Structure, Property and Modelling Studies of a Linear Epoxy Polymer

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

By

Adrian Sebastian Deazle

Structural and Computational Chemistry Group
Department of Chemistry
University of Surrey

February 1994
To Mum, Dad and Karin
Abstract

The aim of this Thesis was to build an atomistic model based on experimental information and to use simulation methodologies and theories to determine the mechanical and physical properties of a linear epoxy polymer. The atomistic behaviour of the polymer was studied during the property determining simulations, in an attempt to gain fundamental atomistic information.

The introductory chapter 1 is made up of four parts. The first section is a very general introduction to polymer science giving a newcomer to the field an appreciation of the concepts used, while the second section introduces the chemistry of epoxy resins and their commercial uses. The third section is a very brief introduction to how molecular modelling can be used to bridge the gap between experimental and theoretical studies, while the final section reiterates the aims, and outlines how the research was conducted.

The characterisation of a linear epoxy polymer by spectroscopic and chromatographic methods is described in chapter 2. The physical and mechanical property tests were also conducted and the results were coupled to structural information. The main object of this section was to quantify the relationship of the physical properties with the degree of cure.

The concept, methodologies and techniques of molecular modelling are introduced and discussed in greater detail in chapter 3. To demonstrate the modelling techniques used, the mechanical properties of simple polyethylene-like models were studied and compared with experimental data.

Chapter 4 characterises the structure of the linear epoxy polymer using representative atomistic models which were based on structural information from chapter 2. Additional crystallographic data was used to validate the force field parameters used in the modelling studies, to justify the motions of the molecular chain, and to qualitatively quantify the response of linear chains to stress and temperature.

The simulation and empirical calculations for the determination of both physical and mechanical properties were calculated and are discussed in chapter 5.
Comparisons were made between all three techniques; experimental, computer experiment and theory, and showed good agreement.

Finally, in chapter 6, a brief summary is given of the results in previous chapters, with further discussion on the implications of these results and suggestions on possible areas of future work.
Acknowledgements

Over the past three years I have had the assistance of many people, for which I would like to take this opportunity to thank. Firstly, I would like to thank my supervisors, Prof. J. R. Jones, Drs. B. J. Howlin, G. J. Baust and J. M. Barton, who were very approachable and showed great willingness to contribute to the work in any capacity.

I would like to express my gratitude to Dr. I. Hamerton, M. Clegg, Dr. A. Regnalfard and R. Whattingham, for their invaluable advice in the making and characterising of the linear polymer system. I am greatly indebted to Drs. S. Ramdas (BP, Sunbury) and E.W. Keller (Queen Mary & Westfield College) who have been exceptionally kind in allowing me to use their computing facilities. I am also very grateful to Dr J. Altman for her time and patience after spending many troublesome days installing POLYGRAF on the CONVEX at ULCC.

I would like to thank Drs D. M. Heyes and P. Mitchell for their invaluable discussions and enlightenment on the complexities and mysteries of molecular modelling. They have spent many hours, beyond the call of duty, to help analyse some of the data. For the past two years Mr. C. R. Herard has also assisted in writing programs for data analysis. I would like to thank him for this and for the many hours spent discussing the implications of our simulation results. I am also indebted to Dr J. Siedman for his expertise in polymer science and the input he has made to this thesis.

There are many people in the department and in the university as a whole who have made my stay very pleasant, especially the Chemistry department’s ‘singing secretaries’. I would like the thank all the friends I have made, for their support and words of encouragement.

Finally, but not at all least, I would like to thank my family, especially my wife Karen, who has been somewhat of a PhD widow this past year. She has been most patient while typing the vast majority of this work. I must add that without her constant support and encouragement it would have been very difficult.

