.1. This polymer is amorphous, so it will be compared with an analogous polymer, namely poly(arylene ether ketone)². Conformational analysis studies, crystal data studies, as well as various molecular dynamic simulations were performed on one oligomer of the poly(arylene ether sulphone). The various linkages present in the oligomer were compared, to ascertain the structure and the most favourable conformations of the oligomer.

4.2 Modelling of the poly(arylene ether sulphone) oligomer

Owing to the nature of the amorphous state, molecules in the poly(arylene ether sulphone) (PIES) are in a random state with little order between them. Consequently little is known about the internal structure and movement of these polymers. By performing various experiments on the system, some details on the internal structure of the PIES are obtained.

![Figure 4.1. Schematic of poly(isopropylidene ether sulphone), i.e., Udel poly(sulphone)™.](image)

4.2.1 Building the poly(arylene ether sulphone) oligomer

The PIES oligomer was made up from the crystal structures of 2,2'-bis(4-cyanatophenyl) isopropylidene³ and bis(4-fluorophenyl)sulphone⁴. The fluoro and the cyanato groups were removed from the individual molecules and then they were joined together, with hydrogen atoms being added until all valences were filled. The joining torsion angle between the two monomers was set to that of the cyanato torsional angle. The atom types were altered to be in the correct format for that of the DreidingII force field⁵ (see appendix 1). Partial atomic charges were added to the structure. Both Gasteiger⁶ and MOPAC⁷ partial charges were
considered. The Gasteiger method was chosen because it gave similar results to MOPAC, with the additional advantage of improved computational speed. The calculation was performed in a fraction of the time compared with the MOPAC method (see appendix 1). Furthermore, this charge calculation method became important when larger systems were considered, because MOPAC was limited to approximately 100 atoms. Minimisation was performed on the system to obtain a low energy conformer of the oligomer. The minimisation technique used was the conjugate-gradients method, with an energy convergence of <0.01 kcal/mol. All future minimisations used the conjugate-gradient technique unless otherwise stated. The results of the final minimisation process are given below in table 4.1.

<table>
<thead>
<tr>
<th></th>
<th>Minimised energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (kcal/mol)</td>
<td>84.74</td>
</tr>
<tr>
<td>Internal energy</td>
<td>48.17</td>
</tr>
<tr>
<td>Bonds</td>
<td>9.70</td>
</tr>
<tr>
<td>Angles</td>
<td>31.98</td>
</tr>
<tr>
<td>Torsions</td>
<td>6.46</td>
</tr>
<tr>
<td>Inversions</td>
<td>0.03</td>
</tr>
<tr>
<td>Non-bonded energy</td>
<td>36.56</td>
</tr>
<tr>
<td>VDW</td>
<td>56.54</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>-19.98</td>
</tr>
</tbody>
</table>

Table 4.1. The strain energy break down of the PIES oligomer.

Having minimised the system, the geometry was obtained by measuring the lengths, angles and torsions of the system as shown in figure 4.2. The results are given in table 4.2.

![Figure 4.2. Schematic showing the geometry of the poly(arylene ether sulphone) oligomer.](image)
Table 4.2. Table showing the geometry of the poly(arylene ether sulphone) oligomer after minimisation.

4.2.2 Conformational analysis

A systematic search was performed on each of the linkages of the PIES oligomer. This systematic search, which explores conformational space by a process of regularly incrementing the torsional angles under test, by a set amount is known as conformational analysis. Initially, the first torsional angle was incremented and the energy was calculated. It was then gradually incremented, until it had performed a full 360° revolution. After the first revolution, the second torsional angle was incremented by the same value. The first torsional angle was now incremented and the energy was calculated. This increment was repeated until another full revolution of the first torsional angle was performed, then the second torsional angle was incremented one further step. This process was repeated until the second torsional angle had also been incremented a full revolution. If a 10° increment angle is used, then 1296 steps are performed. If minimisation follows each step, then the conformational analysis procedure is called a soft search. When no minimisation occurs, it is called an hard search. In the minimisation process of a soft search, the torsional angle under test is kept constant, whilst the rest of the structure is minimised.

Initially, all the linkages were in their cis states with each conformational analysis starting at 0°,0°, with an increment of 10°. The soft search technique was used to minimise the
remainder of the oligomer, i.e., removing any unfavourable close VDW contacts between atoms using either 300 minimisation steps or until an energy convergence of <0.01 kcal/mol. Three analyses using the PIES oligomer were performed on the isopropylidene, the ether and the sulphone linkages, to observe any influence of the other groups in the oligomer. The influence of the other linking groups in the PIES oligomer is required, as these other groups are clearly present in other simulations performed, i.e., the MD simulations. These conformational analyses are shown in figures 4.3 to 4.5, together with the particular linkage under test.
Figure 4.3. Conformational analysis plot of the isopropylidene linkage - $\phi_1$ and $\phi_2$. Minimum values are at $\pm 125^\circ$, $\pm 125^\circ$ and at $\pm 55^\circ$, $\pm 55^\circ$. Energy contour intervals are in kcal/mol.
Figure 4.4. Conformational analysis plot of the ether linkage - $\phi 3$ and $\phi 4$. Minimum values are at $\pm 90^\circ$, $\pm 90^\circ$. Energy contour intervals are in kcal/mol.
Figure 4.5. Conformational analysis plot of the sulphone linkage - \( \phi_5 \) and \( \phi_6 \). Minimum values are at \( \pm 90^\circ \), \( \pm 90^\circ \). Energy contour intervals are in kcal/mol.
4.2.3 Cambridge crystallographic database search of the linking groups

A Cambridge crystallographic database (CCDB) search was made on the various torsion angle linkages present in the oligomer. These linkages were as shown on the conformational analysis diagrams (see figures 4.3 to 4.5). There are no direct experimental methods for determining the likely conformation of bonds within an amorphous polymer. Therefore in an attempt to validate the conformational analysis plots (which ideally determine the likely minimum conformations) and the MD simulations which follow in the next section, an analogous CCDB search was performed. The results for the torsional angle distribution of the isopropylidene, ether and sulphone linkages are shown below.

For the isopropylidene linkage (ψ1 and ψ2), there were 34 hits with a frequency distribution as displayed in figure 4.6.

Fig 4.6. A frequency distribution plot of the % population of isopropylidene torsional angles vs. their dihedral range as found in the CCDB.
For the ether linkage ($\phi_3$, $\phi_4$), there were 419 hits with a frequency distribution as displayed in figure 4.7.

![Frequency distribution plot of ether torsional angles](image1)

**Fig 4.7.** A frequency distribution plot of the % population of ether torsional angles vs. their dihedral range as found in the CCDB.

For the sulphone linkage ($\phi_5$, $\phi_6$), there were 53 hits with a frequency distribution as displayed in figure 4.8.

![Frequency distribution plot of sulphone torsional angles](image2)

**Fig 4.8.** A frequency distribution plot of the % population of sulphone torsional angles vs. their dihedral range as found in the CCDB.
4.2.4 Molecular dynamics simulations at various temperatures

Quenched MD simulations were performed on an isolated PIES oligomer at various temperatures, ranging from 100 to 700°C, using the summed verlet technique\textsuperscript{10}. This means that after each 0.1ps of MD simulation, the system was minimised. In these simulations, up to 300 steps were performed, or until energy convergence of <0.01kcal/mol was reached. The simulation lasted for 50ps, which was enough time for these simple systems to equilibrate. The trajectory files which were produced, were analysed for their energy components and distribution of geometric values, especially the torsional angle distributions.

4.2.4.1 Energy considerations

During the course of a MD simulation, the structure relaxes, explores conformational space and generally obtains an 'equilibrium' energy and position after a certain time of simulation. The time taken to equilibrate the system varies, depending upon the complexity, the temperature and the type of simulation performed. In the case of the above simulations, because of the fairly simple structure, \textit{i.e.}, only one oligomer present, and the minimisation stage after each 0.1ps of MD simulation, the equilibrium energy of the structure was reached fairly quickly. This was typically less than 20ps. Consequently, the last 30ps of the trajectory files were analysed to ascertain the movement and the structure of the PIES oligomer. Clearly, these simulations could have been extended for a longer time period, which may have produced different results. However, it was felt that a 50ps simulation was sufficient to obtain a representative sample of the conformational space which could be explored by the oligomer under the conditions of the MD simulation.

4.2.4.2 Populations and residence plots

Each of the bond lengths, bond angles and torsional angles of the rotatable bonds were analysed in turn. It quickly became apparent that most of the movement of the oligomer came from the torsional angles. The bond lengths and angles remained fairly constant over the length of a simulation (only deviating by 1 or 2\%) whereas the torsional angles moved a great deal. Consequently, only graphs showing the movement and % population of the different types of torsional angles present at specific temperatures are shown. These are at
two different simulation temperatures (300K and 480K), to show a representative view of
the movement of these linkages (see figures 4.9 to 4.20).

Figure 4.9. Graph of the motion of the $\phi_1$ and $\phi_2$ torsional angles vs. time at 300K.

Figure 4.10. Graph of the % population of the torsional angles $\phi_1$ and $\phi_2$ vs. the dihedral range at 300K.
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Figure 4.11. Graph of the motion of the $\phi_1$ and $\phi_2$ torsional angles vs. time at 480K.

Figure 4.12. Graph of the % population of the torsional angles $\phi_1$ and $\phi_2$ vs. the dihedral range at 480K.
Figure 4.13. Graph of the motion of the $\phi_3$ and $\phi_4$ torsional angles vs. time at 300K.

Figure 4.14. Graph of the % population of the torsional angles $\phi_3$ and $\phi_4$ vs. the dihedral range at 300K.
Figure 4.15. Graph of the motion of the $\phi_3$ and $\phi_4$ torsional angles vs. time at 480K.

Figure 4.16. Graph of the % population of the torsional angles $\phi_3$ and $\phi_4$ vs. the dihedral range at 480K.
Figure 4.17. Graph of the motion of the \( \phi_5 \) and \( \phi_6 \) torsional angles vs. time at 300K.

Figure 4.18. Graph of the % population of the torsional angles \( \phi_5 \) and \( \phi_6 \) vs. the dihedral range at 300K.
Figure 4.19. Graph of the motion of the $\phi_5$ and $\phi_6$ torsional angles vs. time at 480K.

Figure 4.20. Graph of the % population of the torsional angles $\phi_5$ and $\phi_6$ vs. the dihedral range at 480K.
4.2.5 Application of stress to the simulation

In addition to the MD simulations above, a series of experiments were run to examine the effect of varying the stress on the system. For this scenario, the oligomer was placed under periodic boundary conditions (PBC), to enable either a compressive or an expansive force in the direction of the z-axis to be applied (which was along the length of the oligomer). Experiments were performed so that the forces which were used, varied from +4GPa to -4GPa in the z-direction (see figure 4.21), whilst atmospheric pressure \( (1.01325 \times 10^{-4} \text{GPa}) \) was applied in the other two directions. The simulations were run for 50ps at a temperature of 300K. Again, the first 20ps of the simulation were ignored, whilst the system was equilibrating. The PBC were set up so that the periodic box remained orthorhombic for the entire simulation, although the cell lengths were allowed to alter.

![Figure 4.21. Schematic of the PIES oligomer under an expansive force in the z-axis direction.](image)

Since the results of the stress analysis, for both torsional angles per linkage are similar, only one graph per linkage is illustrated (see figures 4.22 to 4.24). It was noted that applying stress to the system had little effect on the bond lengths and bond angles in the system, although they did fluctuate about their equilibrium value to a greater extent than under normal conditions.
Figure 4.22. Graph of the % population of the torsional angle $\phi_1$ vs. the dihedral angle at 300K under atmospheric, compressive (-1GPa) and expansive (1GPa) conditions.

Figure 4.23. Graph of the % population of the torsional angle $\phi_4$ vs. the dihedral angle at 300K under atmospheric, compressive (-1GPa) and expansive (1GPa) conditions.
4.2.6 Discussion

Each of the three linkages will be discussed in turn, in relation to their behaviour under the various experiments shown above. The movement and flexibility of the linkages has been analysed using their conformational analysis, from comparison with crystal data and from their MD simulations, i.e., under normal and stress conditions.

First, it was quickly ascertained from the MD simulations, that as expected the major contributory factor to the movement of the PIES oligomer was through the six torsional angles, which make up the three linkages present in the oligomer. The bond lengths and bond angles of each of the three linkages remained fairly constant. They merely fluctuated slightly about their equilibrium values, as obtained from the initial minimisation of the oligomer.

The conformational analysis of $\phi_1$/$\phi_2$ (see figure 4.3), has minimum values at approximately $\pm 125^\circ, \pm 125^\circ$ and $\pm 55^\circ, \pm 55^\circ$ which show good agreement with the published data\textsuperscript{9,11,12,13,14}.
available from a number of different force fields. Calculations using *ab initio* and semi-empirical methods have yielded similar low energy results\(^{15,16,17,18}\). There is also good agreement with the crystal data as shown in figure 4.6. This type of arrangement of the lowest energy conformers at \(\pm55^\circ, \pm55^\circ\) etc. is known as the *twist* arrangement. Using the conformational plot, the energy barrier to rotation was found to be 6kcal/mol. Other workers\(^{11,17,18}\) have obtained similar energy barriers either by MM, *ab initio* or semi-empirical techniques. However Fan *et al.*\(^{12}\) and Sundararajan *et al.*\(^{14}\), who both worked on bisphenol-A poly(carbonates) have produced energy barriers with lower values (\(~3\text{kcal/mol}\)) for the isopropylidene linkage. Fan optimised the Dreiding\(^{\text{II}}\) force field for torsional potentials using the *ab initio* approach, and obtained minimum energies at \(53^\circ\), whereas Sundararajan used different forms of the non-bonding VDW potential. Because of the high energy barrier of rotation obtained in this work, there was a large inaccessible region on the conformational map. Also, for the linkage to move from one minimum to another, a concerted motion of both phenyl rings, by the torsional angles changing conformation needs to take place. This is explained later, when the MD simulation results are discussed. Steric interactions between the nearest neighbouring hydrogen atoms are a major contributor to the energy barrier of rotation, as this non-bonded distance varies from approximately 1.5\(\text{Å}\) in an high energy conformer, to 3.7\(\text{Å}\) in the lowest energy structures (see figure 4.25).

![Figure 4.25. Diagram of one linkage of the oligomer where X can be any of the linking groups and H1 and H2 were the two hydrogens under consideration. The H1-H2 distance varies depending on the linking group X, and the current value of the two torsional angles under test.](image)

It was also shown that the crystal data results compared very well with the conformational analysis, in which the crystal data has four major populations centred around \(\pm130^\circ\) and \(\pm50^\circ\). This shows that the parameterisation of the isopropylidene carbons atoms in the force field was good, due to the correlation between the two results. Due to the high energy barrier to rotation, which was shown by the distinct peaks in the conformational plot, together with the four distinct frequency distributions in the crystal data plot, the
isopropylidene is an inflexible linkage, in which high energy is needed to overcome this energy barrier.

Examining the MD simulation results, especially at lower temperatures (figures 4.9 and figure 4.10) showed that there was little movement of the torsional angles as there was insufficient energy in the system to overcome the high energy barrier to rotation. The majority of the populations for both torsional angles were centred around the 50 to 60° range. Figure 4.9 shows that there was a concerted motion of the two torsional angles when the energy barrier to rotation was overcome. At approximately 26ps, $\phi_2$ flips to a different low energy torsional state: $120^\circ$, whilst the other torsional angle $\phi_1$ simultaneously flips to $-60^\circ$. This ring flip was a concerted motion as one torsional angle movement can not happen without the other torsional angle also moving. The ring flip of the isopropylidene linkage occurred at every simulation temperature which was tried, although the flipping process occurred more often at higher temperatures. These ring flips have also been observed in NMR studies ($^{13}\text{C}$ or $^2\text{H}$) and in semi-empirical calculations on bisphenol-A poly (carbonates). The phenyl rings connected to the central isopropylidene linkage experiences strong resistance to ring rotation due to the repulsions between ortho hydrogens. This repulsion however, may be relieved if the two rings are allowed to rotate synchronously, where they overcome a 5kcal/mol energy barrier. Figure 4.11, shows there was greater movement of the isopropylidene linkage at higher temperatures, as it was easier for the structure to overcome the 6kcal/mol energy barrier, although it still does not happen that regularly. The frequency population plot, as shown in figure 4.12, shows a tetramodal distribution centred around -130°, -60°, 50° and 120°, whereas at lower temperatures (see figure 4.10), the plot tended to be unimodal. This frequency population plot relates the movement of the linkage to that of the conformational plot. At even higher temperatures, the population plot becomes even more regular, with each torsional range containing approximately 25% of the isopropylidene population.

The conformational analysis of $\phi_3\phi_4$ - the ether linkage (see figure 4.4) has minimum values at $\pm 90^\circ, \pm 90^\circ$. This agreed with the findings of some workers. Other researchers who used the MM2 force field and the Tripos force field obtained their lowest energy structures at $\pm 40^\circ, \pm 140^\circ$ and at $0^\circ$ and $180^\circ$ respectively. Jaffe, Kendrick and Schaefer et al. using $ab\ initio$ techniques obtained low energy torsional values at $43^\circ$, $77^\circ$ and $90^\circ$ respectively, showing the difference in results when different basis sets are used to describe
the structure. The arrangement of the ether torsional angles at the lowest energy is known as a butterfly arrangement. The differences in values obtained between this and other work, could be due to force field differences and/or because other workers used model systems, i.e., diphenylether, rather than the PIES oligomer used in this work. Letton calculated the lowest energy conformer to be either at 40°, 40° or 90°, 90° by the semi-empirical CNDO/2 technique. The energy barrier to rotation obtained from MM was 4 kcal/mol which agreed well with other diphenylether moieties, whereas semi-empirically the energy barrier was 8.4 kcal/mol. However, this value was greater because Letton took the energy barrier as the energy difference between the most strained and the least strained structure, although the energy barriers to rotation from the \textit{ab initio} calculations of Jaffe and Kendrick were lower at 2.5 and 3.4 kcal/mol respectively, if the energy barrier at 180° was used.

Lautenschläger et al., working on poly(esters), using the CVFF obtained an energy barrier of 4 kcal/mol, with the lowest energy structures at ±90°, whereas using the AM1 semi-empirical wavefunctions, the lowest energy structures were at ±40°, ±140°, with an energy barrier of 1 kcal/mol. This clearly shows the difference in results between using molecular mechanics and semi-empirical calculations. The lower energy barrier of the ether link, means that more low energy conformational space for the ether linkage can be explored, as compared to the isopropylidene linkage, which explored less conformation space. This is confirmed by DMTA analysis of various poly(sulphones), which showed the isopropylidene linkage to be more inflexible than the ether linkage. However, the conformational plot results do not correlate with those of the crystal data results as is presented in figure 4.7, which has maximum frequency populations at ±180° and 0° respectively. This anomaly is best explained either by crystal packing forces on the ether moiety which are no longer present in the PIES oligomer, or by electron delocalisation of the two lone pairs on the oxygen atom. Allen found the two torsional angle values to be 90°, having optimised the structure using both the AM1 and PM3 semi-empirical wavefunctions. The classic example of this phenomena is the biphenyl unit, which has a central torsional angle of 0° in a crystal structure, yet once minimised or placed into a liquid phase, the lowest energy structures have a central torsional angle which varies between approximately 45° and 60°. These variations are dependant on the force field which is used or the medium in which the structure is placed, whilst if alkyl groups were placed on the phenyl rings the central torsional angle can vary from 44 to 90°.
The motion of $3^4$, i.e., the ether linkage at 300K, is shown in figures 4.13 to 4.14. The movement of the torsional angles was centred around the $-90^\circ$ and $90^\circ$ regions, which was in agreement with the conformational analysis plot. There was movement of the torsional angles from one state to another, but no concerted ring flip as in the case for the isopropylidene linkage. In the population plot (figure 4.14), there was a bimodal distribution of the torsional angles centred around $-90^\circ$, $90^\circ$, but spread over an approximate $30^\circ$ range, either side of the equilibrium point. This was due to the lower energy barrier to rotation of the ether linkage, which can explore greater conformational space, than the isopropylidene linkage. At higher temperatures (see figures 4.15 and 4.16), there was greater movement of the two torsional angles, but still centred around the $-90^\circ$, $90^\circ$ value. The % population plot was very similar to that of the lower temperature population plot, i.e., bimodal. The % population plot at 480K was also similar to other higher temperature plots, e.g., 700K, except that the torsional angle range was larger, with a lower % population maximum at $-90^\circ$ and $90^\circ$.

The conformational analysis of $5_6$ (see figure 4.5) has minimum values at $\pm 90^\circ$, $\pm 90^\circ$ which agreed well with other results$^6,15,18$ and from ab initio data$^17$. Fan et al.$^11$ using the same force field obtained minimum values at $\pm 70^\circ, \pm 70^\circ$ and $\pm 110^\circ, \pm 110^\circ$, but used a model system, i.e., diphenylsulphone. However, in this conformational analysis, the influence of the remainder of the oligomer could slightly alter the result. Kendrick using the STO-3G basis set obtained the optimum low energy torsional angle at $180^\circ$ with an energy barrier at $0^\circ$ of 14.8kcal/mol$^{25}$. However, he concluded that as with the diphenyl sulphide moiety further work was needed with a larger basis set to describe the sulphur atom, so that more reliable results similar to experimental values were obtained. Again, from MM the lowest energy conformations were in the butterfly arrangement. The conformational plot agreed well with crystal data (see figure 4.8), which has two frequency distributions centred around $\pm 90^\circ$. These were spread over a wide range of torsional angles. The energy barrier to rotation was low at 1kcal/mol, which agreed with published results from MM calculations$^6,11$ although from ab initio data the energy barriers was 3.6kcal/mol$^{17}$. Therefore, there was a large area of conformational space which the sulphone moiety could explore. This low energy barrier was mainly caused by the large C-S bond length of 1.74Å. The closest non-bonded H-H distances were moved further away, consequently allowing easier rotation about the linkage, as there were fewer steric effects present. Letton$^{18}$ calculated the sulphone moiety to have an energy barrier of 100kcal/mol, but realised this
value was far too high because the CNDO/2 package was unable to optimise the sulphone
linkage properly. The crystal data (figure 4.8) showed that the torsional angles were centred
around ±90° but also had a large spread of values over nearly every other torsional range.
This, together with the low energy barrier to rotation which the sulphone linkage possesses,
means that the sulphone linkage was the most flexible linkage in the PIES structure.

The motion of _ϕ_5 and _ϕ_6 torsional angles, _i.e._, the sulphone linkage is shown in figures 4.17
and 4.18 for the simulation run at 300K. These graphs show that the sulphone linkage
explores a large amount of conformational space, and is a flexible linkage. There was no
correlation between the movement of the two torsional angles, instead the two torsional
angles moved independently of each other. This was due to the low energy barrier to
rotation, _i.e._, 1 kcal/mol which made it possible for the sulphone linkage to reside in many
low energy conformations. Figure 4.18 shows that the movement of the two torsional angles
was centred about -90° and 90° in a bimodal distribution, but that the distribution was
spread over the whole range of available torsional angles. This result agreed well with that
of the crystal data and the conformational plot. The linkage was in a continuous state of
motion, moving rapidly from one conformer to another because the energy barrier was so
low. When the simulation was run at higher temperatures (figures 4.19 and 4.20), there was
simply greater movement of the sulphone linkage, which gave a similar distribution plot.
This was again bimodal, which was centred about -90°, 90° and spread over all the entire
torsional range. Anwer _et al._ also showed the flexibility of the sulphone linkage, where the
sulphone linkage has one of the shortest persistence lengths to be measured of these
bridging linkages which were examined.