Adrian Sebastian Doazle
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>(i)</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>(iii)</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>(iv)</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Introduction</td>
<td>2</td>
</tr>
<tr>
<td>1.2. Introduction to Polymer Science</td>
<td>2</td>
</tr>
<tr>
<td>1.3. Introduction to Epoxy Resins</td>
<td>12</td>
</tr>
<tr>
<td>1.4. Introduction to Molecular Modelling of Polymers</td>
<td>23</td>
</tr>
<tr>
<td>1.5. Outline of Research</td>
<td>25</td>
</tr>
<tr>
<td>1.6. References</td>
<td>28</td>
</tr>
<tr>
<td>2. Characterisation of a Linear Epoxy Polymer by Experiment</td>
<td>31</td>
</tr>
<tr>
<td>2.1. Introduction</td>
<td>33</td>
</tr>
<tr>
<td>2.2. Spectroscopic Characterisation</td>
<td>33</td>
</tr>
<tr>
<td>2.3. Chromatographic Characterisation</td>
<td>42</td>
</tr>
<tr>
<td>2.4. Physical Property Determination</td>
<td>51</td>
</tr>
<tr>
<td>2.5. Mechanical Property Determination</td>
<td>57</td>
</tr>
<tr>
<td>2.6. Discussion</td>
<td>61</td>
</tr>
<tr>
<td>2.7. Summary</td>
<td>72</td>
</tr>
<tr>
<td>2.8. References</td>
<td>73</td>
</tr>
<tr>
<td>3. Introduction to Molecular Modelling of Polymers</td>
<td>75</td>
</tr>
<tr>
<td>3.1. Introduction</td>
<td>76</td>
</tr>
<tr>
<td>3.2. Molecular Modelling</td>
<td>76</td>
</tr>
<tr>
<td>3.3. Simulation Techniques</td>
<td>80</td>
</tr>
<tr>
<td>3.4. Modelling Hardware and Software</td>
<td>93</td>
</tr>
<tr>
<td>3.5. Introduction to Polymer Modelling</td>
<td>93</td>
</tr>
<tr>
<td>3.6. Discussion</td>
<td>99</td>
</tr>
<tr>
<td>3.7. References</td>
<td>101</td>
</tr>
<tr>
<td>4. Characterisation of a Linear Epoxy Polymer by Simulation</td>
<td>104</td>
</tr>
<tr>
<td>4.1. Introduction</td>
<td>105</td>
</tr>
<tr>
<td>4.2. Conformational Analysis</td>
<td>105</td>
</tr>
<tr>
<td>4.3. Crystal Data Search</td>
<td>115</td>
</tr>
<tr>
<td>4.4. Stress and Temperature Analysis by Boltzmann Distribution</td>
<td>126</td>
</tr>
<tr>
<td>4.5. Discussion</td>
<td>137</td>
</tr>
</tbody>
</table>
# Introduction

1.1. Introduction ....................................................................................................................... 2  
1.2. Introduction to Polymer Science .......................................................................................... 2  
  1.2.1. Polymer Morphology ....................................................................................................... 5  
    1.2.1.1. The Amorphous State .............................................................................................. 5  
    1.2.1.2. Glass Transition Temperature .................................................................................. 6  
    1.2.1.3. Crystalline and Semi-crystalline .............................................................................. 9  
  1.2.2. Polymer Categories ...................................................................................................... 10  
  1.3. Introduction to Epoxy Resins .................................................................................................. 12  
  1.3.1. The Epoxy Group ...................................................................................................... 12  
  1.3.2. History ...................................................................................................................... 12  
  1.3.3. General Reactions ...................................................................................................... 14  
  1.3.4. Curing of Epoxy Resins ............................................................................................... 16  
    1.3.4.1. Catalytic .................................................................................................................. 16  
    1.3.4.2. Co-reactive curing .................................................................................................. 17  
  1.3.5. Other Possible Reactions ............................................................................................. 19  
    1.3.5.1. Etherification .......................................................................................................... 19  
    1.3.5.2. Homopolymerization ............................................................................................. 20  
    1.3.5.3. Cyclisation ............................................................................................................. 20  
  1.3.6. Properties and Application of Epoxy Resins .................................................................. 21  
1.4. Introduction to Molecular Modelling of Polymers ................................................................. 23  
1.5. Outline of Research ............................................................................................................ 25  
1.6. References ........................................................................................................................ 28
Chapter 1 Introduction

1.1. Introduction

This thesis aims to extend the knowledge and understanding of epoxy resins by studying a linear epoxy polymer. The object of the work is to determine the physical and mechanical properties of the linear epoxy polymer using three methods; experimental, theoretical and computer experiments. The latter technique will provide atomistic detail of the behaviour of the molecular chains under thermal and pressure changes.

This chapter introduces the areas of science and outlines the research proposal used in this thesis, it is divided into four sections, for which a general summary is given. The first section deals with polymer science, this gives a newcomer to the field an appreciation of the concepts used in this field. The second section gives a more detailed summary of epoxy resins, a class of polymers the properties of which are investigated both experimentally and theoretically in subsequent chapters. The third section introduces the general philosophy of molecular modelling and its use in calculating polymer properties from atomistic information. The final section gives an outline of the research proposal in the context of previous and ongoing work.

1.2. Introduction to Polymer Science

Polymers are macromolecules synthesised from the repeated co-reaction of small "building blocks" called monomers. They occur in nature and are also readily synthesised. There are two general processes by which monomers polymerise to form large polymeric structures: step growth and addition. The structure of polymers formed by way of a step growth mechanism differ slightly from the monomer structure, with the liberation of small condensation molecules, (e.g. water, acetic acid), whereas polymers formed by an addition process have the same chemical composition as the monomer. Monomers of the latter type may, for example undergo ring opening or multiple bond breaking to form single bonds. The formation of oligomers, linear or large network systems, which contain branches and crosslinks, are dependent on the functionality of the monomers. Any functionality greater than one can result in the cross-linked networks depending on the system considered.
Chapter 1 Introduction

The number of monomer types used to build a polymer is further classified. Homopolymers contain one type of monomer, while copolymers contain two or more. Depending on the monomeric distribution this category is further subdivided into four groups. Statistical copolymers contain a purely random distribution of two monomers while alternating copolymers, as the name suggests, are regular in distribution. Block copolymers contain regions of one monomer joined to regions containing another monomer block, graft copolymers are an example in which a block of one monomer is grafted onto the backbone of another monomer type.

The rate at which monomers react is dependent on factors such as viscosity, temperature and steric factors. Considering the effect of all these factors it is not surprising that polymers rarely have a single well-defined molecular weight, but rather a distribution of various chain lengths and/or degrees of crosslinking within a system. The average or statistical molecular weight of a polymer mixture can be expressed in three different ways:

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \bar{M}_z = \frac{\sum N_i M_i^2}{\sum N_i M_i^2}
\]

where \(N_i\) is the number of molecular species, \(i\), with molecular weight, \(M_i\). \(\bar{M}_n\) is the number average molecular weight, \(\bar{M}_w\), weight average molecular weight, and \(\bar{M}_z\) is the z-average molecular weight. The experimental techniques used to characterise the statistical molecular weights of polymers are summarised in the table below.
<table>
<thead>
<tr>
<th>Method</th>
<th>Principle</th>
<th>Statistical Weight Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-group Analysis</td>
<td>Measures number of end-groups by chemical analysis.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Ebullioscopy</td>
<td>Measures the thermodynamic changes in elevated boiling point of polymer solutions.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Cryoscopy</td>
<td>Measures the thermodynamic changes in the depressed freezing point of polymer solutions.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Osmometry</td>
<td>Measures the osmotic pressure difference between pure solvent and polymer solutes.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Vapour Pressure Osmometry</td>
<td>Measures the vapour pressure difference between solvent drops and polymer solute drops.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Light Scattering</td>
<td>Measures difference in light scattering of solvent and solute.</td>
<td>$M_w$</td>
</tr>
<tr>
<td>Small angle X-ray scattering</td>
<td>Measures differences in x-ray scatter of solute over solvent caused by electron density differences.</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Ultra centrifugation</td>
<td>Measures U.V. absorption changes as sample is spun.</td>
<td>$M_n, M_z$</td>
</tr>
<tr>
<td>Gel permeation chromatography</td>
<td>Separates molecular chains according to hydrostatic volume.</td>
<td>$M_z, M_w, M_x$</td>
</tr>
</tbody>
</table>

Table 1.1. Summary of methods used in characterising the statistical molecular weight of polymer.