Inspection of the stress results for _ϕ_1 of the isopropylidene linkage (figure 4.22) shows that
stress, either expansive or compressive, of magnitude 1 GPa, has an effect on the linkage. In
both cases, the results became more diffuse, but were still centred around the 60° torsional
range. Consequently, the populations fell as the torsional range began to spread out from the
ideal torsional angle of 60°. It was also noted that no ring flips of the isopropylidene linkage
occurred due to the presence of the stress on the system, as no other low energy minimum
areas were explored. Only when higher stresses were applied, were other low energy
minimum regions explored by the _ϕ_1 torsional angle. When a stress of -3 GPa was applied,
some of this force was dissipated, by the _ϕ_1 torsional angle moving to 120°, at the same
time as the _ϕ_2 torsional angle changed to a different torsional range. Again, _ϕ_1 only moved
to a different low energy torsional range if \( \phi \) did the same. At higher expansive forces, e.g., 3GPa, \( \phi \) remained unimodal, centred around 60°, but with a narrower torsional range and an higher percentage population.

Looking at the results for \( \phi \) of the ether linkage (figure 4.23), the effect that stress has on the torsional angle can easily be seen. When an expansive force (1GPa) was applied, the motion of \( \phi \) became centred around -90°, in a unimodal distribution. At higher stresses, the results were the same, except that the population in that range became greater and spread over a smaller torsional range. The same phenomenon occurred for \( \phi \), when the various stresses were applied. When a compressive force (-1GPa) was applied, the motion of \( \phi \) spread over a large range of torsional angles, with a large population centred around 60°. This occurred because the energy of the system has to be dissipated. One way to achieve this was by moving from one torsional angle to another. Also, when the system is populated at lower torsional angles than the normal values, the length of the oligomeric chain is reduced. The reduction of the oligomeric chain length arose from the torsional angles changing their conformational state, as the bond lengths and bond angles do not alter appreciably during the course of the simulation. Similar results were obtained, when either greater compressive forces were used or when \( \phi \) was analysed.

Examination of \( \phi \) of the sulphone linkage (figure 4.24) showed quite surprising results. Having ascertained the flexibility of the sulphone linkage, its flexibility was very much restricted when either expansive or compressive forces were applied. When an expansive force was applied (1GPa), the torsional range became centred around -90°, with a sharp peak, compared to the spread of results the linkage possessed when stresses were not applied to the system. Similar results were obtained for \( \phi \), except the unimodal distribution was centred around 70°. The results were centred around the -90° torsional range for \( \phi \), because the expansive force moved the linkage into its most favourable low energy conformation, causing the length of the oligomer to be increased as the expansive force was applied. When a compressive force was applied (-1GPa), the torsional range became centred around -70° and -130°, in a bimodal distribution range. Clearly, the excess energy in the system was dissipated, by moving the \( \phi \) torsional angles to slightly higher energy conformations. These oligomers could absorb the compressive force which was applied, by changing the \( \phi \) torsional angle away from the obtained default angle of -90°. Similar results were obtained when higher compressive forces were also applied to the oligomer.
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The results calculated from conformational analysis, crystal data studies and MD calculations, showed quite clearly, that for an unhindered oligomer of PIES, the most flexible linkage was the sulphone linkage, followed by the ether, with the isopropylidene linkage being the least flexible of the three. Their energy barriers to rotation obtained from the conformational plots are 1, 4 and 6kcal/mol respectively. This was in agreement with the work of Fan et al., who used minimisation in conjunction with the Monte Carlo technique to ascertain the flexibilities of the individual linkages. However, when a compressive or expansive force was applied to the sulphone linkage, the sulphone linkage became less flexible, as it was unable to adopt all the conformational space which the free linkage possessed.

4.3 Modelling of the poly(arylene ether ketone) oligomer

In addition to modelling the oligomer of the amorphous polymer, PIES, the modelling of the oligomer of the semi-crystalline polymer, poly(arylene ether ketone) (PIEK) was performed. Simply changing the sulphone to a ketone linkage, changes the properties of the two polymers considerably. By modelling the oligomer of PIEK, some of the reasons governing these two different states may be able to be obtained.

4.3.1 Building the poly(arylene ether ketone) oligomer

The PIEK oligomer was made by replacing the sulphone linkage of the PIES oligomer, with a carbonyl linkage. The Gasteiger method was then used to place partial atomic charges on the oligomer (see appendix 2). A low energy conformer of the oligomer was obtained by minimising the structure to energy convergence (<0.01kcal/mol). This process gave energy and geometry values as shown in tables 4.3 and 4.4 and figure 4.26.
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Table 4.3. The energy components of the PIEK oligomer.

<table>
<thead>
<tr>
<th>Energy Component</th>
<th>Minimised Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (kcal/mol)</td>
<td>81.99</td>
</tr>
<tr>
<td>Internal energy</td>
<td>28.25</td>
</tr>
<tr>
<td>Bonds</td>
<td>10.83</td>
</tr>
<tr>
<td>Angles</td>
<td>5.37</td>
</tr>
<tr>
<td>Torsions</td>
<td>11.99</td>
</tr>
<tr>
<td>Inversions</td>
<td>0.06</td>
</tr>
<tr>
<td>Non-bonded energy</td>
<td>53.74</td>
</tr>
<tr>
<td>VDW</td>
<td>63.32</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>-9.58</td>
</tr>
</tbody>
</table>

Table 4.4. Table showing the geometry of the poly(arylene ether ketone) oligomer after minimisation.

<table>
<thead>
<tr>
<th>Bond angle(°)</th>
<th>Torsion angle(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.52</td>
</tr>
<tr>
<td>12</td>
<td>1.52</td>
</tr>
<tr>
<td>13</td>
<td>1.37</td>
</tr>
<tr>
<td>14</td>
<td>1.37</td>
</tr>
<tr>
<td>19</td>
<td>1.38</td>
</tr>
<tr>
<td>110</td>
<td>1.38</td>
</tr>
<tr>
<td>111</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.2 Conformational analysis

A conformational analysis was performed on the ketone linkage ($\phi_7, \phi_8$), using the method as described in section 4.2.2.

![Diagram of ketone linkage]

Figure 4.27. Conformational analysis plot of the carbonyl linkage - $\phi_7$ and $\phi_8$. Minimum values are near $\pm 150^\circ, \pm 150^\circ$ and at $\pm 30^\circ, \pm 30^\circ$. Energy contour intervals are in kcal/mol.
4.3.3 Cambridge crystallographic database search of the linking groups

A similar search for the carbonyl linkage (ϕ7,ϕ8) was performed to that described in section 4.2.3. For the linkage, there were 456 hits with a frequency distribution as shown in figure 4.28.

![Frequency distribution plot of carbonyl torsional angles vs. dihedral range](image)

**Fig 4.28.** A frequency distribution plot of the % population of carbonyl torsional angles vs. their dihedral range as found in the CCDB.

4.3.4 Molecular dynamics simulations at various temperatures

MD simulations were performed at various temperatures on the PIEK oligomer, in a similar manner to those performed in section 4.2.4. The only difference was that the higher temperature runs were made at approximately 40°C less than for PIES, because of the T_g difference between the two polymers. The results for the PIEK oligomer at two temperatures (300K and 440K), are shown in figures 4.29 to 4.32. Again, the first 20ps of the simulation were ignored, as the system was equilibrating in this time period. The results for the isopropylidene and the ether linkage have also been omitted, as they are very similar to those obtained for those linkages in the PIES oligomer.
Figure 4.29. Graph of the motion of the $\phi_7$ and $\phi_8$ torsional angles vs. time at 300K.

Figure 4.30. Graph of the % population of the torsional angles $\phi_7$ and $\phi_8$ vs. the dihedral range at 300K.
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Figure 4.31. Graph of the motion of the $\phi_7$ and $\phi_8$ torsional angles vs. time at 440K.

Figure 4.32. Graph of the % population of the torsional angles $\phi_7$ and $\phi_8$ vs. the dihedral range at 440K.
4.3.5 Discussion

The results from the conformational analysis of $\phi 8$ (see figure 4.27) show minimum values at $\pm 30^\circ, \pm 30^\circ$ and $\pm 150^\circ, \pm 150^\circ$ in agreement with the published data. However, a model structure of diphenylketone using the CNDO/2 semi-empirical package gave the minimum energy structure at $90^\circ, 90^\circ$, whilst from $\textit{ab initio}$ data the low energy conformers were found at $52^\circ$. The lowest energy conformers were in the twist conformation. An energy barrier to rotation of 3.5 kcal/mol was observed in similar agreement with the published data, whilst from $\textit{ab initio}$ data the energy barrier to rotation was 7 kcal/mol. Although the carbonyl linkage has an energy barrier of 3.5 kcal/mol, comparable to that of the energy barrier of 4 kcal/mol of the ether linkage, figure 4.27 showed that there were a large amount of fairly inaccessible conformations which can not be adopted by the linkage. Comparing the sulphone to the carbonyl linkage, the C-C bond length from the phenyl ring to the linking C atom of the carbonyl group is 1.38 Å, compared to the C-S bond length from the phenyl ring to the linking S atom of 1.74 Å. There is more steric interaction between the neighbouring hydrogen atoms in the carbonyl linkage, consequently making the energy barrier to rotation higher and removing some of the conformational space which the linkage can adopt. The crystal data torsional angle distribution (see figure 4.28), showed that there was a slight discrepancy between the two sets of results. Again, this discrepancy was due to crystal packing forces in the crystalline state and the conjugation about the carbonyl linkage.

The results from the MD simulations at 300K are shown in figures 4.29 and 4.30. These show a trimodal population distribution centred around $-150^\circ$, $50^\circ$ and $150^\circ$ which was virtually in agreement which the conformational plot. There was a slight population centred around $-30^\circ$ and if either the simulation was performed for a longer time span, e.g., 100ps, or the simulation was run at a higher temperature, then this torsional range would also be more highly populated. Figure 4.29 showed that there were areas in the simulation where the carbonyl torsional angles remain fairly constant at approximately $30^\circ$ or $\pm 150^\circ$ for up to 5 picoseconds. It is in these areas that the possibility of packing of the polymer chains could take place, and in particular that of the carbonyl linkage. This could explain why poly(arylene ether ketones) are semi-crystalline polymers (see section 4.4 for a fuller explanation). Examination of the graphs clearly showed that there were specific areas where the carbonyl linkage resides, which were very different from that of the sulphone linkage.
The graphs of the higher temperature simulation (figures 4.31 and 4.32) showed that the population distribution became tetramodal, centred around ±150° and ±40°, with the results virtually mimicking those of the conformational analysis. In these higher temperature simulations though, there was less time when the carbonyl torsional angles remained at a fairly constant value, with its torsional angle centred around a particular value. Instead, it would move more often from one low energy population state to another. These specific movements took place because of the intermediate energy barrier the carbonyl linkage possesses, ~3.5kcal/mol. This energy barrier allowed some, but not total freedom of movement to the linkage, to a few well defined minimum energy regions. There were also inaccessible regions where the carbonyl linkage could not explore, which were mainly due to the VDW interactions of hydrogen atoms, when neighbouring phenyl groups came into very close contact.

4.4 Comparison between the two systems

Owing to the inherent similarities between the two polymeric systems, only the differing linkage, i.e., the sulphone and the carbonyl groups will be discussed. By altering this group, the polymer changes from being amorphous to semi-crystalline, and the T_g reduces by approximately 40°C.

From the above simulations, it can easily be seen that the sulphone linkage was far more flexible than the carbonyl linkage. This was shown by the differing energy barriers to rotation which were 1kcal/mol for the sulphone linkage and 3.5kcal/mol for the carbonyl linkage. The population plots also showed this difference, where the sulphone distribution was bimodal, but virtually spread over the whole torsional range, whereas the carbonyl range was tetramodal, but in well-defined regions. Finally, the residence plots showed that the sulphone linkage was continuously changing conformation, whereas the carbonyl linkage remained in a specific conformation for a span of time, before changing to other low energy conformations.

Consequently, because the sulphone torsional angle is more flexible, it would be very difficult for many linkages to 'pack' together to form a crystalline structure. In fact, all poly(sulphones) are amorphous. The only exception being one which was made to crystallise using dichloromethane as solvent. However, this crystallinity disappeared when
the solvent was removed. Attwood et al.\textsuperscript{35} suggested that the crystallinity arose when an adduct was formed between the polymer and the solvent. Other poly(sulphones) have been made specifically to show the crystalline phenomena. They contain few flexible linkages, but many inflexible biphenyl units\textsuperscript{36} instead. Another difference between the two systems was the bond angle and bond lengths of the respective linkages. The ketone linkage has bond angles and lengths of 124.62° and 1.38Å respectively, whilst those of the sulphone linkage were 109.84° and 1.74Å. There is a substantial difference in both values and it has been ascertained that the bond length plays an important role in the flexibility of the sulphone linkage as shown by obtaining the persistence length of the sulphone unit\textsuperscript{9}. The difference in the bond angle between the two linkages is also most important. In PIEK, the bond angle was in a trigonal arrangement and together with the movement of the carbonyl linkage in well-defined regions, may suggest reasons for the occurrence of crystallinity. When the oligomers were in fairly inflexible regions, it is possible for neighbouring oligomer chains to pack tightly and result in the formation of a crystalline region. In contrast, when the oligomer resided in areas where movement was less restricted, the result would be an amorphous domain. In PIES however, the inherent flexibility, together with the tetrahedral arrangement of the sulphone linkage, left little opportunity for close packing and consequently produced an amorphous system.

4.5 Modelling of the cyanurate ring linkage

The cyanurate ring linkage was briefly modelled in chapter 3.5.3. A more thorough investigation was now undertaken, using conformational analysis and MD techniques. As the s-triazine ring is simply a linking moiety, no actual polymer properties can be obtained from the structure. The movement of the cyanurate ring and the groups joined to it are discussed in the latter part of this section.

4.5.1 Conformational analysis

Conformational analysis was performed on the cyanurate ring (see figure 3.11), using the \( \phi \theta \phi \theta \) torsional angles. The conditions used were set out in section 4.2.2. Either of the other two linkages could have been used instead. The conformational plot is shown in figure 4.33.

A CCDB search of the linkage was also performed. However, there were only four hits in the database, and so it was not possible to obtain any statistics from those results.
Figure 4.33. Conformational analysis plot of the cyanurate linkage - $\phi 9$ and $\phi 10$. Minimum values are near $\pm 90^\circ, \pm 90^\circ$. Energy contour intervals are in kcal/mol.
4.5.2 Molecular dynamics simulation at 300K

MD simulations of the cyanurate ring moiety (see figure 3.11) using Gasteiger\(^6\) and MOPAC\(^7\) charges were performed on the system at 300K (see appendix 3). This becomes important when the thermoset polymer was modelled (see chapter 6), as the Gasteiger derived partial atomic charges can be used for many atom systems whereas the MOPAC derived partial charges are limited to approximately 100 atoms. A 50ps simulation was performed, ignoring the first 20ps for analysis as the system equilibrated. Only results from the Gasteiger run and from one arm of the cyanurate ring are shown, although the MOPAC results and those from the other two arms gave similar results. The movement of the torsional angles are shown in figure 4.34. Other torsional angles along with the \(s\)-triazine ring bond angles were also monitored. The bond angles vibrated slightly about their equilibrium values as obtained from the new \(s\)-triazine ring parameter set, but the isopropylidene torsional angles behaved as expected, agreeing with the results in section 4.2.4.2. Results at other temperatures were unnecessary as the \(s\)-triazine ring simply links other oligomers together, forming a thermoset polymer and as such, no polymer properties can be obtained from just modelling a cyanurate ring moiety.

![Figure 4.34](image)

**Figure 4.34.** Graph of the % populations of the torsional angles \(\phi 9\) and \(\phi 10\) vs. the dihedral range at 300K.
4.5.3 Discussion

The conformational plot (figure 4.33) gave minimum values at ±90°±90° for the φ9 and φ10 torsional angles respectively. This gave an energy barrier of rotation of 2kcal/mol for the φ9 linkage, whilst the energy barrier was 4kcal/mol for the φ10 torsional angle (the ether linkage). This result was in agreement with that from the ether segment in section 4.2.2. An energy barrier of 1kcal/mol and lowest energy conformers at approximately 45°45° were observed when an ether linkage was joined to two pyridine rings. It is clear from the plot that the φ9 torsional angle *i.e.*, the linkage nearest the triazine ring is more flexible, than that nearest the phenyl ring. This clearly is due to the N atoms in the triazine ring, replacing the C atoms and their associated H atoms. In this case, there were no hydrogens on the triazine ring, *i.e.*, in the ortho position to hinder motion about the φ9 linkage. There were no steric interactions between neighbouring hydrogen atoms, and no high energy VDW states. This was also the findings of Welsh *et al.* who stated that both the flexibility and the accessibility of coplanar conformations should increase significantly with the number of ortho-CH groups being replaced by aromatic N-atoms. Consequently, there was a low energy barrier to rotation and much conformational space which the φ9 linkage could explore.

This was confirmed from the MD simulation results (figure 4.34), which again showed the φ9 torsional angle to be more flexible than the φ10 torsional angle. In the % population plot, the φ9 linkage has a bimodal distribution centred around ±90°, but spreads over the entire torsional range, exploring the whole possible range of conformational space. In the φ10 case, again there was a bimodal distribution centred around ±90°, but the populations spread only about 40° either side of the equilibrium value in which the % populations were biased to the -90° torsional angle. There was much conformational space which φ10 did not explore, due to the higher energy barrier which the linkage possesses. The φ9 torsional angle rotated freely, often changing from the +90° state, through intermediate states, to the -90° state, whereas the φ10 torsional angle remained, fluctuating locally around the -90° torsional state, before obtaining enough energy to move to the +90° state. When the simulation was performed for longer periods, the % populations in the two states did become more even, for the φ10 torsional angle, but was still confined to exploring the conformations in the ±90° region.
4.6 Conclusion

The results in this chapter, quite clearly indicated the movement and flexibility of the PIES oligomer under ideal conditions. The flexibilities rank in the order, isopropylidene the most inflexible, sulphone the most flexible, with the ether linkage having an intermediate flexibility. Energy barriers to rotation of 6, 1 and 4 kcal/mol were obtained for each linkage respectively. The results also validate changing the sulphur atom parameters, to describe the sulphone linkage more accurately. Having ascertained where the linkages were most likely to reside, a more complete study of the PIES polymer, under bulk conditions was undertaken in the following chapter, taking into account the results from the ideal conditions in this chapter. It has also been shown that the carbonyl linkage has an energy barrier to rotation of 3.5 kcal/mol, which was less flexible than the sulphone linkage. This might be a reason, coupled with the fact that the carbonyl linkage remained in similar low energy conformations for a period of molecular dynamic simulation, why poly(ether sulphone) polymers are amorphous, whereas the poly(ether ketones) polymers are semi-crystalline. Finally, a study of a cyanurate ring linkage was performed, which showed the s-triazine torsional angle ($\phi$9) to be more flexible than the phenyl ether torsional angle ($\phi$10), with a lower energy barrier to rotation of 2 kcal/mol. This was assumed to be due to lack of hydrogen atoms in the ortho position on the s-triazine ring, thus giving little steric hindrance and consequently ease of motion to this ring.

4.7 References

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17 R. L. Jaffe, Polymer Preprints, 30(2) 1-2 (1989).


Chapter 5

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5.1 Introduction

After having characterised the poly(arylene ether sulphone) (PIES) oligomer in the previous chapter, the amorphous polymer PIES was investigated in greater detail, under the influence of bulk conditions. A range of different molecular dynamics (MD) simulations were performed on the amorphous polymer, which ranged from constant pressure to constant volume simulations. This work was performed with and without solvent being present in the simulation. Both physical and mechanical properties of the PIES were obtained from these simulations. In addition, some physico-mechanical properties were obtained using 'additive group contributions', from the theoretical calculations of Van Krevelen\(^1\).

5.2 Modelling two chains of poly(arylene ether sulphone) under bulk conditions

After modelling a single chain of PIES in a vacuum, the next stage was to model two chains of PIES under bulk conditions. Various simulations were performed on the system to examine how the polymer would behave in the presence of other PIES chains and under the influence of periodic boundary conditions (PBC).

5.2.1 Method

Two independent tetramer chains of PIES (using atomic partial charge values obtained from the Gasteiger method\(^2\)), in which the oligomeric repeat unit was based on the one which was characterised in chapter 4. These were built and combined in the 'polymer' module of POLYGRAF\(^3\). They were then converted into an amorphous two-stranded system with a density of 1.24gcm\(^{-3}\)(\(^4\)) at a temperature of 300K. The techniques used to convert the strands of PIES to an amorphous system, use either rotational isomeric state theory (RIS)\(^5\) developed by Flory, or random methodology based on the Monte Carlo (MC)\(^6,7\) technique. This produced a cubic periodic cell of cell length 16.8Å. The periodic cell was then extended in all directions to produce a lattice of 27 periodic boxes, i.e., one 'real' structure and 26 images surrounding the real structure. This structure was then minimised using the conjugate-gradients algorithm\(^8\) at constant volume until energy convergence (<0.01kcal/mol) was reached.
The method utilised in all the studies to obtain these amorphous structures was the random methodology technique, i.e., the MC technique. The main parameters to be specified were the density and the temperature at which the polymer was to be built in the amorphous cell. The values of the rotatable torsion angles were obtained from the MC technique, which assigned random values to the torsional angles. Each torsional angle was systematically searched. The energy was calculated and if the energy was less than the previous result, then the conformation was accepted. If the energy was greater, then it was accepted in proportion to the value of $e^{-\Delta V/kT}$, i.e., the Boltzmann test where $\Delta V$ was the change in potential energy. The procedure ensured that the probability of any conformation was proportional to the Boltzman factor, although high energy conformations were always rejected. This is known as 'bump' checking. If a conformation was rejected, then the process can be repeated up to a maximum of ten times. If the new conformation was not accepted, then the previous torsional angle was recalculated. The procedure was repeated until the amorphous cell has been obtained, which is shown in figure 5.1. When the amorphous cell was generated, the atoms were in an highly energetic state. This high energy however was removed once minimisation and MD simulations had been performed on the cell.

Figure 5.1. Schematic of how the amorphous builder in POLYGRAF works, which creates an amorphous cell of the required polymer.
Canonical dynamics using both constant pressure and temperature (NPT) and constant volume and temperature (NVT) algorithms, using the Nosé formulation were performed on the amorphous cell and its 26 images. The simulations lasted for up to 200ps and were performed at 400K and 600K respectively. This time period gave the structure a reasonable time scale in which to relax fully and explore different conformations of the simulated structure, in the four different simulations which were performed.

5.2.2 Results

The trajectory files obtained from the MD simulations were analysed for a number of properties, including population plots of the constituent torsional angle ranges, and the long and short range order in the structures, i.e., the radial distribution and the un-normalised radial distribution functions. The movement of the structures, i.e., the mean square displacement and the diffusion coefficients were also obtained, and the mobility of the individual torsional angles. These were calculated by obtaining the non-normalised autocorrelation and cross-correlation functions of the torsional angles in the repeat unit of the polymer. The theory of each of these techniques is discussed in turn, before presentation of the results.

The energy and either the volume or pressure values (depending on the type of simulation) from the four trajectory files were analysed to determine whether an equilibrium point had been reached in the simulations. Results similar to figure 5.2 were obtained for all the simulations, in which the constituent parts equilibrated within 50ps. Only the first 50ps of the total energy and the volume fluctuations from the NPT simulation at 400K are shown in figure 5.2. This was simply for ease and clarity in presentation of the results. In the remainder of the simulation, these values simply fluctuated about their equilibrium value.
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Figure 5.2. Graph of the first 50ps of the (NPT) MD simulation at 400K, showing how the potential energy (PE) and volume data equilibrate within the first 50ps of the simulation.