The configuration that a polymer chain adopts (i.e., the three-dimensional arrangement of the molecular chains) is directly related to the conformational space an individual monomer can explore, minus the reduced degrees of freedom of this monomer when incorporated into the polymer chain. The conformational space explored by the monomer is constrained by the height of the rotational energy barriers between steady states. If the rotational energy barrier is low the conformational space explored by this structural motif will be large compared with a system that has a high rotational energy barrier. If a chain has sufficient thermal
energy it will surmount the energy barrier and adopt other low energy conformations. Nuclear magnetic resonance (NMR), electron spin resonance (ESR), X-ray and infra-red spectroscopy (IR) are some of the techniques used to determine the configuration of macromolecules.

1.2.1. Polymer Morphology

Polymers can adopt three types of morphology: amorphous crystalline and semi-crystalline. Each will be discussed in turn.

1.2.1.1. The Amorphous State

In the amorphous state a polymer chain adopts a random orientation. The lack of long range order allows the polymer chain to undergo significant molecular motion below the melting point by virtue of the available free volume. At low temperatures the polymer chains are frozen into a glass-like state, as the temperature is increased so does the motion of the polymer chain, resulting in a greater volume of explored conformational space. The polymer is now in the rubber-like state. Further heating results in a molten state until at high temperatures degradation may occur. These state transitions are classified into five regions, shown in figure 1.1., the glassy state (A-B), elastic state (B-C), rubbery state (C-D), rubber flow state (D-E) and finally the viscous state(E-F).

![Figure 1.1. This illustration is a plot of a temperature dependent property in relation to temperature.](image-url)
A transition through any of these states results in a corresponding change in mechanical and physical properties of the bulk material. The configuration of amorphous polymers can be elucidated from direct experimental measurements. A series of NMR pulse sequences can be used on liquid polymers to elucidate the molecular configuration while solid amorphous configuration studies require specialised equipment and techniques, e.g., cross-polarisation of magic angle spinning (CP-MAS) [1],[2],[3].

1.2.1.2. Glass Transition Temperature

Figure 1.1. shows a marked change in bulk properties from the glassy (A-B) to the rubbery state (C-D). The temperature at this transition region is the glass transition ($T_g$), and is characteristic only in polymers containing amorphous regions. The $T_g$ can be determined by measuring thermodynamic properties [4]: volume expansion coefficient ($\alpha$), heat capacity ($C_p$) and the isothermal compressibility ($K$) of the material. Those transitions that show a sharp discontinuity in the second derivative of the Gibbs energy with respect to temperature or pressure, are considered second-order thermodynamic properties.

First-order thermodynamic transitions are defined [4] as a sharp discontinuity in the first derivative of the Gibbs energy $G$, but a second order thermodynamic transition shows an even greater discontinuity. These thermodynamic property equations are shown in table 1.2.
## Table 1.2. Equations describing the 1st and 2nd-order thermodynamic transitions that occur at $T_g$.

On an atomic level, the free volume that an amorphous molecule possesses is due to the poor packing of the molecular chains. At temperatures below the $T_g$ there is only localised chain motion, by reducing the temperature even further it is possible to freeze out these localised motions. Experimental studies \cite{5} have shown that polymers containing the glycidyl ether structural motif, freeze out at -70°C. On increasing the temperature the polymer attains sufficient thermal energy for main chain motion to occur, it is at this point that defines the $T_g$.

The changes in the specific volume $v$ of a polymer with temperature are schematically represented in the following illustration (figure 1.2) for amorphous, crystalline and semi-crystalline materials. The same discontinuity is seen for $C_p$ and $\alpha$ measurements, although not necessarily the same shape.
Figure 1.2. Illustration of specific volume variation as a function of temperature and morphology.

\[ T_g \] is a function of molecular motion and the temperature at which \( T_g \) is observed is dependent on the chemical nature and structure of the molecules. These dependent properties can be categorised into five groups:

- **Chain flexibility** - by definition the more flexible the rotational bonds along the backbone of the chain the lower the \( T_g \). As the rigidity of the chain increases so the \( T_g \) increases.