5.2.2.1 Population plots

Using the above MD simulations, % population plots were obtained for each of the three individual linkages, by combining all the occurrences of the individual linkages for each of the separate chains present in the simulation. These are shown in the figures 5.3 to 5.6, although only the result from one of the chains is shown.

Figure 5.3a. Combined % population plot of all the isopropylidene linkages for one polymer chain, under constant volume conditions at the specified temperatures.
Figure 5.3b. Combined % population plot of all the isopropylidene linkages for one polymer chain, under constant pressure conditions at the specified temperatures.

Figure 5.4. Graph of one of the isopropylidene linkages, showing the occurrence of ring flips for the linkage and the concerted motion of both torsional angles.
Figure 5.5a. Combined % population plot of all the ether linkages for one polymer chain, under constant volume conditions at the specified temperatures.

Figure 5.5b. Combined % population plot of all the ether linkages for one polymer chain, under constant pressure conditions at the specified temperatures.
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Figure 5.6a. Combined % population plot of all the sulphone linkages for one polymer chain, under constant volume conditions at the specified temperatures.

Figure 5.6b. Combined % population plot of all the sulphone linkages for one polymer chain, under constant pressure conditions at the specified temperatures.

5.2.2.2 Radial distribution function

The radial distribution function (G(r)), is the averaged distribution of inter-atomic vector lengths, which is related to the unnormalised distribution function, (N(r)). It is defined as the probability of finding an atom at a distance r away from another atom. The plots which
were obtained show peaks and troughs, relating to coordination or excluded volume in the
system. \( G(r) \) is useful in revealing overall structure properties, such as packing and ordering
behaviour, \( i.e. \), it determines whether a system is crystalline, where many peaks and troughs
especially encompassing a large distance (\( >6\text{Å} \)) indicate an ordered crystalline structure.

\[
G(r) = \frac{N(r)}{\rho_0^2 4\pi r^2 \, dr}
\]

\( \text{eqn. 5.1} \)

\[
N(r) = \left\langle \sum_{i,j} \delta(r - |r_i - r_j|) \right\rangle
\]

\( \text{eqn. 5.2} \)

where \( \rho_0 \) is the atomic density for periodic systems, \( N(r) \) is the unnormalised distribution
function, \( r \) is the distance under consideration and \( r_i \) and \( r_j \) are two atoms being tested.

The radial distribution function for PIES was obtained from the NPT simulation at 400K
and this figure is shown in figure 5.7, and the unnormalised distribution function is
illustrated in figure 5.8. Similar plots were obtained from the other simulations which are
not shown.

![Radial distribution function (G(r)) of PIES from the NPT simulation at 400K.](image)

**Figure 5.7.** The radial distribution function \( G(r) \) of PIES from the NPT simulation at 400K.
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Figure 5.8. The unnormalised distribution function ($N(r)$) of PIES from the NPT simulation at 400K.

### 5.2.2.3 Mean square displacement

The mean square displacement (MSD) is used to calculate the translational movement of a structure. The value which is generally quoted is the self diffusion constant ($D$), which is obtained from the slope of the MSD vs. time plot.

![Figure 5.9. Schematic showing the displacement ($r$) of an atom from time $t=0$ to time $t=t$, where $D$ is the self-diffusion constant.](image)

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |r(t) - r|^2 \rangle$$  

**eqn. 5.3**

where $\langle |r(t) - r|^2 \rangle$ is the mean square displacement, $t$ is the time and $D$ is the self diffusion constant.

A typical MSD plot calculated from the NPT simulation at 400K is illustrated below in figure 5.10 in which the self-diffusion constant ($D$) is $0.113 \text{Å}^2/\text{ps}/\text{per atom}$. Other $D$ values from other MD simulations are given in table 5.1.
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Figure 5.10. Graph of the MSD vs. time for PIES obtained from the NPT simulation at 400K.

Table 5.1. Table of the self-diffusion constant (D) as obtained from the various MD simulation techniques.

<table>
<thead>
<tr>
<th>MD technique</th>
<th>D (Å²/ps/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVT at 400K</td>
<td>4.02x10⁻⁴</td>
</tr>
<tr>
<td>NVT at 600K</td>
<td>1.55x10⁻²</td>
</tr>
<tr>
<td>NPT at 400K</td>
<td>1.13x10⁻¹</td>
</tr>
<tr>
<td>NPT at 600K</td>
<td>2.12x10⁻¹</td>
</tr>
</tbody>
</table>

5.2.2.4 Correlation plots

The mobility of polymer chains can be characterised by time correlation functions, particularly the cross or autocorrelation. These are functions of the rotatable torsional angles φ in a structure. The autocorrelation function of the rotation of the bond torsional angle φ is evaluated as:

\[
R_\phi(t) = \frac{\cos(\phi(t)) \cos(\phi(0)) - \cos^2(\phi(0))}{\cos^2(\phi(0)) - \cos^2(\phi(0))} \tag{5.4}
\]

where \( R_\phi(t) \) is the correlation coefficient at a particular time and φ is the torsional angle value at time = t or time = 0. Chain mobility is dependant on the temperature of the system, i.e., whether there is enough energy in the system to overcome the energy barriers of particular torsional angles. Clearly there is greater mobility at higher temperature. The non-normalised time correlation function between two quantities is given by:

\[
R_\phi(t) = \frac{\cos(\phi(t)) \cos(\phi(0)) - \cos^2(\phi(0))}{\cos^2(\phi(0)) - \cos^2(\phi(0))} \tag{5.4}
\]
where $\delta A(t)$ is the value of torsional angle $A$ at time $t$, whilst $\delta B(t_0)$ is the value of torsional angle $B$ at time $t = 0$. If $A$ and $B$ are the same torsional angle then the non-normalised autocorrelation is obtained, whereas if $A$ and $B$ are different torsional angles then the non-normalised cross-correlation function is obtained. The FORTRAN computer code used to obtain the non-normalised correlation function is given in Appendix 4 and is based on the programme given in the book by Allen and Tildesley\textsuperscript{10}. A number of correlation functions were obtained from these studies for the torsional angles in the simulations. Results from the simulations are very similar, so only results from the NVT simulation at 400K are illustrated. Some correlation functions of the torsional angles are shown below in figures 5.11 to 5.13. The definitions of the torsional angles were the same as defined in chapter 4, i.e., $\phi_1$ and $\phi_2$ refer to an isopropylidene torsional angle, $\phi_3$ and $\phi_4$ refer to an ether torsional angle, and $\phi_5$ and $\phi_6$ refer to a sulphone torsional angle.

**Figure 5.11.** Graph of the non-normalised autocorrelation function of $\phi_1\phi_1$ from the NVT simulation at 400K.
Figure 5.12. Graph of the non-normalised autocorrelation function of $\phi 6\phi 6$ from the NVT simulation at 400K.

Figure 5.13. Graph of the non-normalised cross-correlation function of $\phi 3\phi 4$ from the NVT simulation at 400K.

5.2.3 Discussion

The graph in figure 5.2 illustrates how the total potential energy and the volume equilibrate for a period of 50ps for the NPT simulation at 400K. Similar results were obtained from the NVT simulation except that in this case, it was the total energy and pressure which
equilibrated over a period of 50ps. In these simulations, there were many more interactions
which needed to be simulated, e.g., the non-bonded intermolecular interactions and
interactions to all the periodic images formed, compared to modelling the PIES oligomer in
a vacuum in chapter 4. Consequently, a much longer simulation time was needed to obtain a
relaxed structure which was near to its equilibrium point.

The constant volume results for the isopropylidene dihedral angle (figure 5.3a), illustrate a
defined tetramodal distribution centred around ±50° and ±130° respectively, for both
temperature ranges. However, the populations are very low in the -130° and 50° range for
the simulation at 600K. The constant pressure simulations at both temperatures for the
isopropylidene dihedral angle (figure 5.3b), show a tetramodal distribution of dihedral
angles centred around ±50° and ±130° in four well defined distributions. This shows that the
linkage can reside in any of the four low energy distributions, which compares well with the
crystal data, conformational analysis and simulation work presented in chapter 4. The
constant pressure simulations seem to allow the polymer chains to explore more of the
available conformational space. This is because the fluctuating volume of the simulated cell
allows the four low energy conformation regions to be explored, whereas the constant
volume simulation has more difficulty exploring these low energy regions. However, if the
NVT simulation lasted longer, then more conformational space would be explored, in which
the results would more than likely resemble those of the NPT simulation.

Although the results were in a tetramodal distribution, the distribution of the torsional
angles which were explored in each of the four populations was spread out over a range of
torsional values. This spread of torsional angles was higher than in the case of the single
oligomer in a vacuum, where the spread was over a very narrow torsional range. This was
due to the influence of the other molecules in the structure, the other polymer chain and the
influence of the PBC. In this situation the torsional angles were forced to explore slightly
higher energy conformations of the isopropylidene linkage and consequently made the
results more diffuse. The movement of the individual dihedral angles was interesting and
showed the phenomenon of ring-flipping. If one of the dihedral angles changed its state
from 120° to 60° then its neighbour changed dihedral states also (see figure 5.4). This
showed that a pair of isopropylidene dihedral angles were totally correlated, i.e., if one
dihedral angle 'flipped' then the other one also flipped in a concerted motion.
Hutnik et al.,\textsuperscript{13} when modelling glassy bisphenol-A poly(carbonate) (PC) observed phenylene ring flips about the isopropylidene group. When a phenylene ring was 'driven' to flip, there was a 'knock-on' effect of other torsional angles in the polymer chain, mainly of torsional angles close to the effect, but also torsional angles up to 30 angles distant from the flipped phenylene ring. When a phenylene ring flip occurs, there has to be a strong cooperative movement of the isopropylidene moiety between the two adjoining phenyl rings. The cooperative motion of the isopropylidene angles is due to largely intramolecular constraints. The system also relaxed via conformational changes in the carbonate group, but as expected, the ring flip altered the structure of the polymer chains more than the carbonate group motion.

Jho et al.,\textsuperscript{14} and Xiao et al.,\textsuperscript{15} using dynamic mechanical thermal analysis techniques on derivatives of PC, suggested that relaxation of the polymer occurs over 6-9 repeat units. Xiao concluded that intrachain interactions were the dominant factor in the cooperative relaxation of the polymer. Meanwhile, Henrichs et al.,\textsuperscript{16} used variable temperature \textsuperscript{13}C NMR to show the occurrence of ring flips in PC. They concluded that the high barrier to methyl rotation indicated that rotation of the methyl groups was coupled to the motion of the aromatic rings. Cholli et al.,\textsuperscript{17} using solid-state \textsuperscript{2}H NMR on deuterated poly(butylene terephthalate), concluded that the phenyl group underwent ring flips, if there was enough conformational space surrounding that site. They observed ring flips in the semi-crystalline polymer and were able to predict the experimental solid-state \textsuperscript{2}H NMR in which particularly at low temperature, there was fair agreement with the experimental data. Kikuchi et al.,\textsuperscript{18}, when modelling poly(ethyl acrylate) noticed two types of motion along the polymer backbone. First, rapid torsional oscillation around equilibrium angles with an amplitude of \(\approx 30^\circ\) and second, conformational jumps that occur at moderately long time intervals. These often took place collectively over closely located monomer units; the so-called segmental motion.

There is a bimodal distribution centred around \(\pm 90^\circ\) for the ether dihedral angles simulated at constant volume (figure 5.5a). There is also a slight population at 0° for the simulation at 400K and an even smaller population present from the simulation performed at 600K. In this case, because of the influence of the other chain and molecules present in the simulation, the ether linkage can become 'trapped' in an high energy state and can not escape from this state because of the limited movement of the structure (see the MSD result in table...
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5.1, which shows little movement of the system during the constant volume simulations. This phenomenon has also been seen in bulk simulations on single chains of PIES at 300K, but these results have not been presented. However, this type of result was hardly seen at 600K, simply because the system has more energy due to the simulation temperature and did not become 'trapped' in high energy conformations as it was possible to overcome the energy barriers to rotation more easily. In this case, it was possible for the polymer to move more freely, explore more space, thus enabling the ether dihedral angles to populate the low energy conformations.

The ether dihedral angle simulated under constant pressure conditions (figure 5.5b) gave at both temperatures ranges, a bimodal distribution of dihedral angles centred around ±90°. This distribution was spread over a large range of dihedral angles. There was more movement between dihedral states at 600K, compared to the NPT simulation at 400K, or either of the NVT simulations performed. This was due to the higher temperature of the run and this consequently increased the velocity and energy each individual atom possessed. Therefore, the chance of overcoming the energy barrier of 4kcal/mol was greatly enhanced. This phenomenon was also increased by the fluctuating volume of the periodic cell, where it was easier for the polymer to relax around the rotatable torsional angles in the polymer backbone. However, unlike the isopropylidene dihedral angles, the movement was independent of any neighbouring ether dihedral angles.

When the sulphone dihedral angles were simulated under constant volume conditions (see figure 5.6a), there was a tetramodal distribution centred around -140°, -20°, 60° and 160° at 400K, but at 600K there was a bimodal distribution centred around -90° and 80°. This strange phenomena for the dihedral angles at 400K was seen again, where the population plot of the sulphone torsional angles was not as expected. This phenomenon was again seen when a strand of PIES was simulated under NVT conditions at 300K, where the sulphone torsional angle distribution was not centred totally around ±90°, rather there was a large population centred around 0°. This phenomenon is likely to occur because the dihedral angles can not explore all the conformation space due to the presence of other atoms and polymer strands in the simulation. This hinders free rotation about the torsional angles. The constant volume of the simulation, the packing constraints which were applied from the other strand and the periodic 'images' of the system in the simulation hinder free movement of the torsional angle. At the higher simulation temperature of 600K, these factors were
overcome, due to the system being in an higher energetic state. Because these linkages have more energy and the whole structure is more mobile, there is less chance of the linkages becoming 'trapped' in high energy conformations. However, due to the constant volume conditions, there was little movement from one low energy torsional state to another.

When the sulphone dihedral angle was simulated under constant pressure conditions (figure 5.6b) at both temperatures there was a bimodal distribution of dihedral angles centred around ±90°. At both temperatures there was frequent to and fro movement between the two low energy torsional states, especially in the simulation at 600K. However, these distributions of torsional angles were large and spread over the whole range of angles which could have been explored. This showed that even when simulating PIES under bulk conditions, the sulphone linkage was the most flexible of the three linkages being studied. This is due to the low energy barrier to rotation and consequently the ease of rotation about the sulphone linkage. The populations obtained at both temperature ranges gave the expected result, which agreed with the crystal data and the MD simulations described in chapter 4, although in these constant pressure simulations more low energy conformational space was explored as compared to the constant volume simulations.

All the results obtained for the three dihedral linkages were in good agreement with those obtained from crystal data (except for the ether angles where the reasons for this have already been described) and with the conformational analysis and MD results as described in chapter 4. The only results which disagreed with this data were from the NVT simulation at 400K, in which the ether and the sulphone linkages gave non-ideal results. Clearly in these situations, there was not enough energy in the system for the structure to relax properly, overcome energy barriers and find low energy conformers. Similar results were also seen when a strand of PIES was simulated under NVT conditions at 300K. The polymer remained 'trapped' in high energy conformations, where the torsional angles were not always the ones of lowest energy. Also, there was a slight anomaly in the isopropylidene result in the NVT MD simulation at 600K, where the % populations at -130° and 50° were very low in these two ranges. It is assumed in this simulation that there was not enough free volume for the linkage to explore and consequently failed to overcome the 6kcal/mol energy barrier. It is assumed that if the simulation was run for a much longer simulation time then these other low energy regions would be explored as well. However, on the whole these anomalous results did not occur at the higher temperature NVT simulation due to the greater
energy of the simulation, or simulations involving the NPT algorithm because of the greater mobility of the polymer, due to the fluctuations in the cell volume in these simulations.

Cagin et al.\textsuperscript{19} simulated poly(ethylene) using both microcanonical MD (Verlet\textsuperscript{20}) and canonical MD (Nose\textsuperscript{21}) techniques and concluded that the Nose algorithm reached thermal equilibrium distributions in about 10ps of MD simulation, whereas the Verlet algorithm had failed to reach thermal equilibrium after 1 nanosecond of simulation. In this simulation, thermal equilibrium was reached when the torsional states were in a 3:1:1 ratio of trans:gauche$^+$:gauche (t:g$^+$:g$^-$), in which the initial state of all the torsional angles was trans. They concluded that canonical dynamics had the advantage of applying energy exchange with that to an external heat bath, where the atoms comprising a particular dihedral angle can gain enough energy to cross the trans-gauche energy barrier ($\sim$4kcal/mol). However, in the microcanonical simulation, there was an uneven distribution of kinetic energy along the segment, due to the constant energy constraint in microcanonical simulations, although given time, it was clear that the thermal equilibrium would be reached. Finally they concluded that canonical dynamics could be used for the study of phase transitions, i.e., melting and $T_g$ transitions in polymers, since the method leads to temperature fluctuations which provide a faithful representation of the physical conditions.

Smith et al.\textsuperscript{21} modelled atactic poly(vinylchloride) (PVC) in the melt and in a vacuum and obtained similar characteristic ratios in both simulations, although the chains in the melt were somewhat extended relative to the isolated chains. Similar results between the two simulations were also found for the distribution of trans dihedral angles against gauche dihedral angles in the system, with the probability of the trans state formation being about 70%. The distribution of torsional angles into the two states is however less temperature dependent than that found for poly(ethylene), due to the chirality of the PVC chains. When poly(styrene) was modelled\textsuperscript{22}, the t:g$^+$:g$^-$ ratio was approximately 2:1:1 for the torsional angles of the polymer backbone, but from the G(r) plots, it was concluded that the phenyl rings on different chains preferentially pack at a separation of $\sim$6Å and have a tendency to align at right angles to each other.

The MSD of the four MD simulations was obtained and the results are shown in table 5.1. The table clearly shows that the polymer movement was much greater under constant pressure simulations. In these simulations, the polymer had opportunities to diffuse and explore more conformational space as the volume of the periodic cell fluctuated. This was
shown by the residence plots and the greater diffusion coefficients obtained from the
constant pressure simulations, where there was up to a 10-fold increase in the self diffusion
coefficient in comparison with the constant volume simulations.

Boyd et al.$^{23,24}$ modelled methane diffusion in poly(ethylene) and poly(isobutylene) (PIB)
and showed that methane diffused faster in poly(ethylene) than in PIB. At 298K, the
self-diffusion constants of methane were 0.12Å$^2$/ps and 0.062Å$^2$/ps respectively.
Furthermore, the self-diffusion constant of the polymer chain for poly(ethylene) was shown
to increase from 0.003 to 0.019Å$^2$/ps when the polymer was simulated at 300 and 400K
respectively. They concluded that the lower self-diffusion constant for methane simulated in
PIB was due to lower mobility and higher density of PIB. In PIB, the specific free volume at
400K was 0.421cm$^3$/g, and in poly(ethylene) the specific free volume at 300 and 400K was
0.458 and 0.534cm$^3$/g respectively. These results confirmed the strong temperature
dependence of the free volume available to a penetrant the size of methane and showed that
a methane molecule saw less free volume in PIB than in poly(ethylene) at a specific
temperature. The movement of the penetrant was also significant. In the poly(ethylene)
simulation at 300K and the PIB simulation at 400K, the penetrant molecules underwent
large 'hops' between long periods of localisation in voids in the polymer structure, whereas
at 400K, the polymer was more mobile and the penetrant was no longer trapped in voids for
lengthy periods.

Müller-Plathe et al.$^{25}$ studied the short term diffusion of oxygen molecules in amorphous
PIB at 300K, where the oxygen molecules generally oscillate in particular cavities, before
'hopping' into a neighbouring cavity$^{26}$, when a channel became available in the polymer
matrix. The occurrence of a sharp peak in the energy of the system at the time of an hop
suggested that there was an energy barrier to overcome. This involved the opening of the
channel between the cavities, and also the actual 'hop' into a neighbouring cavity. There
seemed to be no preference for an end-on or an edge-on hop which indicated that the
channels were big enough to allow the oxygen molecules to pass either way or to allow
them to rotate during the jump. Finally, Coughlin et al.$^{27}$ modelled the diffusion of some
large di-n-alkyl phthalates in amorphous PVC at 363K, and predicted that for a given fixed
molecular volume, compact structures would migrate more slowly than extended ones. The
calculated diffusion coefficients were less sensitive to molecular size than the experimental
results, as the simulated results ranged from 8.29x10$^{-5}$ to 2.53x10$^{-5}$Å$^2$/ps, with $n$ varying
from 5 to 10. The diffusion coefficient for these large molecules were very small, which was not surprising considering the size of the penetrant molecule and was approximately 1000 times slower than for the diffusion coefficient of methane in PIB.

The G(r) plot from either type of simulation (figure 5.7) were very similar. The plot showed no order in the system, i.e., the system although in energetically favourable conditions remained in a state of disorder. There was no evidence of long range order in the system, as there were no major peaks present above approximately 4Å. The peaks shown in the plot describe various bonded and non-bonded distances in the system, e.g., the C-H and C-C bonded distance and the para C-C non-bonded distance which were present at about 3.4Å. The N(r) plot (figure 5.8) showed a similar result, except that above 4Å the value of the curve continued to increase, rather than remaining constant as in the case of G(r).

Fan et al. modelled PC and obtained the G(r) plot by averaging the results from six model structures. In their system, again there was no order, and only the peaks observed at less than 5Å could be assigned to specific distances of connected atoms (1-2, 1-3 and 1-4 type interactions). This type of structural order due to intramolecular connections disappeared at distances greater than 5Å. Beyond this distance, the structure was completely randomised (as in our system). This was evident as there was no visible peak at the well-defined distance (~5.76Å) between the carbon and oxygen atoms in the C-Ph-O segment as seen in the G(r) plot. Hutnik et al. also modelled PC and obtained various G(r) plots of the constituent atoms in the structure. They concluded from these plots that the structure might not be totally amorphous in nature. The isopropylidene-isopropylidene carbon atom intermolecular G(r) plot showed there was a weak intermolecular preference for distances between 5-6Å, which could be an indication of areas of 'enhanced order'. Rigby et al. modelling n-alkane like chains, obtained the intra- and the inter-molecular G(r) of the poly(methylene) type structure, in which various conformational sequences of the polymer could be seen in the intra-molecular plot. These were swamped however, when the two contributions were combined. As the temperature was lowered below the T_g, the short range order improved accordingly because of increased density. This reduced thermal motion and extended the chain conformation of the polymer. Theodorou et al. obtained G(r) plots for the various constitutional species of atactic poly(propylene) and found no order in the amorphous system. However, the inter-molecular G(r) plots were more interesting. The first coordination shell of the methyl-methyl G(r) plot was shown to be at approximately 3.5Å,
approximately equal to the sum of the VDW radii of the species involved. The skeletal carbon-carbon \( G(r) \) plot showed a broad hump at approximately 6.3 Å, because the substituents on the chains kept these C-C atoms far apart. The skeletal carbon-methyl \( G(r) \) plot showed the first coordination shell to be at 3.9 Å.

The correlation plots (figures 5.11-5.13) show the movement of the linkages and how the specified torsional angles relax over a period of time. The autocorrelation plot of \( \phi_1 \phi_1 \) shows the linkage relaxing over a time of 25 ps, and then simply fluctuating about this value for the remainder of the simulation. However, the autocorrelation plot of \( \phi_6 \phi_6 \) shows a more intense relaxation of the linkage at the beginning of the simulation, because of the greater mobility of the sulphone torsional angles, which reach equilibrium after 30 ps. This increased mobility is shown in population plots of the constituent linking groups in figures 5.3 to 5.6. In either type of MD simulation or at the two temperatures specified, more conformational space is explored by the sulphone linkage as compared to the isopropylidene linkage. The cross-correlation of \( \phi_3 \phi_4 \) shows the linkage relaxing over a period of 40 ps, before fluctuating around this point for the remainder of the simulation. As the system had relaxed after 50 ps of simulation to as low an energy as possible, the results presented, i.e., the \( G(r) \) and the MSD plots (figures 5.7 and 5.10 and table 5.1) have been calculated from energetically relaxed structures.

Doherty et al. have modelled \( C_{21} \) n-alkane crystals and obtained the auto, the \( (1,2) \) and the \( (1,3) \)-torsion angle pair cross-correlation function of all the torsional angles averaged over all the 12 chains in the crystalline cell. They concluded that the autocorrelation function showed that the individual torsional motions were periodic, but the cross-correlation function indicated strong reverse coupling between \( (1,3) \)-torsional pairs, and the \( (1,2) \)-torsion angle pair cross-correlation function showed little coupling. Takeuchi et al. modelled poly(ethylene) in the bulk at and above its \( T_g \). They obtained the dihedral angle autocorrelation function which indicated an appreciable degree of chain mobility, in which this mobility depended only slightly on the torsional potential present in the poly(ethylene) model. They concluded that the reorientation process, i.e., the relaxation of the polymer was affected by two components, namely on a short time scale, conformational transitions and on a large time scale, the presence of surrounding chains, where surrounding chains can constrain the relaxation unless they too were allowed to move. They also observed from the time-correlation plots, that the relaxation times
increased as the temperature was lowered, as the chain length increased and as the bond under consideration was further removed from the chain ends\textsuperscript{12}. Theodorou \textit{et al.}\textsuperscript{32,36} modelling glassy atactic poly(propylene) obtained the directional correlation of the atom pairs in the structure, in which strong directional correlations were seen between neighbouring atoms, which decreased 'quasi-exponentially' with distance. Consequently, there was no correlation at large distances. Theodorou \textit{et al.} also obtained the directional correlation of the displacements of atoms belonging to the same chain, in which strong directional correlation was seen at small separations, but which dropped quickly to almost zero after a distance of 10 bonds. They concluded that the deformation in the glass was accompanied by coordination displacement of chain segments approximately 10 bonds long.

\textbf{5.3 Modelling of poly(arylene ether sulphone) in a solvent}

It has been stated earlier in this thesis, that few poly(ether sulphone) crystallise and if they do so, it is only under certain conditions and in specific solvents. Generally, this solvent is dichloromethane (DCM). Consequently, in this section of work, when some DCM solvent molecules were included in the simulation, then perhaps some PIES-solvent interactions, or some ordering in the system could be seen, after a time period of MD simulation. This could possibly explain the process of crystallisation of the polymer in this particular solvent.

\textbf{5.3.1 Method}

Prior to the modelling studies, the solvent molecule had to be generated. This was performed by making up a DCM molecule, adding Gasteiger charge\textsuperscript{2} to the molecule and minimising to energy convergence. This minimised DCM molecule was then placed into the solvent user library of POLYGRAF\textsuperscript{3}, to enable it to be accessed in the same way as other solvent molecules.

A PIES trimer was built, using Gasteiger charge\textsuperscript{2} and was built up into an amorphous structure of density 1.24gcm\textsuperscript{-3}\textsuperscript{6}. DCM solvent molecules were then introduced around the PIES oligomer, to which 688 solvating molecules were added. The structure was then energy minimised under constant volume conditions for 2000 iterations. Total energy convergence was not critical as a further MD simulation would relax the solvated structure still further. Constant pressure MD simulations (NPT), using the Nosé technique\textsuperscript{9} were
performed on the structure at 300K for ~50ps. (It was intended to have a much longer simulation, but unfortunately due to the central processing unit (cpu) and disk space constraints, the simulation was terminated after approximately 50ps). This time constraint clearly showed that in the simulation most of the time was used in simulating the solvent, rather than the PIES oligomer. The data from the simulated trajectory files was analysed for the torsional angle populations of the various linkages, plus the radial distribution function, the MSD and some correlation plots, to observe how the PIES behaviour under these solvated conditions.

5.3.2 Results

The results from the simulation are given in the following graphs. Figures 5.14 to 5.16 show the total torsional angle distributions of the isopropylidene, ether and sulphone linkages respectively. Figure 5.17 shows the radial distribution of the polymer including the solvent molecules from the whole simulation, and figures 5.18 to 5.20 show the non-normalised correlation function plots of some torsional angles present in the polymer backbone. The MSD was obtained and the self-diffusion constant $D$ was found to be $0.353 \text{Å}^2/\text{ps}/\text{per atom}$.

![Graph of the % population of the isopropylidene torsional angles vs. the dihedral angle for PIES in CH$_2$Cl$_2$ as solvent.](image-url)
Figure 5.15. Graph of the % population of the ether torsional angles vs. the dihedral angle for PIES in CH$_2$Cl$_2$ as solvent.

Figure 5.16. Graph of the % population of the sulphone torsional angles vs. the dihedral angle for PIES in CH$_2$Cl$_2$ as solvent.
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Figure 5.17. G(r) plot of solvated PIES in CH$_2$Cl$_2$ solvent.

Figure 5.18. Graph of the non-normalised autocorrelation function of $\phi_1 \phi_1$ from the CH$_2$Cl$_2$ solvated NPT simulation at 300K.
5.3.3 Discussion

Once the MD simulation was underway, the energy of the system equilibrated, when the potential energy of the system fluctuated around -800 kcal/mol. This comprised of a very
low non-bonded energy value (-3500 kcal/mol) and a very high bonded energy value (2700 kcal/mol). The low non-bonded energy term was almost entirely due to VDW interactions, which involved solvent-polymer and solvent-solvent non-bonded interactions. There was some H-bonding present in the system (approximately -3 kcal/mol throughout the simulation). This was due to the opportunities for H-bonding to occur between the ether oxygens of the PIES oligomer and the hydrogen atoms of the surrounding DCM molecules. This was because both the PIES and DCM were charged and in close proximity to each other, due to the presence of 688 DCM molecules in the simulation.

A further study was made of the flexibility of the torsional linking groups present in the backbone of the oligomer, although the flexibility was likely to be hindered by the presence of nearby solvent molecules in the simulation. In solvent MD simulations, much of the time is spent simulating the solvent molecules, where they fluctuate around during the simulation. This is shown by the high self-diffusion coefficient of the simulation as compared to a non-solvated simulation under the same conditions but at higher temperature. Also the movement or flexibility of an individual linkage seems small because many solvent molecules need to be displaced before a moiety can overcome energy barriers and move to a different low energy dihedral conformation.

All the dihedral angle populations of the isopropylidene linkages were combined to give a tetramodal population plot (see figure 5.14) with values centred around -120°, -50°, 60° and 130° respectively. This gave four narrow population bands in the four lowest energy regions, which corresponded to the lowest energy plots from a potential energy vs. torsional angle plot. The movement of each individual dihedral angle was monitored and no 'flip' of the dihedral angle was observed. The energy barrier of 6 kcal/mol was too high for the isopropylidene angle moiety to overcome at the simulation temperature, due to the presence of all the solvent molecules. Displacement of many solvent molecules would be necessary to incur flipping of the isopropylidene linkage. However, should the simulation be run for a much longer time period, then ring flips might be observed, because they had been observed during the Tg simulation of PIES at 300K, (see section 5.4), although the result is not shown. An example of an isopropylidene ring flip, simulated in the bulk phase was obtained when two strands of PIES were simulated. This phenomenon is shown in figure 5.4.
Inspection of the ether torsional angle distribution in figure 5.15, shows a bimodal distribution centred around ±90°, which was in good agreement with other data obtained for this torsional angle linkage. Due to the fairly low simulation temperature and the influence of bulk and solvent conditions, there was little movement of the ether linkages throughout the simulation. There was however a slight fluctuation about their mean values and at the beginning of the simulation when the angles were seeking their optimum value. At this temperature of 300K, the ether linkages were 'locked' into position, i.e., in one or other of the two low energy torsional states, due to the H-bonding interaction between the DCM molecules and the PIES oligomer. The dihedral angles were unable to rotate freely at this temperature and consequently were unable to fluctuate between the two different lowest energy dihedral states.

Finally, looking at the sulphone torsional angle distribution in figure 5.16, this was still the most flexible linkage present in the system, although the movement was highly reduced compared with a non-solvated simulation. There was a bimodal distribution centred around ±90°, but there were two deviations centred around -20° and 160° respectively. However, there was again no jumping to different dihedral states for individual dihedral angles, instead they just fluctuated about the mean value. This was again due to the DCM molecules, where movement of the sulphone linkages was damped, compared with a non-solvated system, where transitions to and from the two low energy dihedral states were fairly common at a temperature of 300K. This shows that the solvent hindered movement of the sulphone linkages, either by the formation of H-bonds or just by its presence in the simulation. In this case, it would be necessary to displace many solvent molecules to allow the sulphone moiety to change dihedral states. The H-bonds could make it easier for sulphone linkages to pack together, as they would be changing dihedral states rather less than in a non-solvated case. However, much longer simulations are necessary to ascertain the nature of the packing and any degree of crystallisation of PIES in DCM as solvent.

The G(r) plot (figure 5.17) shows no order in the distribution of the polymer and the solvent. There was a mass of interactions around 0-3 Å gradually tailing off until the cut off point of 9 Å. Because of the number of interactions in the 0-1 Å range, where there should be none due to the length of VDW radii of the simulated atoms, the result showed that the system was not fully relaxed after the 50ps of MD simulation and as such should have been simulated for a longer simulation time. Instead any plot should have had its first peak at
approximately 1Å, the length of a C-H bond, with the rest of the plot beginning from that point. The plot showed though that there was no order in the solvent layers of DCM, unlike the order of the solvent layers shown in a G(r) plot of the simulation of water molecules. In a G(r) plots peaks at approximately 2.5Å and 6Å show up the order in the first and second layers of water in a simulation involving this solvent. Depner et al. modelled poly(oxyethylene) in benzene, showed that the first ordered layer of benzene molecules from a G(r) plot was between 5-6Å, and a G(r) plot of the oxygen atoms and the centre of mass of the benzene molecules, indicated that neither the gauche nor the trans positions of the neighbouring O-C-C-O torsional angles were preferred.

The self-diffusion constant at 300K (0.353Å²/ps/per atom) incorporating the solvent molecules was greater than D of PIES when simulated at 400K (0.113Å²/ps/per atom). This illustrated the mobility of the CH₂Cl₂ atoms, where D has increased by a factor of three, although the simulation temperature and the movement and the flexibility of the polymer chain has decreased. Depner et al. modelling poly(oxyethylene) in benzene at 300K, obtained D for the benzene molecules to be 0.31Å²/ps, whilst D for the polymer chain was 0.08Å²/ps. This showed the enhanced movement of the solvent molecules compared to the polymer chain. Lodge et al. modelled poly(styrene) and a number of poly(butadienes) in solvent near their Tg's and concluded that the presence of the polymer chain may be felt some significant number of solvent diameters (i.e., more than 2-3) away from the polymer chain. Furthermore, the polymer chain can have a substantial influence on the reorientational dynamics of the solvent molecules. Poly(styrene) was shown to slow down the relaxational mobility of the solvent, whereas poly(1,4-butadiene) accelerated solvent relaxation.

The correlation plots shown in figures 5.18 to 5.20 show the relaxation of the linkages over a period of approximately 50ps, where complete relaxation of the linkages has not occurred. Relaxation of the linkages takes longer in these MD simulations, due to the presence of the solvent molecules. It is more difficult to overcome the energy barriers to rotation in the short simulation time span due to the solvent molecules being present and consequently obtain low energy conformations of the structure. Although the energy of the system relaxed in a short time span, the structure of the polymer together with the solvent molecules were not relaxed fully. This was shown by the G(r) plot in figure 5.17, where there was a mass of interactions around the 0-3Å distance. The autocorrelation of φ1φ1 (figure 5.18) shows the
linkage relaxing over a period of 40ps. However, the autocorrelation function of $\phi_6\phi_6$ (figure 5.19) shows that the linkage had not relaxed after 50ps of MD simulation even though there was intense fluctuation of the linkage in the first few picoseconds of the simulation. The relaxation of both linkages was hindered by the lower simulation temperature and by the solvent molecules. The % population plot of the sulphone linkage (figure 5.16) showed two deviations at -20° and 160° indicating that the linkage was not fully relaxed at the end of the 50ps simulation. The cross-correlation plot of $\phi_3\phi_4$ (figure 5.20) shows the linkage relaxing over the time span of the simulation, unlike the linkage in the non-solvated simulation, which had not relaxed after 200ps of simulation. Clearly, in this case, the ether linkage found itself in a low energy conformation and as it was unable to change dihedral states due to the presence of H-bonding via the DCM molecules, it quickly relaxed into a stable, low energy structure.

5.4 Calculation of the physical and mechanical properties of poly(arylene ether sulphone)

In this section, some of the physical and mechanical properties of PIES were calculated. These include the $T_g$ of the PIES system via molecular simulation, the solubility parameter and various mechanical properties obtained from both the elastica module of POLYGRAF and from the theoretical calculations of Van Krevelen.

5.4.1 Calculation of the $T_g$ and the thermal expansion coefficients of poly(arylene ether sulphone)

A PIES trimer was built in the polymer module of POLYGRAF, using the oligomer as characterised in the previous chapter. Using this structure, 15 different PIES trimers were built in the amorphous builder at a temperature of 300K, with a density of 1.24gcm$^{-3}$ in a cubic cell of length 12.1Å. These 15 random, amorphous structures were examined and the 'best' structure was extracted for further use. Its periodic image was extended in the 'c' direction and tail-correction was performed, to take into account the end effects of the oligomer and so were less pronounced. In this scenario, 'best' means that when tail correction was performed, the two atoms joined, i.e., the head atom of the structure and the tail atom of the image were fairly close. With these two atoms being fairly close when they are joined, this effects the rest of the structure as little as possible, when minimisation was
performed on the structure. This procedure has been used by Takeuchi et al\textsuperscript{11,35} to minimise the end-effects of a poly(ethylene) chain. The structure was then minimised at constant volume until energy convergence was achieved (<0.01 kcal/mol).

Canonical dynamics - constant pressure and temperature (NPT) using the Nosé\textsuperscript{9} algorithm was performed on the system starting at 700K and finishing at 100K. The temperature was dropped by 100K every 250ps. The last monomer 'snapshot' at a particular temperature was extracted and used as the starting structure for the next temperature range. This large time period was used so that the volume of the system had a long time to equilibrate, to obtain an average volume at each temperature. The temperature was decreased rather than increased from 100K, so that various high energy transitions could be frozen out from the movement of the polymer.

After obtaining the trajectory files from the above experiments, at temperatures between 100 and 700K, the trajectory files were analysed to calculate the T\textsubscript{g}. This was performed from volume fluctuations at the various temperatures in which the polymer was simulated. At the beginning of each individual simulation, the structure, the volume and the PE of the system were equilibrating. The structure was trying to overcome any deviations which it may have possessed, \textit{i.e.,} VDW interactions and internal stresses, whilst from the MD simulation technique, the external heat sink used in the simulation needed time to equilibrate to its appropriate temperature. Consequently, the first 50ps of simulation were ignored and the calculations were performed using the remaining 200ps present.

The same formula was used to obtain the T\textsubscript{g} was the one used to obtain the volume thermal expansion coefficient (VTEC) of the polymer\textsuperscript{42}. From this, the linear thermal expansion coefficient (LTEC) was calculated. The LTEC is simply one third of the VTEC. The VTEC was obtained by finding \(\Delta V/V\) at a particular temperature where:

\[
V\text{TEC} = \frac{\Delta V}{V} = \frac{V - V_0}{V} \quad \text{eqn. 5.6}
\]

where \(V\) is the averaged volume at a particular temperature and \(V_0\) is the original volume.

The results for PIES (averaged over 200ps) with an initial volume of 1812.5 Å\textsuperscript{3} are shown in table 5.2.
Chapter 5: Modelling of poly(arylene ether sulphone) under bulk conditions

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Energy (kcal/mol)</th>
<th>Volume (Å³)</th>
<th>ΔV/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>80.4</td>
<td>1967.9</td>
<td>0.079</td>
</tr>
<tr>
<td>200</td>
<td>132.0</td>
<td>1998.7</td>
<td>0.093</td>
</tr>
<tr>
<td>300</td>
<td>186.9</td>
<td>2050.1</td>
<td>0.116</td>
</tr>
<tr>
<td>400</td>
<td>242.5</td>
<td>2062.5</td>
<td>0.121</td>
</tr>
<tr>
<td>500</td>
<td>280.5</td>
<td>2068.8</td>
<td>0.121</td>
</tr>
<tr>
<td>600</td>
<td>342.2</td>
<td>2206.23</td>
<td>0.178</td>
</tr>
<tr>
<td>700</td>
<td>384.6</td>
<td>2251.4</td>
<td>0.195</td>
</tr>
</tbody>
</table>

Table 5.2. Table of the energy, the volume and the change in volume (ΔV/V) values as used in the determination of the Tg of PIES.

These values from table 5.2 were plotted to obtain the Tg of the PIES as shown in figure 5.21.

![Graph of the Tg of PIES by MD simulation showing a Tg of 490K.](image)

Figure 5.21. Graph of the Tg of PIES by MD simulation showing a Tg of 490K.

From figure 5.21, the Tg of PIES was shown to be 490K (217°C), whilst the literature value was 468K (195°C). Using figure 5.21, the VTEC for both the glassy (αg) and liquid (αl) states were also calculated and from these results the LTEC was ascertained. These results are given in table 5.3.

Table 5.3. Table of the VTEC and the LTEC in the glassy and liquid states of PIES.

<table>
<thead>
<tr>
<th></th>
<th>VTEC</th>
<th>LTEC</th>
<th>Literature$^{44}$ (VTEC)</th>
<th>Literature$^{44}$ (LTEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_g$ (K$^{-1}$)</td>
<td>1.29x10$^{-4}$</td>
<td>4.30x10$^{-5}$</td>
<td>1.65x10$^{-4}$</td>
<td>5.50x10$^{-5}$</td>
</tr>
<tr>
<td>$\alpha_l$ (K$^{-1}$)</td>
<td>3.70x10$^{-4}$</td>
<td>1.23x10$^{-4}$</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

5.4.2 Calculation of cohesive energy and Hildebrand's solubility parameter

The cohesive energy is defined as 'the increase in the internal energy $U$ per mole of substance if all the intermolecular forces are eliminated'. The cohesive energy is calculated as follows.

$$E_{\text{cohesive}} = U_{\text{chain}} - U_{\text{bulk}}$$

where $U_{\text{chain}}$ is the energy of the polymer in the free state and $U_{\text{bulk}}$ is the energy of the polymer in the bulk. Hildebrand's solubility parameter ($\delta$) was obtained to quantify the solubility of polymers in solvents. It was introduced by Hildebrand in 1949$^{48}$, and is as follows.

$$\delta = \left( \frac{E_{\text{cohesive}}}{V_m} \right)^{1/2}$$

where $\delta$ is Hildebrand's solubility parameter and $V_m$ is the molar volume.

Using a MD simulation (NPT) of a PIES tetramer at 300K, the trajectory file was analysed for the 10 structures with the lowest energy. These were minimised with and without PBC to obtain the cohesive energy and also the solubility parameter. The cohesive energy was calculated to be 55.7±19.2kcal/mol, and the solubility parameter was 6.25±1.08cal$^{1/2}$cm$^{-3/2}$, compared to the literature value of 9.31cal$^{1/2}$cm$^{-3/2}$(48).
5.4.3 Calculation of the mechanical properties of poly(arylene ether sulphone) from the 'elastica' module

The trajectory files obtained from the T_g simulation of PIES were used to calculate the elastic constants of the polymer. This was possible because the simulation contained less than 200 atoms and consequently could be used in the elastica module\(^\text{^\textregistered}}\). The underlying theory of this process based on the work of Theodorou \textit{et al.}\(^\text{\textsuperscript{47}}\) together with the theory on the calculation of the elastic constants is given in chapter 6. The structures used were from the trajectories simulated at 300, 500 and 700K respectively. The ten lowest energy structures from each trajectory were extracted, minimised to energy convergence (<0.01 kcal/mol) and then placed into the elastica routine\(^\text{^\textregistered}}\). Typical results of the stiffness and compliance matrices are given in tables 5.4 and 5.5 respectively.

\[
\begin{pmatrix}
6.522 & 4.993 & 2.303 & -0.394 & 0.081 & -0.745 \\
4.993 & 8.543 & -1.825 & -0.594 & 1.165 & 0.001 \\
2.303 & -1.825 & 8.107 & 0.239 & 0.138 & -0.206 \\
-0.394 & -0.594 & 0.239 & 0.803 & 0.096 & -0.051 \\
0.081 & 1.165 & 0.138 & 0.096 & 1.741 & -0.212 \\
-0.745 & 0.001 & -0.206 & -0.051 & -0.212 & 1.833
\end{pmatrix}
\]

Table 5.4. Typical results of the stiffness matrix for PIES.

\[
\begin{pmatrix}
0.279 & -0.043 & -0.146 & 0.325 & 0.154 & 0.302 \\
-0.043 & 0.353 & -0.293 & 0.097 & -0.017 & -0.102 \\
-0.146 & -0.293 & 0.549 & -0.257 & -0.067 & -0.284 \\
0.325 & 0.097 & -0.257 & 1.587 & -0.610 & 0.600 \\
0.154 & 0.017 & -0.067 & 0.610 & 0.504 & 0.402 \\
0.302 & 0.102 & -0.284 & 0.600 & 0.402 & 0.617
\end{pmatrix}
\]

Table 5.5. Typical results of the compliance matrix for PIES.

The elastic constants were calculated from these matrices. Due to the low number of atoms simulated, the calculation was repeated many times to obtain averaged values for the elastic constants. These averaged results together with their standard deviations are given in table 5.6.
Chapter 5: Modelling of poly(arylene ether sulphone) under bulk conditions

### Table 5.6

<table>
<thead>
<tr>
<th>Property</th>
<th>Value by Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk modulus B (GPa)</td>
<td>4.23±2.14</td>
</tr>
<tr>
<td>Compressibility (GPa)</td>
<td>0.23±0.16</td>
</tr>
<tr>
<td>Poisson's Ratio $\nu$</td>
<td>0.44±0.14</td>
</tr>
<tr>
<td>Young's modulus E (GPa)</td>
<td>2.54±0.81</td>
</tr>
<tr>
<td>Lambda $\lambda$ (GPa)</td>
<td>3.83±1.76</td>
</tr>
<tr>
<td>Shear modulus G (GPa)</td>
<td>2.19±0.90</td>
</tr>
</tbody>
</table>

The table above is Table 5.6, which shows the elastic constants of PIES obtained from the 'elastica' module in POLYGRAF.

### 5.4.4 Properties of poly(arylene ether sulphone) from group contributions

In this section, various properties of PIES were obtained from the theoretical calculations of Van Kreveien. This is also known as group theory contributions where various structural units, e.g., phenyl rings, structural linking groups etc., are given constitutional values, which when summed together, give a theoretical prediction of various polymer properties. Different values are used to obtain different properties, in which properties such as density, $T_g$ and the various elastic constants can be predicted.