- **Molecular structure** plays an important role in the motion of chains. Bulky groups increase the observed \( T_g \) whereas, for example, smaller groups would result in less steric hindrance resulting in greater chain motion. The tacticity of substituted groups on the chain or cis-trans isomerism in polydienes alter the chain flexibility and therefore the \( T_g \) and \( T_m \).

- **Molecular weight** - as the polymer grows, the chains become more tangled, therefore more thermal energy is required to increase main chain motion, resulting in increased \( T_g \).
**Degree of crosslinking** - with the introduction of crosslinking the number of degrees of freedom are dramatically reduced, therefore there is an increase in $T_g$ as the degree of crosslink density is increased.

**Thermal history** - The $T_g$ is not a genuine second order thermodynamic transition but has a kinetic element to its nature. This is demonstrated by an apparent reduction in the $T_g$ value as the cooling rate is lowered \([6],[7]\). The opposite behaviour is observed when the cooling rate is increased.

The $T_g$ of a material is experimentally determined by measuring these observed thermodynamic discontinuities and mechanical property changes with temperature. Differential scanning calorimetry (DSC) measures changes in heat capacity $C_p$, thermal mechanical analysis (TMA) measures the changes in the sample volume, to give the thermal expansion coefficient $\alpha$, while dynamic mechanical thermal analysis (DMTA) apparatus measures the changes in the modulus as a function of temperature. Experimental information about the DSC and TMA techniques will be discussed in detail in chapter 2, the DMTA technique is discussed below.

In a DMTA experiment a known sinusoidal stress is applied to the test sample at a given frequency (typical range 0.01-200 Hz, depending on modulus and sample type). The corresponding lagged sinusoidal strain of the material is measured over a desired temperature range. Below the $T_g$ the modulus is at its maximum value, while above the $T_g$, the modulus falls. Depending on how the sinusoidal stress is applied to the material the following moduli can be determined: torque, tensile, shear and flexural moduli. In polymeric materials some of the stress energy applied to a sample is stored as potential energy which is a measure of the storage modulus and applies to the elastic component of the material. The energy lost as heat, is measured by the 'loss tangent' $\tan \delta$ and is due to internal friction of the material. From this information the loss modulus can be determined. The moduli, $T_g$, $T_m$ and $\tan \delta$ measured by DMTA are all frequency dependant.

1.2.1.3. Crystalline and Semi-crystalline

Owing to the long range order of crystalline materials, there is no free volume therefore no $T_g$ is observed. When the temperature is sufficiently high the crystal will melt at a temperature $T_m^\circ$, see figure 1.2. Semi-crystalline materials contain
both amorphous and crystalline regions, which result in both thermodynamic transitions $T_g$ and $T_m$ being observed.

A detailed discussion about the crystalline and semi-crystalline states is beyond the scope of this thesis, but is discussed briefly here for completeness. The properties of a crystalline or semi-crystalline material are very different to their amorphous counterpart. A method to elucidate the presence of a crystalline region in a polymer can be studied from changes in enthalpy ($\Delta H$) as a function of temperature, using DSC. A characteristic crystallisation exotherm is observed along with its corresponding melting point as the temperature is increased. X-ray scattering experiments are used to precisely determine the 3-D structure of the crystalline polymers, while X-ray powder diffraction patterns are generated from semi-crystalline materials.