Properties obtained from this approach have already been calculated from molecular simulation, or can be compared with experimental results. The results are shown in Table 5.7 and the elastic properties are given in Table 5.8. Details explaining how these values were obtained are given in appendix 5.

### Table 5.7

<table>
<thead>
<tr>
<th>Property</th>
<th>Value by group contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $\rho$ (gcm$^{-3}$)</td>
<td>1.19</td>
</tr>
<tr>
<td>$T_g$ (K)</td>
<td>472.9</td>
</tr>
<tr>
<td>VTEC $\alpha_g$ (K$^{-1}$)</td>
<td>1.95x10$^{-4}$</td>
</tr>
<tr>
<td>VTEC $\alpha_l$ (K$^{-1}$)</td>
<td>4.23x10$^{-4}$</td>
</tr>
<tr>
<td>LTEC $\alpha_g$ (K$^{-1}$)</td>
<td>6.50x10$^{-5}$</td>
</tr>
<tr>
<td>LTEC $\alpha_l$ (K$^{-1}$)</td>
<td>1.41x10$^{-4}$</td>
</tr>
<tr>
<td>Cohesive energy $E_h$ (kcal/mol)</td>
<td>33.9$^\tau$</td>
</tr>
<tr>
<td>Solubility parameter $\delta$ (cal$^{1/2}$/cm$^{3/2}$)</td>
<td>9.53$^\tau$</td>
</tr>
</tbody>
</table>

Table 5.7 shows some of the properties of PIES as obtained from theoretical calculations$^1$, where $^\tau$ means that in that calculation, one of the contributions was estimated from other values.
Mechanical properties by Theoretical calculations

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk modulus B (GPa)</td>
<td>4.19</td>
</tr>
<tr>
<td>Compressibility $\beta$ (GPa)</td>
<td>0.24</td>
</tr>
<tr>
<td>Poisson's Ratio $\nu$</td>
<td>0.43</td>
</tr>
<tr>
<td>Young's modulus $E$ (GPa)</td>
<td>1.76</td>
</tr>
<tr>
<td>Lambda $\lambda$ (GPa)</td>
<td>3.78</td>
</tr>
<tr>
<td>Shear modulus $G$ (GPa)</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 5.8. Table of the elastic constants of PIES as obtained from theoretical calculations.

5.4.5 Discussion

The value of the $T_g$ of PIES from the two different methods, were 490K from the simulation technique, and from the theoretical calculation, the value was 472.9K. Both these values were in good agreement with the experimental value of 468K\textsuperscript{49}. The MD simulation took approximately 1000 hours (~6 weeks) of cpu time, whilst the theoretical calculation was performed within an hour. This clearly demonstrates the advantage of the theoretical approach, as the calculation was performed much more quickly. However, there are some disadvantages; namely that there were not values for all functional groups in the calculations considered, (in the $T_g$ case all the functional groups were present, but in other calculations, e.g., the solubility parameter calculation, some of the functional group values were missing). Furthermore, the method does not work for thermoset polymers. Consequently, only simulation can be used in thermoset polymer cases (see chapter 6) to calculate the $T_g$ and the various mechanical and physical properties of these systems. In the theoretical calculation, the result vindicated the use of the given values and clearly showed that each functional group considered has been parameterised well. Hopfinger et al.\textsuperscript{48} have combined molecular modelling and group contribution theory\textsuperscript{1} in which the $T_g$ was assumed to be a function of conformational entropy and mass moments of the polymer. These two molecular properties were estimated in terms of torsional angle units comprising the polymer backbone using conformational energy calculations. A universal $T_g$ equation was derived using 30 structurally diverse polymers. This theory has the advantage that it is not restricted by lack of group contribution theory parameters and takes advantage of three-dimensional molecular information, but it was necessary to develop 'designer' $T_g$ equations for acrylate and
methacrylate polymers. Finally, Carlier et al.\textsuperscript{49} have developed a simple method to predict the T\textsubscript{g}'s of poly(sulphones) and poly(ketones), by utilising the rigidity of the groups in the backbone of the polymer.

The model used to describe the simulated T\textsubscript{g} results, i.e., the PIES trimer and the Gasteiger charge also seems accurate, as the result was in good agreement with the literature value. This showed that after each stage of MD simulation at a particular temperature, the energy and the volume of the structure was fully relaxed. In this state the volume of the cell had plenty of time to relax, fluctuate and obtain an equilibrated value which gave rise to the accurate T\textsubscript{g} result. However, it would be possible to improve this result by increasing the number of repeat units in the backbone of the polymer and by repeating the calculation several times using different starting models. This would then give the result more credence, as an averaged value would be obtained, but with a larger usage of cpu time. However, the result clearly demonstrated that molecular modelling and in particular molecular simulation can be used for the prediction of T\textsubscript{g}.

The LTEC in the glassy (\(\alpha_g\)) and liquid states (\(\alpha_l\)) were obtained from the gradient of the slopes in the T\textsubscript{g} graph (see figure 5.21). These were 4.30\times10\textsuperscript{-5}K\textsuperscript{-1} and 1.23\times10\textsuperscript{-4}K\textsuperscript{-1} respectively, in which the \(\alpha_g\) value agreed well with the literature value of 5.50\times10\textsuperscript{-5}K\textsuperscript{-1}\textsuperscript{(44)}. The theoretical results gave values of 6.50\times10\textsuperscript{-5}K\textsuperscript{-1} and 1.41\times10\textsuperscript{-4}K\textsuperscript{-1} for \(\alpha_g\) and \(\alpha_l\) respectively. The value of \(\alpha_g\) value agrees well with the literature, whilst the \(\alpha_l\) value is similar to the simulated value. The result showed that the formula obtained by Van Krevelen\textsuperscript{1} to predict \(\alpha_g\) from the T\textsubscript{g} was accurate. Fan et al.\textsuperscript{42} simulated \(\alpha_g\) for UDEL poly(sulphone) using a much larger model of 12 repeat units and obtained a value of 7.20\times10\textsuperscript{-5}K\textsuperscript{-1}. It is interesting to note that the literature value is approximately midway between our value and the value obtained by Fan et al. Clearly their model described UDEL poly(sulphone) more accurately, in which they were at the upper limit of the \(\alpha_g\) value, whereas in our result, we were at the lower end of the \(\alpha_g\) value. This showed that a less accurate model can be used to obtain similar results, even though the results were at the lower end of the \(\alpha_g\) value.

The cohesive energy has been calculated by both simulation and theoretical methods. Because the value varies depending on the size of the polymer chain, it is not possible to compare with the experimental result. Instead the solubility parameter, which is normalised
by dividing by the molar volume, is a better method of comparison. However, the theoretical result should be treated with a certain amount of caution, because the value for the sulphone group was estimated from sulphur and oxygen contributions. This gave a result of 9.53cal$/cm^{32}$ for the theoretical result and a value of 6.25cal$/cm^{32}$ for the simulated result as compared to the experimental value of 9.3cal$/cm^{32}$. Unfortunately, not much of a comparison can be made between the two results, for reasons given above, although the simulated result is clearly not very accurate compared to the experimental value. This could be due to the small number of repeat units used, where the value of the non-bonded energy term was just not accurate enough, consequently lowering the simulated solubility parameter value. Theodorou et al.\textsuperscript{32} in their studies of atatic poly(propylene) calculated the solubility parameter from simulation to be 6.94cal$/cm^{32}$, which virtually agreed with the experimental value\textsuperscript{1} of 8.21cal$/cm^{32}$. Hutnik et al.\textsuperscript{29} modelled PC and obtained a solubility parameter of 9.48cal$/cm^{32}$, which was in excellent agreement with the experimental value of 9.92cal$/cm^{32}$. In both cases, a 'tail correction' factor was included in the $U_{\text{bulk}}$ term, in which an extra term was calculated, to give a better description of the non-bonded energy interactions, which had been splined in the minimisation stage. This factor made the results for both systems much more accurate, as compared to our simulated value. Ludovice et al.\textsuperscript{50} also modelled atatic poly(propylene) and calculated the solubility parameter from constant stress molecular dynamics (CSMD) at 275 and 500K to be 7.08 and 6.29cal$/cm^{32}$ respectively. The difference in these values came from the different thermal histories of the two samples. The solubility parameter obtained by minimising the initial structure was 7.56cal$/cm^{32}$ which was nearest to the literature value. This indicated that energetically the minimisation process produced a relatively relaxed structure. However, the high intramolecular energy of the sample, suggested a drastically different final structure, when compared with the structures obtained from minimisation followed by CSMD simulation. Boyd et al.\textsuperscript{24} in simulating the diffusion of penetrants through amorphous PIB, where there were 18 polymer chains of PIB containing 12 repeat units in a periodic cell of length 33Å, obtained the solubility parameter at a few temperatures. Extrapolation of the result to 298K gave a value of 7.9cal$/cm^{32}$. This agreed very well with the experimental results of 7.7-8.1cal$/cm^{32}$.

The density of the system, from theoretical calculations was either 1.19g/cm\textsuperscript{3} in the glassy state or 1.28g/cm\textsuperscript{3} in the rubbery state, whilst the experimental density was 1.24g/cm\textsuperscript{3}\textsuperscript{30}, which was the value used in the preceding MD simulations. Too much reliance should not
be placed on the theoretical value because the contribution to the volume of the sulphone group had to be taken individually from contributions both from a sulphur and ether groups, although the volume used would be about the correct value. When Fan et al.\textsuperscript{42} modelled the density of UDEL poly(sulphone), with a starting density of either 1.20 g cm\(^{-3}\) or 1.30 g cm\(^{-3}\), the resulting density in both cases was 1.17 g cm\(^{-3}\), and when modelling PC\textsuperscript{28}, with an initial starting density of either 1.20 g cm\(^{-3}\) or 1.40 g cm\(^{-3}\), the final simulated density was \(~\!1.18\text{ g cm}^{-3}\). This was in excellent agreement with the experimental value of 1.20 g cm\(^{-3}\).\textsuperscript{44} This showed that the MD algorithms were able to optimise the densities of structures even when the initial density was not necessarily the correct value. This became important (see chapter 6), where the density of the 6-ringed PIES dicyanate thermoset polymer was not known and had to be estimated when the polymer was created from the amorphous builder.

The mechanical properties of the system obtained from both simulation and theoretical calculations were generally in good agreement with experimental values. The main two elastic properties of interest, namely Young's modulus and Poisson's ratio have simulated values of 2.54 GPa and 0.44, whilst the theoretical values were 1.76 GPa and 0.43.

Experimental values from the literature were 2.69 GPa and 0.37 respectively\textsuperscript{44}. As the simulated results were similar to the experimental results, this showed that by performing a large number of simulations and averaging the results, accurate results were obtained, and that any anisotropic nature of the polymer was overcome. The only inaccurate value was the shear modulus, where the simulated value of 2.19 GPa, differed significantly from the literature value of 0.92 GPa\textsuperscript{44}. In general, the simulated results were at the maximum values possible for the polymer. These results showed that the parameterisation of the system \textit{via} the DreidingII force field was fairly accurate, which justified the reparameterisation of the sulphone linkage moiety. The results from the theoretical calculations were also in good agreement with the literature values, where all the results have been ascertained from the Bulk modulus result. This showed again that the parameters describing the various linkages present in the polymer have been described well. Poisson's ratio was ascertained from this result by using the intercept in a graph. Consequently the other elastic constants were calculated according to the equations given at the beginning of chapter 6. The theoretical results would have been even better if the literature value of Poisson's ratio had been used in the calculation.
Fan et al. have modelled UDEL poly(sulphone) to obtain the elastic constants. Their model contained ten repeat units and they produced their results by averaging the results of 10 structures into one stiffness matrix, before obtaining the elastic constant results. Their simulated results were accurate, with errors between 20-40%, when the Young's, Bulk and Shear moduli were 3.88, 3.02 and 1.60 GPa respectively. Their results were also consistently higher than experimental values, although the Poisson's ratio result of 0.24 was surprisingly low. They concluded that the difference in results might result from the idealised interactions between atoms and molecules, forcing the results to be higher than the experimental values. Both Fan et al. and Hutnik et al. modelled the elastic constants of PC, and obtained results which were greater than their experimental equivalent. These results and other work, which describe the results of the simulation of elastic constants for other polymeric systems by various methodologies are discussed at the end of chapter 6.

5.5 Conclusions

In this chapter, the MD simulations gave a good description of the PIES system. The isopropylidene ring flips, the % population plots centred around the lowest energy conformations of the particular torsional angles and the G(r) plot describe the structure of the PIES very well. The self-diffusion constant indicated increased movement of the polymer at higher temperatures. Only the lower temperature simulation using NVT MD showed a slight anomaly in the % population results. In general, the % population results obtained from modelling PIES under bulk conditions were in good agreement with results from the simulation of a PIES oligomer in a vacuum and from the crystal data results from chapter 4. In general, despite the fact that the bulk simulated results were more diffuse and spread over a larger torsional range, they nevertheless occupied the same lowest energy torsional values as the PIES oligomer, when simulated in a vacuum.

The results of the mechanical and physical properties of the polymer, either from simulation or from theoretical calculations, agreed well with the literature values. This showed that the model used to describe the simulated polymer, which was used to obtain the \( T_g \) was accurate, in which the polymer was in a relaxed and low energy state. The measured \( T_g \) (217°C) agreed well with the simulated value, being only 20°C higher than the experimental value. The calculated thermal expansion coefficients were accurate as well, with \( \alpha_g \) being 4.30x10^{-5} K^{-1} whilst the literature value was 5.50x10^{-5} K^{-1}, but unfortunately the \( \alpha_l \) of
3.70x10^{-4} \text{K}^{-1} \text{ could not be compared to a literature value. The elastic constants obtained from the same model were also very accurate. The Young's modulus and Poisson's ratio only deviated by 6 and 15\% when the results were averaged, which was within the error which Theodorou et al.\textsuperscript{47} obtained in their original modelling study of the elastic constants of atactic poly(propylene) in 1986. The results calculated from the group theory contributions of Van Krevelen\textsuperscript{1} gave good results with the mechanical properties and the T_g results particular good. This shows that if a linkage or grouping was present in the parameter tables, then for a particular polymeric system accurate results could be calculated.}

A simulation of PIES in DCM was also performed, in which the time period of the simulation was insufficient to obtain any conclusive results concerning the simulation of the polymer in the solvent. The results showed that the polymer was less mobile in the solvent as the \% population plots had narrower dihedral ranges. However, they were still positioned in the lowest energy conformations of the dihedral angles. The self-diffusion constant was high, which indicated a lot of movement of the DCM solvent molecules. The correlation plots of the linking groups together with the G(r) plot illustrated that the time period of the simulation (~50ps) was not long enough to obtain a relaxed structure of the polymer. However, simulation of the non-solvated system showed that the linkages were generally relaxed after 50ps of MD simulation.

After modelling the thermoplastic PIES under bulk conditions and obtained various conformational, physical and mechanical properties, e.g., the T_g and the elastic constants, the final stage of this thesis was to model various properties of a thermoset polymer. This polymer was formed when the repeat unit of the poly(arylene ether sulphone) dicyanate ester oligomer was cured, i.e., a thermoset polycyanurate with a 6-ringed poly(arylene ether sulphone) backbone as synthesised and characterised in chapter 2.

5.6 References

3 Molecular Simulations Inc. 16 New England, Executive Park, Burlington, MA 01803-5297.


40 Elastica module in Professional POLYGRAF (3.2.1) manual, page EL1-EL8 (1993).


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Chapter 6: Modelling of cyanurate ring thermoset polymers

6.1 Introduction

The thermoplastic polymer, poly(arylene ether sulphone) (PIES) was modelled using bulk modelling techniques, described in the previous chapter. From these calculations various mechanical and physical properties of this polymer were obtained. Bulk modelling studies of two thermoset cyanate ester polymers was performed in this chapter. The polymers modelled were the same two polymers which were synthesised and characterised in chapter 2 - namely the bisphenol-A dicyanate polymer (BPADC) and a 6-ringed poly(arylene ether sulphone) dicyanate polymer (6-ringed PIES dicyanate). These were both modelled using the elastica module\(^1\), using the professional POLYGRAF molecular modelling software package. The results of this modelling will be discussed and compared with the experimental results derived in chapter 2 and with the results of other polymer simulations on mechanical properties obtained from the literature. Furthermore, the \(T_g\) of the 6-ringed PIES dicyanate polymer, together with the thermal expansion coefficients were calculated from molecular simulation. These will also be compared with other \(T_g\) simulations found in the literature.

6.2 The elastica module

The elastica module\(^1\) in professional POLYGRAF was used to obtain various mechanical properties of the polymers under consideration. This module has an atom limit of 200 atoms, because a second derivative energy minimisation, which needs to be calculated is computationally very expensive and dependent on the memory limits of the machine. Due to the limited number of atoms available for analysis, a large number of similar simulations were performed, to obtain an average result of the systems. The underlying theory behind the process will be discussed first, followed by a discussion of the modelling methods and the results obtained from this work.

6.2.1 The theory behind the elastica module

The mechanical properties of a polymeric material can be calculated after an initial energy minimisation, followed by a second derivative energy minimisation calculation under a small fixed strain. The expression used to calculate the potential energy of the system, under a small strain is as follows:
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\[ U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial U^2}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j + \ldots + \frac{1}{n} \sum_{ij} \frac{\partial U^n}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j \]  

\text{eqn. 6.1}

where \( U \) is the energy, \( U_0 \) is the equilibrium energy, and \( \varepsilon \) is the strain. The second derivative of the energy is used to calculate the components \( C_{ij} \) of the stiffness matrix, where the stiffness matrix is related to the energy by:

\[ C_{ij} = \left( \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \right) / V \]

\text{eqn. 6.2}

where \( C_{ij} \) is the stiffness matrix, \( U \) is the total energy, \( V \) is the volume and \( \varepsilon_i \) and \( \varepsilon_j \) are the strain applied to the system. Theodorou et al.\(^2\)\(^3\) having modelled glassy atactic poly(propylene), have shown that this stress method for calculating mechanical properties of polymeric glasses was within 15% of experimental values. They obtained a Young's modulus of 2.79GPa, whereas the experimental value was 2.65GPa\(^2\). In this stress method for calculating the elastic constants, very small strains were applied to the system, in which case there was a corresponding change in each strain component. Because of the strain-energy function, and the fact that Theodorou et al.\(^2\) were dealing with an isotropic material, \textit{i.e.}, poly(propylene), there is a relationship \( C_{ij} = C_{ji} \) with \( C_{ij} \) being the stiffness matrix. From these relationships, an isotropic stiffness matrix can be obtained. The compliance matrix is the inverse of the stiffness matrix. The elastic constants of interest can be calculated from these matrices (see section 6.2 for further details on the elastic constants and method of calculation from these two matrices).

The stiffness matrix is defined as follows:

\[ C_{ij} = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{pmatrix} \]

\text{eqn. 6.3}
The stiffness matrix, written in terms of the two Lamé constants ($\mu$ and $\lambda$) (see section 6.2.6) in terms of an isotropic material is as follows:

$$C_{ij} = \begin{pmatrix}
2\mu + \lambda & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & 2\mu + \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & 2\mu + \lambda & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu \\
\end{pmatrix} \text{ eqn. 6.4}$$

whilst the compliance matrix, which is the inverse of the stiffness matrix, for an isotropic material is as follows:

$$S_{ij} = \begin{pmatrix}
S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{22} & S_{12} & 0 & 0 & 0 \\
S_{12} & S_{12} & S_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 & 0 \\
0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 \\
0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \\
\end{pmatrix} \text{ eqn. 6.5}$$

The mechanical properties of a polymer can be calculated from the above matrices. These are the Young's modulus, Poisson's ratio, Bulk modulus, Shear modulus and the Lamé constants. Their derivation from both experiment and theory is given below.
6.2.2 Young's modulus

The Young's modulus \( E \) of a material is the strain \( \varepsilon \) per unit length, when a force \( F \) per unit cross-sectional area \( A \), i.e., the stress \( \sigma \) is applied.

![Schematic of Young's modulus](image)

**Figure 6.1.** Schematic of the operation of Young's modulus on a material.

\[
E = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta L/L_0}
\]

where \( E \) is the Young's modulus, \( \sigma \) is the stress, \( \varepsilon \) is the strain, \( F \) is the force applied, \( A \) is the cross-sectional area, \( \Delta L \) is the change in length and \( L_0 \) is the original length.

Three values for the Young's modulus can be found from the compliance matrix for the three directions under consideration, i.e., \( x \), \( y \) and \( z \) directions, but for an isotropic system all three values are expected to be the same.

\[
E_x = \frac{1}{S_{11}}, \quad E_y = \frac{1}{S_{22}}, \quad E_z = \frac{1}{S_{33}}
\]

**eqn. 6.7**
6.2.3 Poisson's ratio

Poisson's ratio (\(\nu\)) of a material is obtained when a uniaxial tensile force (\(F\)) is applied to a material. There is a change in the length per unit length, in addition to a corresponding change in the width per unit width of the material. This process is also known as necking.

\[
\nu = \frac{\Delta W / W_0}{\Delta L / L_0} = \frac{-\varepsilon_t}{\varepsilon_l}
\]

where \(\nu\) is the Poisson's ratio, \(\Delta W\) is the change in width, \(W_0\) is the original width, \(\Delta L\) is the change in length, \(L_0\) is the original length, \(\varepsilon_l\) is the longitudinal strain and \(\varepsilon_t\) is the transverse strain.

The compliance matrix gives Poisson's ratio in its different directions in space as:

\[
v_{xy} = -\frac{S_{21}}{S_{11}}, \quad v_{yx} = -\frac{S_{21}}{S_{22}}, \quad v_{zx} = -\frac{S_{31}}{S_{33}}
\]

\[
v_{xz} = -\frac{S_{31}}{S_{11}}, \quad v_{zx} = -\frac{S_{32}}{S_{22}}, \quad v_{yy} = -\frac{S_{22}}{S_{33}}
\]
6.2.4 Bulk modulus

The Bulk modulus \( (B) \) is the volume change per unit volume when an hydrostatic pressure \( (P) \) is applied to a material.

\[
\text{Figure 6.3. Schematic of the operation of bulk modulus on a material.}
\]

\[
B = \frac{pV_o}{\Delta V}
\]

where \( V_o \) is the original volume and \( V \) is the volume after the deformation force \( F \) has been applied. This force can be expressed as the external pressure \( p \). \( \Delta V \) is the volume change.

The compliance matrix gives the bulk modulus as:

\[
B = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{21} + S_{31} + S_{32})}
\]

eqn. 6.11
6.2.5 Shear modulus

The shear modulus \( G \) is the shear force per unit distance \( d \) between shearing surfaces, when a force \( F \) per unit cross-sectional area \( A \) is applied to a material.

![Schematic of the operation of shear modulus on a material.](image)

**Figure 6.4.** Schematic of the operation of shear modulus on a material.

\[
G = \frac{F/A}{s/d} = \frac{F/A}{\tan \gamma} = \frac{\tau}{\tan \gamma}
\]

where \( G \) is the shear modulus, \( F \) is the applied shear force, \( A \) is the cross-sectional area, \( d \) is the length and \( s \) is the shear length.

The compliance and stiffness matrices give the shear modulus as:

\[
G = \frac{1}{2} (S_{11} - S_{12}) = \frac{1}{2} (C_{44} + C_{55} + C_{66})
\]

6.2.6 Lamé constants

Two Lamé constants can be calculated. First, the constant \( \mu \), which is related to the more common shear modulus \( G \).

\[
\mu = G = \frac{E}{2(1 + \nu)}
\]

where \( E \) is the Young's modulus and \( \nu \) is the Poisson's ratio.

Second, the Lamé constant \( \lambda \), which has no direct physical meaning and applies only to isotropic materials.
\[
\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)} \quad \text{eqn. 6.15}
\]

From the stiffness matrix, the Lamé constant \( \lambda \), is as follows:

\[
\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}) \quad \text{eqn. 6.16}
\]

The elastic constants above are interrelated by the equation below.

\[
E = 2G(1+\nu) = 3B(1-2\nu) \quad \text{eqn. 6.17}
\]

In most cases, it is sufficient to determine two elastic constants as the others can be obtained from equation 6.17. The volume compressibility \( \beta \), which is the inverse of the bulk modulus is another elastic constant which can be calculated.

### 6.3 Modelling of a bisphenol-A dicyanate polymer network

After having obtained the elastic constants of the BPADC thermoset polymer by experimental characterisation techniques (chapter 2.4), these values were also calculated by molecular simulation techniques. As the elastic module was limited to 200 atoms, which clearly is not excessive, many different structures of the polymer were produced and simulated by molecular dynamics (MD). These results were then analysed so that they could be averaged to produce the simulated elastic constants.

#### 6.3.1 Method

The BPADC polymer was built, using the crystal data and the results from section 4.5, on the modelling of the cyanurate ring linkage. One of the terminal methyl groups was removed and the segment joined to another phenyl ring. The other two arms from the \( \pi \)-triazine ring were also removed. This process gave a repeat unit shown in figure 6.5.
Chapter 6: Modelling of cyanurate ring thermoset polymers

Figure 6.5. The repeat unit of the BPADC oligomer, as used in the POLYGRAF package to model the network structure. The hydrogen tail atoms are removed and the head atom of the next oligomer joins at this point, so that the polymer can grow into a 3-D polymer network structure.

The structure was given an *head* and two *tails*, so when polymerised, the polymer would be built correctly. This takes place by removal of the tail atoms, which are replaced by the head atom. Five repeat units can then be attached, before the 200 atom limit is exceeded. Partial atomic charges were assigned to the structure using the Gasteiger method. From this modelled structure, 15 random structures of the polymer were built in the amorphous builder of POLYGRAF, using a density of 1.26 at 300K. The Monte Carlo (MC) technique was chosen to build the random structures, (for details on the MC technique, see section 5.2.1), to produce polymers with periodic boundary conditions (PBC), having a cell length of 12.95Å. These 15 random structures were examined, and the 'best' six were chosen to have their PBC extended. Tail-correction was carefully used to join the simulated cell to the imaginary cells, to simulate the bulk thermsoset nature of the polymer. In the above, 'best' related to the structures of the 15 random polymers produced, where it was the easiest to perform tail-correction on the structure. This means that the head atom of the structure and the tail of the image were as close to each other as possible before joining, to avoid major disruption of the rest of the polymer structure, when minimisation was performed on the structure. These structures were then minimised using the conjugate-gradients algorithm (this algorithm was used exclusively to minimise the structures in this chapter) to energy convergence (<0.01kcal/mol). Constant volume conditions were used to remove any close VDW contacts and to give low energy structures of the polymer.

Constant pressure MD simulations (NPT), using the Nosé algorithm at temperatures of either 300 or 400K, were performed on the six model random polymers for a time period of 100ps. In these time spans, there was plenty of time for the polymers to adopt many different low energy conformations of the BPADC polymer network. This was achieved by
removing any close VDW contacts that might have occurred when building the structures in the amorphous builder and which might not have been removed from the energy minimisation stage. From these six trajectory files, the six lowest energy structures were extracted from each trajectory file. These were generally in the latter half of the trajectory file. Their PBC were unextended, so that only the original cell and the structure remained, which was energy minimised once again before being placed into the elastica module.

During the MD stage, the structure moved away from its cubic shape to an anisotropic form. In the elastica module, the 'triclinic' function was used to calculate the elastic properties, to take into account the anisotropic nature of the periodic cell. In order to keep the structures very close to an isotropic state, a far greater detailed model of the BPADC polymer would be necessary. Clearly, this was beyond the limits of the program. The module calculated the elastic constants as if the structure was in a vacuum at 0K. The MD simulation was only performed to produce many different low energy conformers of the BPADC polymer, which were extracted and placed into the elastica module.

6.3.2 Results

The results for the elastic constants were compiled from the 36 structures which were obtained from the MD simulation. Typical results for the stiffness and compliance matrices are given in tables 6.1 and 6.2 respectively. The values which were not zero in the corners of the compliance matrix, showed that the structure was in an anisotropic state. Other authors working on the elastic constants of bisphenol-A poly(carbonate) (PC) obtained a fairly isotropic stiffness matrix, by averaging their results from six simulated structures. This gave just one stiffness matrix from which the elastic constants were obtained.

\[
C_y = \begin{pmatrix}
6.632 & 3.470 & 4.993 & 0.475 & -0.546 & -0.086 \\
3.470 & 9.548 & 5.041 & 1.288 & -0.843 & 0.245 \\
4.993 & 5.041 & 9.007 & -0.081 & -1.796 & -0.334 \\
0.475 & 1.288 & -0.081 & 2.483 & -0.171 & 0.006 \\
-0.546 & -0.843 & -1.796 & -0.171 & 1.147 & -0.298 \\
-0.086 & 0.245 & -0.334 & 0.006 & -0.298 & 1.186 \\
\end{pmatrix}
\]

Table 6.1. Typical results of the stiffness matrix for BPADC.
Table 6.2. Typical results of the compliance matrix for BPADC.

\[
S_y = \begin{pmatrix}
0.180 & -0.039 & -0.077 & -0.021 & 0.119 & -0.013 \\
-0.039 & 0.184 & -0.070 & -0.178 & -0.059 & -0.114 \\
-0.077 & -0.070 & 0.244 & 0.108 & 0.033 & -0.021 \\
-0.021 & -0.178 & 0.108 & 0.921 & 0.088 & -0.074 \\
0.119 & 0.059 & 0.033 & 0.088 & 0.892 & -0.132 \\
-0.013 & -0.114 & 0.021 & -0.074 & -0.132 & 1.458
\end{pmatrix}
\]

The averaged results for the BPADC polymer together with their standard deviations are given in table 6.3.

<table>
<thead>
<tr>
<th>Mechanical properties of BPADC by simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus E (GPa)</td>
</tr>
<tr>
<td>Poisson's Ratio ν</td>
</tr>
<tr>
<td>Bulk Modulus B (GPa)</td>
</tr>
<tr>
<td>Compressibility β (GPa)</td>
</tr>
<tr>
<td>Shear Modulus G (GPa)</td>
</tr>
<tr>
<td>Lambda λ (GPa)</td>
</tr>
</tbody>
</table>

Table 6.3. The mechanical properties of the BPADC polymer as obtained from molecular simulation which were obtained from the *elastica* module which is incorporated in the POLYGRAF modelling package.

### 6.4 Modelling of a 6-ringed poly(arylene ether sulphone) dicyanate network

The elastic properties of the 6-ringed PIEX dicyanate polymer, as synthesised and cured in chapter 2.3 and 2.5 were also obtained from molecular simulation. A similar modelling method was employed to the one which was used when BPADC was modelled. As in the case of the results calculated from modelling BPADC, these properties were compared to those of experimental data in section 6.6.
6.4.1 Method

The repeat unit used to build the 6-ringed PIES dicyanate network is shown in figure 6.6.

This was built by simply using the repeat unit used in section 4.2, adding on a bisphenol-A type moiety and a 5-triazine ring unit. Partial atomic charges were added to the structure via the Gasteiger charge method, and the structure was given one head and two tails, to enable the network polymer to be formed from the resulting repeat unit.

\[
\begin{align*}
&\text{O}-(\quad)\text{-O}\quad(\quad)-\text{O}-(\quad)\text{-N}^+ \\
&\text{where } h \text{ is the head atom and } t \text{ are the tail atoms}
\end{align*}
\]

Figure 6.6. The repeat unit of the 6-ringed PIES dicyanate oligomer, as used in the POLYGRAF package to model the network structure. The hydrogen tail atoms are removed and the head atom of the next oligomer joins at this point, so the polymer can grow into a 3-D polymer network structure.

In this scenario, it was only possible to use 2 repeat units before the 200 atom limit was passed. Consequently, many different models of the polymer were produced to give an average structure for the network, using a combination of PBC, tail-correction and different starting structures of the network. The method used to prepare the structure was based on the one used for the BPADC networked polymer, with a few adjustments. First, the density was reduced to 1.20 g/cm$^3$. It was felt that this structure would have a lower density than BPADC because of the lower cross-link density of the structure, due to its longer repeat unit. Throughout the MD simulation, the density of the structure was in a constant state of equilibrium, which was altered accordingly as necessary by the modelling package. This phenomenon has been demonstrated by the work of Fan et al., who obtained a simulated density of 1.17 g/cm$^3$, for an amorphous poly(sulphone), when the starting density was set at either 1.20 or 1.30 g/cm$^3$ respectively. This showed that even if the starting density was not quite correct, the modelling package was able to optimise the density to a more appropriate value. Second, the size of the periodic cell obtained from the amorphous builder was 15.1 Å. The six 'best' structures were then extracted and had their PBC extended. Tail-correction was then performed on the head and tail atoms to give a better description of the networked thermoset polymer. These structures were then energy minimised under constant volume conditions. MD simulations using the Nosé algorithm were performed at constant pressure.
and temperature (NPT) at either 300 or 400K for the six minimised structures. The simulations lasted for 100ps when the six lowest energy structures from each of the newly produced trajectory files were extracted, so they could be placed through the *elastica* module. Again, the PBC were unextended and then the structure was minimised, before calculating the elastic properties *via* the *elastica* module.

### 6.4.2 Results

The results of the elastic constants from the 36 structures were averaged and placed in table 6.6. The results of a typical stiffness and compliance matrix for the 6-ringed PIES dicyanate polymer network are shown in tables 6.4 and 6.5 respectively.

\[
C_{ij} = \begin{pmatrix}
1.841 & 1.353 & 2.779 & -0.190 & 0.227 & -0.479 \\
1.353 & 3.529 & 1.880 & 0.108 & -0.049 & -0.249 \\
2.779 & 1.880 & 2.172 & 0.796 & 0.646 & 0.592 \\
-0.190 & 0.108 & 0.796 & 0.538 & -0.260 & -0.101 \\
0.227 & -0.049 & 0.646 & -0.260 & 0.570 & 1.465 \\
-0.479 & -0.249 & 0.592 & -0.101 & 1.465 & 0.885
\end{pmatrix}
\]

**Table 6.4.** Typical results of the stiffness matrix for the 6-ringed PIES dicyanate.

\[
S_{ij} = \begin{pmatrix}
0.327 & -0.141 & -0.070 & -0.038 & 0.123 & 0.140 \\
-0.141 & 0.570 & -0.094 & 0.117 & -0.003 & 0.228 \\
-0.070 & -0.094 & 0.149 & 0.052 & 0.007 & 0.128 \\
-0.038 & 0.117 & 0.052 & 0.504 & 0.259 & 0.433 \\
0.123 & -0.003 & 0.007 & 0.259 & -0.193 & -0.102 \\
0.140 & 0.228 & 0.128 & 0.433 & -0.102 & 1.067
\end{pmatrix}
\]

**Table 6.5.** Typical results of the compliance matrix for the 6-ringed PIES dicyanate.
Table 6.6. The mechanical properties of a 6-ringed PIES dicyanate polymer obtained from molecular simulation, which were calculated from the \textit{elastica} module in the POLYGRAF modelling package.

6.5 Modelling the \(T_g\) of a 6-ringed poly(arylene ether sulphone) dicyanate network

Having obtained some mechanical properties of the 6-ringed PIES dicyanate network in the previous section, the \(T_g\) of the polymer was also obtained by molecular simulation. A series of MD calculations were performed at various temperatures and the volume fluctuations of the periodic box were obtained. From these fluctuations, the \(T_g\) and the volume thermal expansion coefficient were calculated, as given from the formula (eqn. 5.6) from section 5.4.1.

6.5.1 Method

The method used to build the model was similar to that of the previous section (6.4.1), except that a larger model was used, because there were no constraints on the size of the model from the computer. The only 'real' constraint was the length of the simulation considering all the different temperatures used in the study of the system. Consequently, a model containing 6 repeat units (see picture 6.1) was used to simulate the polymer, using the repeat unit as shown in figure 6.6. Once again Gasteiger partial charges were assigned to the atoms. The MC technique was used to build the amorphous cell, using an initial density of 1.20gcm\(^{-3}\) at a temperature of 300K. The cell length was 17.1Å, which gave a starting volume of 4983.6Å\(^3\). Ten different starting models of the polymer were obtained from the amorphous builder. The model with the 'best' starting structure was chosen to have its PBC extended to 26 image cells and have tail-correction performed, to give a structure which gave the best description of the thermoset network of the polymer.
Picture 6.1. Model of the 6-ringed PES dicyanate used in the Tg simulation
The structure was minimised to energy convergence of <0.01 kcal/mol using a constant volume algorithm. Having obtained a low energy starting configuration, canonical MD (NPT) was performed using the Nosé algorithm. The starting temperature was 800K. This temperature was chosen as it was clearly an high temperature and is assumed to be a much greater temperature than the actual \( T_g \). All the simulations lasted for up to 250ps or until the volume was fairly constant for approximately 50ps. The last structure was extracted from the trajectory, to start the next simulation at 100K lower than the previous temperature. This was repeated until the final simulation was performed at a temperature of 100K. The temperature was ramped downwards, to enable high energy molecular transitions to be frozen out. The volume and energy fluctuations were monitored carefully throughout the whole of the simulation. Generally, the energy equilibrated quickly, generally within 25ps, whereas the volume often took longer to reach equilibrium. Consequently, when obtaining the average volume at each simulation temperature, the first 50ps of the simulation was ignored, assuming that the volume was equilibrating in this time period.

### 6.5.2 Results

The results of the average energy and volume at the particular temperatures for the polymer simulations are given in table 6.7. The starting structure had a volume \( V_0 \) of 4983.6Å and an energy of 760.2kcal/mol. The theory of the \( T_g \) and the thermal expansion coefficients calculations by molecular simulation is given in section 5.4.1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Energy (kcal/mol)</th>
<th>Volume (Å³)</th>
<th>( \Delta V/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>807.4</td>
<td>5626.9</td>
<td>0.114</td>
</tr>
<tr>
<td>200</td>
<td>899.6</td>
<td>5884.9</td>
<td>0.153</td>
</tr>
<tr>
<td>300</td>
<td>1030.4</td>
<td>5798.2</td>
<td>0.140</td>
</tr>
<tr>
<td>400</td>
<td>1035.2</td>
<td>6217.3</td>
<td>0.185</td>
</tr>
<tr>
<td>500</td>
<td>1338.7</td>
<td>6424.3</td>
<td>0.204</td>
</tr>
<tr>
<td>600</td>
<td>1343.2</td>
<td>6283.3</td>
<td>0.207</td>
</tr>
<tr>
<td>700</td>
<td>1630.9</td>
<td>6525.5</td>
<td>0.236</td>
</tr>
<tr>
<td>800</td>
<td>1790.8</td>
<td>7093.1</td>
<td>0.297</td>
</tr>
</tbody>
</table>

Table 6.7. The average energies, volume and the change in volume \( (\Delta V/V) \) of the 6-ringed PES dicyanate network structure used in ascertaining the \( T_g \) of the polymer.
The $T_g$ and the various thermal expansion coefficients are obtained by plotting the values given in Table 6.7 (see Figures 6.7 and 6.8).

![Graph of $\Delta V/V$ vs. temperature for the 6-ringed PIES dicyanate, showing the $T_g$ point at 490K (217°C).](image1)

![Graph of the total energy $V$ vs. temperature for the 6-ringed PIES dicyanate, showing the $T_g$ point at 495K (222°C).](image2)

Figures 6.7 and 6.8 show the $T_g$ to be 490K (217°C) and 495K (222°C) respectively.

The volume thermal expansion coefficient (VTEC) and consequently the linear thermal
expansion coefficient (LTEC) were obtained from the gradients in figure 6.7. This gave from the two gradients, both the thermal expansion coefficients, \( \alpha_g \) and \( \alpha_l \) in the glassy and liquid states respectively.

<table>
<thead>
<tr>
<th>Simulation results (K(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>VTEC ( \alpha_g )</td>
<td>1.89x10(^{-4})</td>
</tr>
<tr>
<td>( \alpha_l )</td>
<td>3.09x10(^{-4})</td>
</tr>
<tr>
<td>LTEC ( \alpha_g )</td>
<td>6.29x10(^{-5})</td>
</tr>
<tr>
<td>( \alpha_l )</td>
<td>1.03x10(^{-4})</td>
</tr>
</tbody>
</table>

Table 6.8. Table of the thermal expansion coefficients obtained from molecular simulation for the 6-ringed PIES dicyanate polymer network.

### 6.6 Comparison of the modelling with the experimental results

After having obtained various mechanical and physical data via experimental and simulation techniques, for both the BPADC polymer and the 6-ringed PIES dicyanate polymer, the results were compared. Reasons for similarities and differences between the results from simulation and practical work were considered. In the calculation of the elastic properties, there are differences between the experimental and simulation techniques. In the simulation case, the final mechanical results were obtained in a vacuum and at a temperature of 0K. But experimentally, the results were obtained at room temperature ~295K. Therefore, no account of thermal motion was incorporated into the model to describe the structure. Another major problem was the limit of 200 atoms, although the *elastica* module does take PBC into consideration. Consequently the polymer structure becomes an idealised model. There were also small amounts of catalyst and diluent solvent remaining in the 'real' polymer, which also contained tiny air pockets, voids, cracks and abrasions on the polymer. These phenomena are not included in the model used to describe the thermoset polymer. Despite this, the similarity between the mechanical properties for both polymers via the two different techniques is encouraging. Finally, the \( T_g \) simulation of the 6-ringed PIES dicyanate network gave a value of 217°C, which is approximately 80°C higher than the experimental value of 140°C. However, the result for the simulated linear glassy expansion coefficient (6.29x10\(^{-5}\)K\(^{-1}\)) correlated well with the experimental value (7.52x10\(^{-5}\)K\(^{-1}\)).
6.6.1 Bisphenol-A dicyanate results

Table 6.9 shows the elastic constants obtained for the BPADC polymer network, using both simulation and practical techniques. Examination of the results shows a similarity between the values of the elastic constants, although the standard deviations for the simulated results were much larger. This was due to the large number of 'models' which were constructed to obtain the elastic constants. This was overcome by averaging many results which led to quite large standard deviations. Ideally, an isotropic model should be built. However, there is a probability of building a model which displays some anisotropic nature, due to the atom limit in the simulation, in spite of relaxing the structure via MD simulations. Therefore, the elastic constants of the different models vary according to the degree on anisotropy. Consequently, by having many models of the system, the anisotropic nature of the models is largely overcome, although the standard deviations are large as a result of this process. Conversely, the standard deviations of the experimental results were very much smaller, due to the purity, void free nature and isotropic nature of the samples which were used in the mechanical tests.

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>BPADC by Experiment</th>
<th>BPADC by Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus E (GPa)</td>
<td>3.39 ± 0.16</td>
<td>4.04 ± 2.14</td>
</tr>
<tr>
<td>Poisson's Ratio ν</td>
<td>0.35 ± 0.01</td>
<td>0.39 ± 0.13</td>
</tr>
<tr>
<td>Bulk modulus B (GPa)</td>
<td>3.79 ± 0.28</td>
<td>3.89 ± 2.04</td>
</tr>
<tr>
<td>Shear Modulus G (GPa)</td>
<td>1.25 ± 0.05</td>
<td>1.28 ± 0.75</td>
</tr>
<tr>
<td>Lambda λ (GPa)</td>
<td>2.95 ± 0.25</td>
<td>4.32 ± 2.17</td>
</tr>
</tbody>
</table>

Table 6.9. Table of the elastic constants for the BPADC polymer network from experimental and simulation studies.

The Lamé constant λ was the only elastic constant to be appreciably over the 15% error margin as mentioned by Theodorou², when atactic poly(propylene) was modelled. This constant has no direct physical meaning, and is generally only applied to isotropic materials, so it is not surprising that the simulated value is much higher than the experimental result. In this and other simulation work¹²¹⁴, the elastic constants were generally higher than experimental values. These were always at the upper limit of the values that are possible for
a polymer to possess. Reasons for these higher values of the elastic constants from simulation are that the applied stress in the experiment is much greater than the simulated stress. The temperature difference between the simulation (0K) and the experiment (room temperature) may also affect the values.

A problem with the BPADC model was that, whilst most of the BPADC cyclotrimerises to form a 3D thermosetting network, a small amount forms a BPADC cage, which is synthesised from three oligomeric units. This cage structure has been observed in mass spectroscopy\(^\text{15}\), with a M/E of 834, in which this moiety was broken down into fragments by the mass spectrophotometer in different ways to the uncaged moiety. This BPADC cage structure shown in figure 6.9 is similar to that of cage bicyclophanes\(^\text{16}\). It is not known by how much this cage structure effects the mechanical properties reported.

![Diagram showing the BPADC cage structure made up of three BPADC oligomers.](image)

Gupta et al.\(^\text{17,18,19}\) have developed an algorithm which simulates the structure buildup process during the homopolymerisation of monomers. They used this procedure to model the trimerisation of BPADC using the MC method to generate many different structures of the oligomer. They found that gel conversion occurred at 68\%, but experimentally, it has been found to be between 50-65\%\(^\text{17}\), due to diffusion limitations. Furthermore, this value did not alter if longer monomers were used. They concluded that the formation of the
polycyanurate network occurred via a step growth mechanism. This reaction was not controlled by the mobility of the molecules, because the percentage conversion at the gel point has been obtained at various temperatures, but rather by steric hindrances of functional sites. Consequently, these cyclotrimerisations reactions only occur in localised areas. This is because the BPADC molecules are extremely rigid, due to the presence of the two aromatic rings in the oligomer backbone\textsuperscript{17}, which is in agreement with the results obtained in chapters 4 and 5 on the modelling of the isopropylidene linkage.

### 6.6.2 6-ringed poly(arylene ether sulphone) dicyanate results

The elastic constants for the 6-ringed PIES dicyanate network from both simulation and experimental studies are given in table 6.10. The results show a trend, in which the simulated results are consistently higher than the experimental results, although they are in the same order of magnitude. This has been found consistently for a range of polymers\textsuperscript{12,14}, where the simulated results were up to 100% greater than the experimental results.

<table>
<thead>
<tr>
<th>Mechanical properties of the 6-ringed PIES dicyanate</th>
<th>Experimental results</th>
<th>Simulation results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus E (GPa)</td>
<td>2.50 ± 0.04</td>
<td>3.64±1.86</td>
</tr>
<tr>
<td>Poisson's Ratio ( \nu )</td>
<td>0.33 ± 0.02</td>
<td>0.35±0.19</td>
</tr>
<tr>
<td>Bulk Modulus B (GPa)</td>
<td>2.53 ± 0.28</td>
<td>3.68±2.43</td>
</tr>
<tr>
<td>Shear Modulus G (GPa)</td>
<td>0.89 ± 0.10</td>
<td>1.12±0.79</td>
</tr>
<tr>
<td>Lambda ( \lambda ) (GPa)</td>
<td>1.91 ± 0.29</td>
<td>3.45±2.54</td>
</tr>
</tbody>
</table>

Table 6.10. Table of the elastic constants for the 6-ringed PIES dicyanate network, from experimental and simulation studies.