1.2.2. Polymer Categories

A polymer can be categorised further depending on the properties it possesses. These categories are summarised in table 1.3. It must be noted that these are not fixed definitions and in some cases many types of polymers exhibit a range of categories depending on how it has been processed, nevertheless it is a useful guide.
<table>
<thead>
<tr>
<th>Type of Polymer</th>
<th>Description</th>
<th>Examples</th>
<th>General Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elastomers</strong></td>
<td>Exhibit large reversible elongation under tensile load, i.e. low modulus. Possess good flexibility and toughness.</td>
<td>Natural rubber, Styrene-butadiene rubber (SBR), Silicon rubber.</td>
<td>Tyres, window and door sealants, flexible moulds.</td>
</tr>
<tr>
<td><strong>Fibres</strong></td>
<td>Polymers that can be drawn into fibres and when woven exhibit high durability and toughness. High modulus.</td>
<td>Nylon-6,6 (Urylon).</td>
<td>Clothing, bristles, upholstery, carpets.</td>
</tr>
<tr>
<td><strong>Thermoplastics</strong></td>
<td>Display plastic deformation above the $T_g$ and can be reformed. This cycle can be performed repeatedly, but not indefinitely.</td>
<td>Low and high density Polyethylene, Polypropylene, Poly(vinyl chloride) PVC, Polystyrene, Polycarbonate.</td>
<td>Kitchen products, toys, toilet products, pipes.</td>
</tr>
<tr>
<td><strong>Thermosetting Plastics</strong></td>
<td>Form insoluble, intractable products which do not soften when heated. The molecular structure is cross-linked. High $T_g$, excellent abrasion and dimensional stability.</td>
<td>Epoxy resins, Phenolic resins, Amino resins, polyester resins.</td>
<td>Surface coatings, adhesives, composites.</td>
</tr>
</tbody>
</table>

Table 1.3 Summary of polymer categories related to their properties.
1.3. Introduction to Epoxy Resins

1.3.1. The Epoxy Group

Epoxy resins are a family of 'pre-polymers' which contain one or more epoxide groups (or oxirane rings). The epoxide group is highly reactive. This is mainly due to the high polarity of this 'special type' of ether group and the ease with which this highly strained ring can be opened (the C-O-C angle is approximately 60°).

![Illustration of an epoxy group](image)

Figure 1.3. Illustration of an epoxy group

1.3.2. History

Like many other synthetic innovations, the commercial utilisation of epoxy resins increased rapidly after World War II. There were initial discoveries by McIntosh and Wolford [9],[10], Blumer [11], Fonrobert and Lemmer [12] and many others [13],[14],[15] who paved the way to full commercialisation of epoxy resins, in the early 1930's. However, Greenlee and Castan were the first to synthesise epichlorohydrin-bisphenol A resins as they are known today. Ciba A.G. of Basle were the first to manufacture epoxy resins commercially after Castan licensed the patent to them. In the early 1940's parallel work took place in the US where the Shell Chemical Corporation was granted the licence for the patent [16] by Greenlee and co-workers to start production.

There have been many new developments and products since those early days. Nevertheless, diglycidyl ether type epoxy resins represented 95% of the epoxy market by the late 1960's. Today there are three main producers of epoxy resins, accounting for over 70% of the world market; Ciba-Geigy (Araldite and Aracast),
Dow Chemicals Co. (D.E.R and D.E.N) and Shell Chemical Co. (EPON and Epikote).

Bisphenol-A diglycidyl ether (BADGE) is one of the most common types of epoxy resins, made from epichlorohydrin and Bisphenol A. Epichlorohydrin is commercially made from propylene and chlorine in a basic medium while bisphenol-A is synthesised from acetone and phenol. The preparation of BADGE was patented by Goppel [17] and is outlined below.

\[
\begin{align*}
\text{CH}_3\text{-CH} & \quad \text{O} \quad \text{Cl}, \\
\text{HOC} & \\
\text{NaOH} & \\
\text{Strong Acid Catalyst} & \\
\text{Cl} & \quad \text{CH}_2\text{-C} & \quad \text{NaCH} & \\
\text{Epichlorohydrin} & \\
\text{Bisphenol-A} & \\
\text{NaCH} & \\
\text{Bisphenol-A Epoxy Resin} &
\end{align*}
\]

Figure 1.4. Scheme highlighting the commercial synthesis of BADGE.

By varying the length of the average repeat unit (n), there is a marked change in the molecular weight, viscosity and epoxide content. This is achieved by adjusting the epichlorohydrin:bisphenol-A molar ratio. To obtain pure BADGE, a minimum ratio of 10:1 is commercially used. Obviously, there are many variations in formulating epoxies. For example to make very low viscosity epoxides, the bisphenol-A portion of the molecule can be replaced by an aliphatic group. The
Epoxy Equivalent Weight (EEW) is used commercially to characterise the amount of epoxy groups present in the molecule. It is defined as the weight of epoxide (in g/m's) containing 1 g/m (chemical equivalent) of epoxide. For BADGE this is equal to half the molecular weight.