The results in table 6.10 show that the simulated results are higher than the experimental results, but are in the same order of magnitude. The results differ by between 6 to 80%, in which the Lamé constant \( \lambda \), which has no direct physical meaning, has the largest deviation. It is interesting to note, that the experimental results were in better agreement with the simulated elastic constants for the BPADC network, than with the results for the 6-ringed PIES dicyanate network. This is related to the fact that more repeat units of BPADC were present in its model, in contrast to the 6-ringed PIES dicyanate model, which contained
fewer repeat units. This is where the 200 atom limit of the *elastica* module has a limiting effect, although it can be used to predict trends as shown with the results in tables 6.9 and 6.10. Clearly, the simulation and experimental results would be in better agreement if it had been possible to simulate a greater number of atoms. This development should soon be available with the advent of faster computers and improvements in software. Consequently, as long as simulation results are used to predict approximate values, rather than defined values and that any simulation work is backed up with experimental data, then there is no reason why simulation and experimentation should not be compatible. A further source of error in the simulation, is the fact that the model of the polymer represents an *ideal system*, *i.e.*, macroscopic defects such as voids, cracks and incomplete cure of the system are discounted. This leads simulated elastic constants to be higher than expected. In the remainder of this section, the work of other authors on the simulation of various polymers will be discussed, showing in some cases that by specifically reparameterising various parameters, similar results to the experimental values can be obtained. Having parameterised certain structural units, it should be possible to model more accurately similar polymers which contain similar structural groups.

Hutnik *et al.*[^14] who have simulated glassy PC and characterised their system *via* molecular mechanics (MM) and MC techniques[^14,20,21], obtained Young's and Shear moduli of 5.60±1.70 GPa and 2.1±0.65 GPa respectively by averaging their results over 13 structures. These were almost twice the experimental values of 2.40 and 0.95 GPa respectively[^14], although their Poisson's ratio and Bulk modulus results of 0.36±0.06 and 6.70±1.60 GPa were similar to the experimental values of 0.42 and 5.50 GPa respectively[^14]. They concluded that a reason for the over estimation of the simulated moduli was that the rigid segments of the PC molecule are larger and have fewer degrees of freedom per unit volume than poly(propylene)². Therefore, the size of the simulation cells is more limiting for PC than poly(propylene). Nonetheless, they concluded that by taking the standard deviation errors into account, the agreement with the experimental results was still quite satisfactory. Fan *et al.*[^12] optimised the DreidingII force field with *ab initio* data, to improve the backbone torsional potentials for PC. They also obtained similar simulated results to Hutnik *et al.*[^14], by averaging the results of six structures into one compliance matrix, which showed a large degree of isotropy. Their simulated results for Young's and Shear moduli were 5.03±0.81 GPa and 2.02±0.47 GPa respectively. These were nearly double the experimental results, although the Poisson's ratio and Bulk modulus values were fairly low at 0.24±0.09

[^14]: Hutnik *et al.*
and $3.68\pm0.74\text{GPa}$ respectively. They concluded that their results were at 'the upper limit of the polymer'. This was due to the idealised structure of the simulated polymer which would not contain any microscopic and/or macroscopic defects. Also, because the experimental stresses applied were far greater than in the simulation studies ($0.05\%$), this produced higher values for the simulated results. It is also interesting to note, that the standard deviations from the above simulations, and especially the standard deviations from Hutnik et al. are similar to the standard deviations given in this thesis. This shows that by averaging many structures to obtain accurate elastic constants, there is a trade-off where larger standard deviations are obtained.

Qian et al. using the QUANTA/CHARMm molecular modelling package, obtained the Young's and Bulk moduli of a range of polymers including poly(vinyl chloride) (PVC), poly(styrene) (PS), poly(ethylene terephthalate) (PET), poly(methyl methacrylate) (PMMA) and Nylon 6. They used the technique of constant stress molecular dynamics (CSMD) to obtain an equilibrated structure, from which either the Young's or the Bulk moduli were calculated. The Young's moduli were obtained from the simulated stress/strain curve after applying an uniaxial tensile stress to the equilibrated structure, whereas the Bulk moduli were calculated by the application of an isotropic pressure of 500 atmospheres. Many of the simulated results were in good agreement with experimental data, but with other results, the agreement with experimental values was not very good.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (gcm$^{-3}$)</th>
<th>E (GPa)</th>
<th>E (GPa) lit.$^{22}$</th>
<th>B (GPa)</th>
<th>B (GPa) lit.$^{22}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.05 (1.05)$^{22}$</td>
<td>1.10</td>
<td>3.4</td>
<td>1.7</td>
<td>5.0</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.15 (1.17)</td>
<td>0.81</td>
<td>3.2</td>
<td>8.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>1.12 (1.08)</td>
<td>1.80</td>
<td>1.9</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>PET</td>
<td>1.25 (1.33)</td>
<td>3.30</td>
<td>3.0</td>
<td>6.2</td>
<td>&gt;4</td>
</tr>
<tr>
<td>PC</td>
<td>1.12 (1.20)</td>
<td>2.00</td>
<td>2.5</td>
<td>4.7</td>
<td>5.0</td>
</tr>
<tr>
<td>PVC</td>
<td>1.28 (1.39)</td>
<td>0.63</td>
<td>2.6</td>
<td>1.4</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 6.11. Table of the density (literature values in brackets) and the Young's and Bulk moduli of a variety of polymers simulated using constant stress molecular dynamics, where the Young's moduli were obtained from a stress/strain curve at a particular temperature.

The results suggest that some polymers were represented better by the force field and by the simulation approach which was used, e.g., the PVC results were not particularly good,
because there was no account taken of the hydrogen bonding-like interaction between methylene hydrogens and the chlorine atoms. Moreover, difficulties in generating a reasonable initial structure for PS, due to the bulky side groups may be a problem. This emphasises the importance of averaging the results over several trial structures. The results also indicated that specific polymers may require modifications to their force field or simulation approach to produce better agreement with experimental results. The density results were also interesting, as the original starting densities of the polymers were often quite different from the actual densities of the polymer, where the densities had a long time period of MD simulation in which to equilibrate. These simulated densities were generally very close to the actual experimental densities, highlighting that molecular simulation can be used to obtain accurate densities of polymeric systems.

Termonia et al.\textsuperscript{24} modelled poly(ethylene) fibres \textit{via} a MC method, where the chains were represented as an array of nodes and bonds, in which constants described the bonding and the non-bonding interactions within and between polymer chains. The numerous weak non-bonding (VDW) terms represent the crystallinity, which provides the initial stiffness of the material. The accompanying stress-strain plots at various molecular weights ($M_w$) (1.4x10$^3$ to 3.3x10$^5$), model the Young’s modulus well, particularly when the $M_w$ was greater than 1x10$^4$, which gave a value of approximately 300GPa. These plots though, show rapid, but not sudden decrease in stress with increasing strain after the point of maximum stress. On the other hand polymer samples display abrupt, catastrophic failure. Termonia \textit{et al.}\textsuperscript{25,26} in further work with poly(ethylene) and particularly the stress-strain behaviour of various molecular weight polymers, predicted different morphological changes. These changes were observed in the deformation of polymers when the entanglement spacing (spacing factor) was altered. The simulation of the polymers which were deformed due to breakage of weak VDW 'non-bonds', together with chain slippage was carried out using a random MC method. This was continued at time intervals, $\delta t$, until the network failed. This resulted in very accurate simulated and experimental polymer morphologies of poly(ethylene) at different spacing factor values.

Yang \textit{et al.}\textsuperscript{27} modelled crystalline poly(ethylene) and poly(p-phenylene terephthalamide) (PPTA) using the stress method developed by Theodorou \textit{et al.}\textsuperscript{2}, in which deformations were applied in the various planes considered. They obtained accurate elastic constants for poly(ethylene), especially the Young's modulus value of 298GPa, which compared very
well with the literature value of 290GPa from neutron scattering experiments. In their simulation of PPTA, they obtained an high simulated value of 335GPa which was approximately 100% greater than the literature value of 153GPa, where most of the energy of deformation was applied to the bonds and valence angles energy terms. They concluded that degree of crystallinity, packing defects, lattice distortion and segmental orientation can effect the experimental modulus. Boyd et al. modelled glassy poly(methylene), with an unfixed and a fixed volume of 1.01cm³/g, to obtain the elastic constants. Their results were sensitive to the specific volume of the polymer. They obtained a shear modulus of 0.7GPa when the cell volume was allowed to fluctuate, but a value of 1.5GPa (literature value 2GPa), when the volume, i.e., the density was kept constant.

Karasawa et al. modelled poly(ethylene) to obtain mechanical properties and accurate force field parameters of the crystalline polymer. This was performed by altering various parameters via the Gaussian ab initio package, until theoretical results were similar to experimental data. Not surprisingly, their simulated Young's moduli of 337GPa and 318GPa at 0 and 300K respectively were similar to the experimental values of 324 and 329GPa calculated from spectroscopic techniques. From these parameterisations, accurate calculations of the elastic constants of other similar n- and branched alkanes should be possible. Karasawa et al. have also modelled crystalline poly(vinylidene fluoride) (PVDF) crystals by MD simulations. They used their force field, the Hessian-biased force field, to describe this moiety, which contained changes to the charge, VDW, torsional and valence parameters, in which they obtained these new parameters from quantum mechanical calculations. The experimental Young's modulus of one of the crystalline forms of PVDF from X-ray diffraction was 177GPa, which was calculated assuming an homogeneous stress. The elastic modulus gave a value of 283GPa from simulation techniques. They concluded that the discrepancy was mainly due to the difficulty in extracting the properties of a pure crystal from samples which contained a mixture of crystalline and amorphous regions. Similar results were found for poly(ethylene), where the x-ray method gave a Young's modulus of 235GPa, whilst neutron scattering, Raman and theory (see above) gave values of approximately 320GPa.

Nicholson et al. modelled PET using both MOPAC and POLYGRAF. They used the techniques of either imposing a strain on the system and measuring the change in energy, or by imposing an external stress in a specific direction and then calculating the strain. The
calculated Young's moduli were far higher than the experimental result of 110 GPa\textsuperscript{31} obtained from x-ray diffraction. This was mainly because only one repeat unit under PBC was used in the simulation, which enabled a perfect lattice to be modelled giving results of 244 and 198 GPa respectively. These results were at the upper bounds of the modulus of the real material and they concluded that work to improve the force field was necessary, as there were problems with the force field parameters which described the PET structure. Finally, Sun et al.\textsuperscript{32} modelled syndiotactic PS and obtained an elastic modulus of 83 GPa, which was very similar to the literature value of 86 GPa\textsuperscript{32}. They applied varying stresses to a periodic box containing PS oligomers and measured changes in the unit-cell dimensions to measure the resultant strain. The elastic modulus was estimated from the resulting slope of the graph.

### 6.6.3 $T_g$ results of a 6-ringed poly(arylene ether sulphone) dicyanate

The $T_g$ of the 6-ringed PIES dicyanate network polymer by molecular simulation was 217°C, whilst from the practical work reported in chapter 2, the $T_g$ by DMTA was 140°C. The modelling result was quite high, when compared with the experimental result. There were a number of reasons for this phenomenon. First, the model of the system may not have been sufficiently accurate to describe the interactions of the polymer bulk properties, \textit{i.e.}, more repeat units of the oligomer were necessary to give a better description of the interactions present. Second, the simulation time may not have been sufficiently long to fully relax the structure, \textit{i.e.}, perhaps another 200 ps of MD at each temperature may have relaxed the structure into other lower energy and lower total volume conformers, and consequently reduced the $T_g$ of the polymer. Third, running the simulation every 100 K may be insufficient to describe transitions which occur around the $T_g$ of the polymer, so possibly a difference of 50 K between each simulation, or more points around the $T_g$ were necessary. This technique however, would only be appropriate if the $T_g$ was already known, or if an initial cruder study had already been performed. Finally, the experiment should be run several times using different models, keeping the number of repeat units constant, to enable average results to be presented. In this way, local fluctuations and discontinuities in the simulated polymeric system should be overcome.

Despite the previous statements, a compromise between the model of the polymer, the speed of the computer and the amount of time required to perform the work has to be considered. Consequently, considering all the above factors, it was assumed that the model used to
describe the polymer was the best available. Ideally, a more substantial model would and could have been used, which hopefully would increase the accuracy of the result.

From the simulation of the T_g, the thermal expansion coefficients were obtained. The expansion coefficient obtained was the VTEC, which was easily converted to the LTEC. The LTEC was also obtained experimentally by TMA in chapter 2, and therefore allowed either of the expansion coefficients to be compared. Here, the result under discussion is the LTEC and these results are shown in table 6.12, although for completeness, the VTEC are also shown in this table.

<table>
<thead>
<tr>
<th>Simulation results (K^{-1})</th>
<th>Experimental results (K^{-1})</th>
</tr>
</thead>
<tbody>
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<td>VTEC ( \alpha_g )</td>
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</tr>
<tr>
<td>( \alpha_l )</td>
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<tr>
<td>( \alpha_l )</td>
<td>1.92x10^{-4}</td>
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</tbody>
</table>

Table 6.12. Table of the VTEC and the LTEC for the 6-ringed PIES dicyanate network in the liquid and glassy states which the polymer possesses, from simulation and experimental studies.

The results in table 6.12, show that the model has given a fairly good simulation of \( \alpha_g \), but as the temperature increases and the polymer moves into its liquid phase, \( \alpha_l \) has been described less adequately. This is likely to be due to the limiting size of the model of the polymer used, whereas a structure containing more repeat units is likely to give a more accurate result. However, initial degradation of the sample between approximately 100 to 200°C (see figure 2.17), i.e., heating up and decomposition of some residual solvent could mask the expansion of the polymer piece and consequently give the \( \alpha_l \) value a slightly false reading. However, this is unlikely to make a major difference to the final experimental value. Fan et al.\(^3\) obtained the linear expansion coefficient of UDEL poly(sulphone) of 7.2x10^{-5}K^{-1} (literature value is 5.5x10^{-5}K^{-1}) which showed that the \( \alpha_g \) value can be modelled fairly well, although unfortunately the MD simulation was terminated at 400K, hence the \( \alpha_l \) value was not calculated. Theodorou et al.\(^2\) having obtained the elastic constants of glassy atactic poly(propylene) also obtained the value of the expansion coefficient, 1.08±0.23x10^{-4}K^{-1} (literature value is 2.5x10^{-4}K^{-1}). They concluded, that perturbations in the potential parameters, unlike those of the elastic constants, can cause
significant changes with small changes in the potential energy parameters, i.e., a slightly inappropriate choice of the van der Waals radii may be responsible for the discrepancy. The expansion coefficient results, particularly the $\alpha_1$ would be improved significantly in the 6-ringed PIES dicyanate polymer, if the $T_g$ simulation result was closer to the experimental value. Consequently, the model used to describe the $T_g$ of the system more adequately must be improved, i.e., by simulating more repeat units in the polymeric system or by running the simulation more than once to obtain averaged results. This should have a knock-on effect on the simulated expansion coefficients of the polymer and consequently give a result which is nearer to the experimental result.

Roe et al. studied the $T_g$ of amorphous poly(ethylene) by obtaining the specific volume at various temperatures. They produced a value of 188K and 212K for an 150 and a 500 monomer system of poly(ethylene) respectively. Literature values for the $T_g$ of poly(ethylene) vary between 150 to 300K, so few conclusions can be drawn from this result. Roe et al. suggested that more accurate results could be produced with improvements in the model of the system and by altering the time scale of the cooling rate. They suggested that their model was not ideal for three reasons. First, their use of the united-atom approach, where hydrogen atoms are removed but incorporated with the carbon atoms. Second, the Lennard-Jones 12-6 potential had been truncated at a short distance (5.7Å) to improve computational speed and the density of the simulated system was variable and not kept at the experimental value. Third, the simulation was run for 100ps at each temperature before simulation at the next temperature range. Consequently, as there was clearly an huge difference in time scales for the cooling rate between simulation and experimental work, they concluded that this would cause a deviation in the $T_g$ of approximately 30°C. Boyd and co-workers using NPT dynamics have simulated the $T_g$ of a number of polymers, by plotting the average specific volume of a polymer chain, averaged over a long time period (up to 2 nanoseconds (ns) in most cases) against the simulation temperature. An inflexion in the curve represented the $T_g$. Single chain polymers were simulated, in which the molecular weight being modelled varied from 8000 to slightly above 10000. Some atoms were represented by the united atom approach, i.e., the hydrogens attached to carbon atoms were removed, but the molecular weight of the carbon atoms were increased to 14 atomic mass units. In the varying temperature simulations of the various single chain polymers under PBC, the volume of the polymers being simulated at higher temperatures equilibrated more quickly. Their results showed good correlation with
experimental data in which the $T_g$ of poly(isobutylene) was 222K (literature value was 198K), the $T_g$ of poly(propylene) was 270K (literature value was 260K) and the $T_g$ of PS was 370K (literature value was 372K). This good agreement was due to the large models of the polymers which were used (i.e., the high molecular weight) and the use of very long simulation times, $\sim$2ns, to relax the simulated polymers. The trend in their results indicated that molecular simulation results slightly over estimate the $T_g$, as we found to a larger extent in our work. However, they concluded the errors in the simulated $T_g$ values were small enough to allow useful material predictions from molecular simulation in the future. Finally, that although the calculations were computationally very 'expensive', they were practical calculations which will be utilised more in the future. A more serious drawback they concluded was the need for the development of reliable potential function parameters required to describe a variety of polymers.

6.7 Conclusions

Comparison of the experimental with the theoretical results showed an high degree of agreement. When Theodorou et al. developed the 'stress' method to obtain mechanical properties, the error in the results for atactic poly(propylene) were not greater than 15%. Virtually all the subsequent papers, including one by the co-author, have reported higher simulated values from polymeric systems of between 20 and 100%. Consequently, errors in the results of the BPADC polymer of between 5 and 40% and between 6 and 80% for the 6-ringed PIES dicyanate polymer are regarded as being very acceptable. As stated earlier, these results could be improved by increasing the atom limit in the elastica module. It is noteworthy, that for both systems, the value which gave the biggest error was the Lamé constant $\lambda$, which should only be applied to isotropic values. The percentage error for both systems would drop to approximately 20 and 45% respectively by disregarding this result. Throughout these simulations averaged values have been used to report the elastic constants which were obtained. The anisotropic nature and the extreme values of the elastic constant results of the simulated polymer were reduced by averaging a large number of values. Finally, the results of the $T_g$ simulation were less accurate than we hoped, although similar $T_g$ results were given from either the change in volume or the energy method. It was also possible to obtain expansion coefficients in which the $\alpha_g$ value was more accurate than the $\alpha_l$ result, by using the change in volume method to obtain these values.
6.8 References


36 J. Han, R. H. Gee and R. H. Boyd, *Macromolecules*, 27, 7781-7784 (1994) and references within.
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Conclusions and future work

7.1 Conclusions

In this thesis, both molecular modelling and practical synthetic techniques have been used to probe thermoplastic and thermoset polymers, based on the repeat unit of the UDEL poly(sulphone) backbone. In the thermoset polymer, this backbone has been linked by cyanurate rings to form a network polymer.

In this thesis, the modelling work was divided into three stages. First, a single oligomer of a poly(arylene ether sulphone), namely, poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulphonyl-1,4-phenylene) (PIES) was characterised in a vacuum using molecular mechanics (MM) and molecular dynamics (MD) techniques. The Dreiding II force field was used to describe the simulated polymers. The parameters used to describe the sulphone torsional angle and the bond angles of the 6-triazine ring were altered slightly, to describe these moieties more accurately. From these studies the flexibilities of the linkages were obtained using a number of techniques. It was found by utilising the DreidingII force field, that the sulphone linkage was the most flexible, then the ether linkage and finally the isopropylidene linkage was found to be the least flexible. The lowest energy conformational torsional angles resided at ±90°, ±90° for the sulphone torsional angle, ±90°, ±90° for the ether torsional angle and ±55°, ±125° for the isopropylidene linkage. These results agree with data from the Cambridge Crystallographic database, except for the ether linkage. Reasons for these differences have already been explained. Their energy barriers to rotation were ascertained from a soft conformational search and found to be 1, 4 and 6 kcal/mol respectively. In further work, another oligomeric system was simulated, where the sulphone linkage was replaced by a carbonyl linkage to form a poly(arylene ether ketone) (PIEK). The energy barrier to rotation of the carbonyl linkage was found to be 3.5 kcal/mol. The lowest energy conformational torsional angles of the carbonyl linkage resided at ±30°, ±150°.

Second, bulk modelling of the PIES thermoplastic polymer under periodic boundary conditions was performed. In these simulations constant volume and temperature (NVT) and constant pressure and temperature (NPT) MD simulations were performed on the system. The NPT simulations described the system more accurately, due to the fluctuations in the size and shape of the periodic cell. Results from these simulations were in good agreement with the results from the simulation of the PIES oligomer in a vacuum. From these
simulations greater movement of the polymer was observed at higher simulation temperatures. This was ascertained from population plots of the constituent linking torsional angles and from mean square displacement plots of the atoms in these simulations. Also the radial distribution plot indicated the amorphous nature of the polymeric system. Physical and mechanical properties of the polymer were ascertained from a number of modelling techniques. The results calculated for the mechanical properties of the system from either group contribution theory or from the elastic module in POLYGRAF were in good agreement with the experimental values. Various physical properties, e.g., the glass transition temperature (T_g) and the isopropylidene ring flips were modelled and simulated well. Modelling of a solvated PIES in dichloromethane was also performed. Relaxation of the system and the actual experiment took much longer to perform, due to all the extra atoms and non-bonded interactions which require simulation. It has been shown that in solvated systems most of the time is utilised simulating the solvent, rather than the polymer, where displacement of many solvent molecules is necessary before movement of the polymeric system can occur.

Third, molecular modelling of a thermoset polymer which has a PIES backbone, in which the repeat units were linked together by cyanurate rings to form a 3D network structure was performed. Mechanical properties were again modelled, and the agreement with synthetic results was found to be satisfactory. The T_g and the thermal expansion coefficients were also obtained. The T_g was calculated to be 217°C, and the glassy and liquid thermal expansion coefficients were 6.29x10^{-5}K^{-1} and 1.03x10^{-4}K^{-1} respectively. A model system based on a commercial polymer was also modelled, namely bisphenol-A dicyanate. This had a smaller repeat unit, in which more accurate mechanical properties were predicted, simply due to the enhanced accuracy of the atomistic model which could be used to describe this polymeric structure.

In the synthetic part of the project a 6-ringed poly(arylene ether sulphone) dicyanate (6-ringed PIES dicyanate) was synthesised from bisphenol-A. This starting group needed to be protected, otherwise high polymers were formed, whereas only a short oligomeric repeat unit was required. The final stage required a cyanation reaction to convert the oligomer to a cyanate ester. The synthesised cyanate ester oligomer was then cured by metal catalysis to form a 3D thermoset polymer network. This structure was then characterised using classical techniques, e.g. solid state NMR and FTIR studies. These showed a high degree of
Conclusions and future work

conversion to the 3D thermoset polymer network. A commercial system, namely bisphenol-A dicyanate was also cured, and used as a comparison with the synthesised polymer. Various mechanical properties of the systems were obtained using an Instron universal testing apparatus, whilst physical properties were obtained by differential scanning calorimetry, dynamic mechanical thermal analysis and thermal mechanical analysis experiments.

Finally, the mechanical and physical properties obtained from experimental techniques and those from the modelling techniques were compared. A similar set of results were obtained from these techniques. Clearly the results from the modelling techniques were not identical to the synthetic values, but they did indicate a range of values for the systems, as the results were fairly accurate and always of the same degree of magnitude as the experimental results. A variety of mechanical properties were simulated, e.g., the Young's moduli and the Poisson's ratios of the two polymers and these agreed well with the experimental values. However, the simulated \( T_g \) of the 6-ringed PIES dicyanate was approximately 80°C higher than the experimental value of 140°C. The expansion coefficients were also calculated, where the expansion coefficient in the glassy phase was described well, whereas the value of the expansion coefficient in the liquid phase needed some improvement.

In this thesis, it has been shown that polymers can be well characterised by the use of molecular modelling techniques. Simulation of various properties was accomplished, where good results were produced by averaging many values over many different models of the system. This nullifies any spurious results or anisotropic nature which may have been present in the modelled structure. Although the results may not be totally accurate, the results can be used to predict trends in polymeric systems. The polymer systems have been described well, due to the accuracy of the force field and to the subsequent changes made to it, and by the use of various algorithms in the modelling package to obtain the various properties$^{4,5}$. Consequently, as the speed of computers increase, coupled with improvements in the speed of software and the methodologies used to model polymers, the results of polymer modelling studies can only improve. Finally, it must be remembered that whenever possible, future modelling studies should be backed up with good experimental data.
7.2 Future work

As a follow-up to this thesis, there are a number of areas of work in which future studies are possible. These are either synthetic tasks or modelling work. Some of the modelling could be currently performed with present commercial software, whilst more advanced studies could be performed in the future, as computers and simulation methodologies improve.

Further modelling studies which are possible include the $T_g$ simulation of bisphenol-A dicyanate (BPADC). From these studies, it should be possible to ascertain the accuracy of the $T_g$ simulation and to work out the optimum model for the structure. Different models could be utilised, i.e., the number of repeat units could be altered to observe the effect of the number of repeat units on the accuracy of these results. From these simulations, it would then be straightforward to obtain the various expansion coefficients in the glassy and liquid states. Having modelled the $T_g$ of the 6-ringed PIES dicyanate network and obtained a rough value for the result, a more accurate model could be used, either by increasing the number of repeat units or by simulating the system at a greater number of temperatures around the $T_g$. Consequently, by having more data points in the vicinity of the $T_g$, it should be possible to calculate a more accurate $T_g$.

Examination of the simulated mechanical properties also shows that further improvements are possible. First, it is now possible with the new generation of polymer modelling software\textsuperscript{10,11}, to model the stress/strain behaviour of polymers, and to predict the corresponding stress/strain curves, from initial strain to rupture point of the polymer. It is now also possible to obtain the mechanical properties at various temperatures, whereas in this thesis, the mechanical properties were only obtained at 0K. Second, the new software has no limits on the size of the structures used to model the mechanical properties, i.e., any number of atoms can be simulated within the constraints of the machine, hence more accurate mechanical properties should be predictable for neat resin polymeric systems. In these simulations, constant stress molecular dynamics algorithms\textsuperscript{12} are used, to apply varying stresses to the simulated polymers, to predict the mechanical properties and stress/strain diagrams.

Having modelled the repeat unit of the PIEK oligomer, it would be appropriate to model this system under more rigorous conditions, i.e., under bulk conditions to observe the behaviour
Conclusions and future work

of the system. The modelled $T_g$ of the system would be a suitable property to test, to see if it followed experimental trends and was less than the $T_g$ of the PIES system. Finally, it would be of interest to model the PIEK linked to cyanurate rings as a thermoset polymer, to observe how its mechanical properties would vary with the corresponding 6-ringed PIES dicyanate system and also the synthesised poly(arylene ether ketone) dicyanate thermoset polymer.

In the synthetic work, a comparison between the properties of the 6-ringed PIES dicyanate polymer and a polymer where the size of the repeat unit of the PIES was very much enhanced, e.g., variation of the repeat unit between a molecular weight of approximately 1000 to 10000. Clearly, in this situation, the differing lengths of the PIES chain would have an effect on the calculated properties. It was stated in chapter 1 that cyanate esters are often cured and blended with bis-maleimides to improve the properties of both systems. The change in mechanical and physical properties of the cyanate ester polymer due to the variation of the amount of bis-maleimide in the system, e.g., from 0 to 50% would be another suitable area for further study, in which modelling studies of these systems could also be performed.

Finally it would be of interest to synthesise and model a 6-ringed poly(arylene ether ketone) dicyanate. This could probably be synthesised by the same method as the corresponding sulphone structure is synthesised in chapter 2, except that it maybe necessary to change the chloro group to a fluoro group to provide a more powerful electron withdrawing group in the initial ketone starting moiety. It was stated that high polymers of PIEK can not be formed under normal conditions\(^{13}\) (see chapter 1) as they crystallise out from solution, but as the synthesis would involve only one ketone linkage, then hopefully this would not be a problem. Using the resulting polymer obtained from the cured oligomer, the mechanical and physical properties could be compared with those obtained using modelling techniques.

All these systems have been modelled or characterised as a neat resin, whereas in one of their major uses as an high performance engineering polymer, they are used as a composite. Consequently, it would be appropriate to test all the above systems as a composite and also to model their composite behaviour. However, modelling of a composite is a complex problem!! as many different factors need to be considered. Consequently, resolution of this problem is still in the distant future. Further improvements in computing power and
methodologies will be required, before any attempt can be made to solve this problem. Any models produced would need to be very well validated using all the available characterisation data.

### 7.3 Future trends

In conclusion, it has been shown that the physical and mechanical properties of the simulated polymers have been well described, by the atomistic models which were used. Eventually, as computers and software methodologies improve, it should be possible to describe systems more accurately, and hence obtain even more accurate results.

Over the next few years, it will be an advantage if the modelling of larger polymeric network systems can be accomplished\textsuperscript{14,15,16}. This is likely to be conducted via random walk or Monte Carlo techniques, where some of the atomistic detail of the polymer would be removed. If MD simulations were used, these would last for a very lengthy period and it would be necessary to analyse a great deal of data. Using these calculations, more advanced work involving blends of other polymers, \textit{i.e.}, forming some kind of interpenetrating network\textsuperscript{2,17} and the influence of carbon fibres, \textit{i.e.}, composite materials will need to be considered. Other advances which would be advantageous are the prediction of stress/strain curves of polymeric systems from initial strain to yield point at various simulation temperatures, for which software has recently been developed\textsuperscript{10,11}. Also, the use of continuum models, which could be used to model solvated systems, where the solvent is 'present' in the simulation, but not modelled as an atomistic model. In this case the speed of solvated calculations would be considerably enhanced. Finally as stated previously, by using modelling and synthesis in tandem, where accurate models and parameters can be obtained by 'fixing' them to synthetic results, it will be possible to calculate the properties of similar polymeric systems, using the newly obtained model parameters.
7.4 References

4 S. Nosé and M. L. Klein, Molecular Physics, 50, 1055-1076 (1983).
7 Elastica module in Professional POLYGRAF (3.2.1) manual, page EL1-EL8 (1993).
8 Molecular Simulations Inc., 16 New England Executive Park, Burlington, MA 01803-5297, USA.
10 Cerius 2, The new molecular modelling package offered from Molecular Simulations Inc. (address as reference 8).
11 Insight2/Discover, The new molecular modelling package offered from Biosym Technologies. 9685 Scranton Road, San Diego, CA 92121-3752, USA.
Appendices

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Appendix 1 - Charge calculations on the poly(arylene ether sulphone)

The partial atomic charges on the poly(arylene ether sulphone) (PIES) oligomer were calculated using MOPAC and Gasteiger charges. These results are shown below.

![Figure A.1. The atom numbers of the PIES oligomer.](image)

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Table A.1. The atom numbers, the atom types and the atomic partial charges calculated from the Gasteiger and the MOPAC charge methods on the atoms in the PIES oligomer.
where H is an hydrogen atom, C_R is an aromatic carbon, C_3 is an sp\(^3\) hybridised carbon, O_3 is an sp\(^3\) hybridised oxygen, O_2 is an sp\(^2\) hybridised oxygen and S_3 is a sp\(^3\) hybridised sulphur atom.

Appendix 2 - Charge calculations on the poly(arylene ether ketone)

The partial atomic charges on the poly(arylene ether ketone) (PIEK) oligomer were calculated using MOPAC and Gasteiger charges. These results are shown below.

![Figure A.2. The atom numbers of the PIEK oligomer.](image)

<table>
<thead>
<tr>
<th>Atom number</th>
<th>Atom type</th>
<th>PIEK - Gasteiger</th>
<th>PIEK - Mopac</th>
</tr>
</thead>
<tbody>
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</tr>
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Table A.2. The atom numbers, the atom types and the atomic partial charges calculated from the Gasteiger and the MOPAC charge methods on the atoms in the PIEK oligomer.
where H is an hydrogen atom, C_R is an aromatic carbon, C_2 is an sp² hybridised carbon, C_3 is an sp³ hybridised carbon, O_3 is an sp³ hybridised oxygen and O_2 is an sp² hybridised oxygen.

**Appendix 3 - Charge calculations on the cyanurate linkage**

The partial atomic charges on the cyanurate linkage were calculated using MOPAC and Gasteiger charges. These results are shown below.

![Figure A.3. The atom numbers of the cyanurate moiety.](image)

<table>
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</table>

Table A.3. The atom numbers, the atom types and the atomic partial charges calculated from the Gasteiger and the MOPAC charge methods on the atoms in the cyanurate linkage.

where C_R is an aromatic carbon, N_R is an aromatic nitrogen, C_3 is an sp^3 hybridised carbon and O_3 is an sp^3 hybridised oxygen. Hydrogen atoms were not included in the table as all the charges on the hydrogens were fairly low and between ±0.06q.
Discussion of the calculated atomic partial charges

Examination of the partial charges returned from both techniques, i.e., the Gasteiger or MOPAC methods show that there are a number of key atoms in the structure. These are the linking atoms and the carbon atoms joining these linking groups to the phenylene rings.

For the PIES oligomer, the partial charges returned are similar from either method apart from small discrepancies in a number of cases. These discrepancies are either the isopropylidene hydrogens or the aromatic carbons where the partial atomic charge is usually very low, but often the two methods give values of opposite sign. The key linking atoms, however, give similar charges from either method. The charges around the isopropylidene linkage are very small with similar results from either method. The exception is the two Csp³ atoms which gave values of opposite sign changing from the Gasteiger to MOPAC methods. The charges around the ether linkage are also similar, although the charge on the Osp³ atom varies slightly between the two methods. Finally, the results of the sulphone are similar, with the exception of the two linking carbon aromatic atoms, in which the partial charges on each atom vary to a large extent. Despite these discrepancies between the partial charges on a few atoms, the results from both methods are similar, hence the Gasteiger charge method was chosen. The advantages of the Gasteiger method was that the atom limit was infinite and that the result was calculated within seconds, whereas with the MOPAC charge method, the number of atoms is limited and the calculation took several hours. These advantages become more important when larger systems are simulated, e.g., the networked thermoset polymer systems.

Examination of the charges returned for the PIEK oligomer, indicate that except around the carbonyl linkage the charges are mainly similar to those for the PIES oligomer by either method. The charges around the isopropylidene linkage are very similar to those in the PIES oligomer (as expected) with the same discrepancies, i.e., the two Csp³ atoms have small charges but different signs depending on the method. The ether linkage is again well described, but with a small error in the value of the Osp³ value. The partial charges of the carbonyl linkage are described quite well, with a slight error in the value of the Csp² charge, although the charge and the sign difference of the adjoining carbon atoms is very apparent. Again, Gasteiger charges were used in the simulation of the PIEK oligomer, although quite clearly the MOPAC charges could also have been used. In this case, a valid reason for using
the Gasteiger charges was that as the PIES and the PIEK oligomers were being compared, the most suitable comparisons are with structures which have been simulated in as similar a way as possible.

Examination of the partial charges in the cyanurate shows that both methods give similar results. The charges returned for the \( \text{5'-triazine ring} \) are similar, with only the magnitude of the charges, especially those of the aromatic nitrogen atoms differing by a significant amount. However the aromatic carbon atoms of the \( \text{s-triazine ring} \), together with the linking \( \text{Osp}^3 \) atoms have similar values. The magnitudes of the carbon atoms of the three phenyl rings from either method are also similar. Again however, the charges of the \( \text{Csp}^3 \) atoms of the isopropylidene linkage have charges of opposite sign depending on which method is used. Although similar atomic partial charge values are obtained by either method, the Gasteiger charge method was chosen. This reason for this is that in the simulation of the thermoset polymers in chapter 6, oligomeric lengths of PIES would be attached to the cyanurate rings; thus increasing the size of the structure. Only the Gasteiger method could cope with the application of partial charges to that size of polymeric structure.

**Appendix 4 - Code written to obtain the correlation functions**

**The non-normalised correlation coefficient**

The Microsoft FORTRAN code used to obtain the non-normalised correlation coefficient is given in the following lines of FORTRAN code. If \( \text{JCOR1} \) equals \( \text{JCOR2} \) then the non-normalised autocorrelation function is obtained, whilst if \( \text{JCOR1} \) does not equal \( \text{JCOR2} \) then the non-normalised cross-correlation function is obtained.

```fortran
PROGRAM CORR

C
C   -- PROGRAM TO OBTAIN THE NON-NORMALISED CORRELATION COEFFICIENT OF
C   -- VARIOUS ANGLES IN THE BACKBONE OF A POLYMER CHAIN
C
C   -- CREATED: 5-DEC-93  CRH
C
C
```
PARAMETER ( JAMONT = 2500, JCOR = 6 )  
DIMENSION TORS (JAMONT, JCOR)  
REAL COREL(JAMONT)  
CHARACTER*80 CFILE  
CHARACTER*1 CREPLY  

C  
C -- READ IN DATA FILE AND PUT DATA INTO A PROCESSING ARRAY  
C  
10 CONTINUE  
WRITE(*,*) ' ENTER DATA FILE ? '  
READ(*,' (80A)' , ERR=10) CFILE  

C OPEN (UNIT = 5, FILE = CFILE, ERR = 10 )  
JTIME = 0  
20 CONTINUE  
JTIME = JTIME + 1  
READ(5,* ,END=100) (TORS(JTIME,J),J=1 ,JCOR)  
GOTO 20  
100 CONTINUE  
CLOSE(5)  

C  
C -- COSINE ALL ANGLES  
C  
DO 200 J = 1, JTIME  
DO 202 J1 = 1, JCOR  
TORS(J,J1) = COS(TORS(J,J1))  
202 CONTINUE  
200 CONTINUE  

C  
C -- PROCESS THE DATA TO GET THE NON-NORMALISED CORRELATION FUNCTION  
C  
205 CONTINUE  
WRITE(*,*) ' ENTER TWO NUMBERS TO GET THE CORRELATION OF ? '  
READ (*,*) JCOR1  
READ (*,*) JCOR2
C
C   --  CLEAR OUTPUT ARRAY
C
   DO 210 J = 1, JTIME
      COREL(J) = 0
   210 CONTINUE
   CONTINUE

   WRITE(*,*) '  ENTER NAME OF OUTPUT FILE ?  '
   READ(*,'(80A)') CFILE
   OPEN (UNIT = 6, FILE = CFILE, ERR = 220 )

C   --  LOOP OVER ALL STRUCTURES SO AS TO OBTAIN AN AVERAGED ENSEMBLE OF RESULTS
C
   DO 230 J = 1, JTIME - 1
      DO 240 J1 = J + 1, JTIME
         COREL(J1) = COREL(J1) + TORS(J,JCOR1) * TORS(J1,JCOR2)
      240 CONTINUE
   230 CONTINUE

   DO 250 J = JTIME, 2, -1
      COREL(J) = COREL(J)/J
   250 CONTINUE

C

   DO 260 J = 1, JTIME
      WRITE(6,*) COREL(J)
   260 CONTINUE
   CONTINUE
   CLOSE(6)

C
   WRITE(*,*) '  DO YOU WANT ANOTHER GO (Y/N) ?  '
   READ(*,'(1A)') CREPLY
   IF ( CREPLY .EQ. 'Y ' .OR. CREPLY .EQ. 'y ' ) GOTO 205

C
   END
Appendix 5 - Calculation of elastic properties of poly(arylene ether sulphone) from group contribution theory

All the calculations below were obtained from the book by Van Krevelen, in which the properties calculated could either be compared with simulated or literature values. In this appendix a more detailed strategy of the method of calculation of these values is shown.

a) Density

The density can be calculated in the glassy state.

\[ \rho = \frac{M}{V} = \frac{M}{\sum V_g} = \frac{442}{372.2} = 1.19 \text{ gcm}^{-3} \]

where \( M \) is the molar mass of the oligomer and \( V_g \) is the volume of the glassy state of the constituent parts. The value of the sulphone unit has been estimated from the values of a sulphur and two oxygen units where \( V_g (\text{phenylene}) = 4 \times 65.5, V_g (\text{ether}) = 2 \times 10, \)
\( V_g (\text{sulphone}) = 37.8 \) and \( V_g (\text{isopropylidene}) = 52.4 \).

The density can also be calculated in the rubbery state.

\[ \rho = \frac{M}{V} = \frac{M}{\sum V_r} = \frac{442}{345} = 1.28 \text{ gcm}^{-3} \]

where \( M \) is the molar mass of the oligomer and \( V_r \) is the volume of the rubbery state of the constituent parts. The value of the sulphone unit has been estimated from the values of a sulphur and two oxygen units where \( V_g (\text{phenylene}) = 4 \times 61.4, V_g (\text{ether}) = 2 \times 8.5, \)
\( V_g (\text{sulphone}) = 32 \) and \( V_g (\text{isopropylidene}) = 50.35 \).
b) $T_g$

$$T_g = \frac{\sum Y_{gi}}{M} = \frac{209000}{442} = 472.9 \text{K}$$

where $M$ is the molar mass of the oligomer and $Y_{gi}$ is the contribution of each structural unit to the $T_g$ where $Y_{gi}$ (p-phenylene) = $4 \times 32000$, $Y_{gi}$ (ether) = $2 \times 4000$, $Y_{gi}$ (sulphone) = $58000$ and $Y_{gi}$ (isopropylidene) = $15000$.

c) Volume thermal expansion coefficients $\alpha_g$ and $\alpha_l$.

$$\alpha_l = \frac{0.20}{T_g} = \frac{0.20}{472.9} = 4.23 \times 10^{-4} \text{K}^{-1} \quad \alpha_g = \frac{\alpha_l}{2.17} = \frac{4.23 \times 10^{-4}}{2.17} = 1.95 \times 10^{-4} \text{K}^{-1}$$

where $\alpha_g$ and $\alpha_l$ are the expansion coefficients in the glassy and liquids states of a polymer respectively.

d) Cohesive energy $E_{coh}$

$$E_{coh} = \Delta U = \sum E_i = 141840 \text{ J/mol} = 33.9 \text{ kcal/mol}$$

where $E_i$ is the group contribution of each unit to the cohesive energy. The sulphone unit has been ascertained from values obtained for the sulphur and two oxygen units where $E_i$ (p-phenylene) = $4 \times 25140$, $E_i$ (ether) = $2 \times 6290$, $E_i$ (sulphone) = $15000$ and $E_i$ (isopropylidene) = $13700$.

e) Solubility parameter $\delta$

$$\delta = \left( \frac{E_{coh}}{V_g} \right)^{\frac{1}{2}} = \left( \frac{33900}{372.2} \right)^{\frac{1}{2}} = 9.53 \text{ cal}^{\frac{1}{2}} / \text{cm}^{\frac{1}{2}}$$

where $V_g$ is the volume of the oligomer in the glassy state.
f) Elastic constants

As shown from equation 6.17, if two elastic constants have been calculated, then the other three constants can be obtained from this equation. From group theory contributions, the Bulk modulus and Poisson's ratio can be obtained.

\[ B = \left( \frac{\sum U_i}{V_g} \right)^6 \rho = \left( \frac{21300}{372} \right)^6 1.19 = 4.19 \times 10^6 \text{ g/cm}^2 = 4.19 \text{ GPa} \]

where \( U_i \) is the group contribution of each unit to the bulk modulus, \( V_g \) is the volume of the oligomer in the glassy state and \( \rho \) is the density and \( U_i (\text{p-phenylene}) = 4 \times 4100 \), \( U_i (\text{ether}) = 2 \times 400 \), \( U_i (\text{sulphone}) = 1250 \) and \( U_i (\text{isopropylidene}) = 2850 \).

Compressibility is defined as the inverse of the bulk modulus, i.e.,

\[ \beta = \frac{1}{B} = \frac{1}{4.19} = 0.24 \text{ GPa}. \]

Poisson's ratio can be ascertained from group contribution theory from a graph of \( \frac{1}{2} \beta / \rho \) vs. \( \nu \) using values from the literature. A least squares line fit through the points gives a reference line. By plotting the \( \frac{1}{2} \beta / \rho \) value on the graph \((1.76 \times 10^6 \text{ Nm/kg})\), the intercept with the slope of the curve gives a Poisson's ratio of 0.43.

Having obtained \( B \) and \( \nu \), the other elastic constants can be calculated.

\[ E = 3B(1-2\nu) = 3 \times 4.19 \times 10^6 \times 0.14 = 1.76 \text{ GPa} \]

\[ G = \frac{3B}{2} \left( \frac{1-2\nu}{1+\nu} \right) = \frac{3}{2} \times 4.19 \times 10^6 \left( \frac{0.14}{1.43} \right) = 0.62 \text{ GPa} \]

\[ \lambda = B - \frac{2G}{3} = 4.19 \times 10^6 - \frac{2}{3} (0.62 \times 10^6) = 3.78 \text{ GPa} \]
Erratum

Page 4, line 5 monomer should be replaced with monomers.
Page 5, section 1.2.3. line 5 effected should be replaced with affected (and elsewhere in the thesis).
Page 6, line 3 dependant should be replaced with dependent.
Page 8, section 1.2.4. line 1 dependant should be replaced with dependent.
Page 8, section 1.2.4. line 2 M_w should be defined as molecular weight.
Page 8, last paragraph <M>_z should be replaced with <M>_w.
Page 9, Figure 1.7, the text should read <M>_n, <M>_w, <M>_z.
Page 12, Figure 1.9, C(CH_3)_3 should be replaced by C(CH_3)2.
Page 12, middle 'sufficiently flexible to show..... than 150^\circ C' should be replaced with 'sufficiently flexible to show ease of motion or processability at temperatures greater than 150^\circ C.'
Page 15, 3 lines from bottom M<n> and M<w> should be replaced with <M>_n and <M>_w.
Page 17, line 1 the second terms in the sentence need not be present.
Page 41, section 4.2.1, melonex should be replaced with melinex (and elsewhere in this chapter).
Page 48, line 3, liquid should be replaced with rubbery.
Page 48 TGA discussion thermo-oxidative in the 2nd sentence need not be present, because thermo-oxidative stability is inaccurate for samples run in nitrogen.
Page 69 Conjugate-gradients method does not have the ability to find the global minimum of a structure.
Page 132, Figure 5.3a 400v should be defined as a constant volume simulation run at 400K, and 600v should be defined as a constant volume simulation run at 600K.
Page 133, Figure 5.3b 400p should be defined as a constant pressure simulation run at 400K, and 600v should be defined as a constant pressure simulation run at 600K.
Page 158, line 6 monomer should be replaced with polymer.
Page 172, line 4 was should be replaced with were.
Page 191, line 4 effect should be replaced with affect.
Page 198, last paragraph decomposition should not be present as the water/solvent simply evaporates as it is heated, but does not decompose.
Page 208, paragraph 3 line 4 a more powerful electron withdrawing group should be replaced with a more facile leaving group.