Another type of epoxy are the novolak (phenolic) resins. They are not as widely used as conventional epoxy resins, but nevertheless are made commercially. They are produced by the reaction of phenol and formaldehyde in acid solution to form a novolak resin. Subsequent reaction with epichlorohydrine results in an epoxidised novolak resin, as shown below.

![Structure of a typical epoxidised novolak resin.](image)

The epoxidised novolak resin can be cured in a similar way to epoxy resin. The conditions can be adjusted to give tailored properties [18].

1.3.3. General Reactions

The epoxy ring is easily cleaved by nucleophilic attack, in the presence of both acid and base catalysts. Both mechanisms are $S_N2$ with the nucleophile attacking 'anti' to the oxygen.

In acid catalysed cleavage, the epoxide is protonated (figure 1.6). This accelerates the breaking of the C-O bond and assists in the attack of the carbon, in the transition state. The nucleophile $HX$: will preferentially attack a more hindered carbon, by virtue of the inductive effects of substituents.
Protonation

\[ \text{V} \text{O}^+ + \text{H}_2\text{O} \rightarrow \text{HO}^+ + \text{VO}^- \]

Nucleophilic Attack

\[ \text{HX}: \ne \text{V} \text{O}^- \rightarrow \text{XOH}^+ \rightarrow \text{XOH}^- + \text{H}_2\text{O} \]

Figure 1.6. Illustration of acid catalysed nucleophilic attack.

In base catalysed cleavage of the epoxide, the leaving group is an alkoxide, which is not as good as the hydroxyl group in acid catalysed reactions, therefore stronger nucleophilic reagents are needed, e.g. phenoxides, ammonia. There is no strong positive charge, therefore the position of attack by the nucleophile is at the less hindered carbon.

Figure 1.7. Illustration of base catalysed nucleophilic attack.
1.3.4. Curing of Epoxy Resins.

The cure process involves the formation of a three dimensional infusible network by cross-linking the resin chains and is a valuable property of epoxy resins. This is the process that gives the resin its characteristic mechanical and physical properties. There are two types of curing reactions, i) catalytic and ii) co-reactive.

1.3.4.1. Catalytic

The catalytic process does not influence the final structure, but aids the breakage of the epoxy ring. There are three types of catalysts that are briefly outlined below:

- **Lewis bases** - an example of a Lewis base cure is the reaction of tertiary amines (\(\text{NR}_3\)) on an epoxide group. This opens the epoxy ring forming a zwitterion that is then protonated by hydroxide groups in the resin. The resulting nucleophile reacts with another epoxy ring to form an ether bond.

- **Lewis acids** - an example is the reaction of BF\(_3\) which is initially complexed with an amine (BF\(_3\).NH\(_2\)R) and then reacts with the epoxy group. This has been proved to be very successful in curing BADGE [19],[20].

- **Photoinitiated cationic curing agent** - These are salts, the anions of which have low nucleophilicity. Upon u.v. irradiation, they yield a Lewis or Bronsted acid, which initiates curing. An example of this is triarylsulphonium salts- \(\text{Ar}_3\text{S}^+\text{PF}_6^-\), which yield \(\text{Ar}_2\text{S}^+ + \text{Ar}^- + \text{PF}_6^-\) on irradiation.

These catalytic curing agents induce homopolymerisation, a reaction discussed in section 1.2.5.2.
1.3.4.2. Co-reactive curing.

In 1933, Schlack [21] documented the reaction of several diepoxides with organic acids and amines. Today amines are the most widely used curing agents and will be discussed in greater depth.

In this case the curing agent acts as a co-monomer reacting with the epoxy and hydroxyl groups to form a linear or cross-linked network system, depending on the functionality of the co-monomer and the number of epoxy groups on the molecule. Unlike the catalytic curing agents, stoichiometric amounts of the curing agent are used. Aliphatic [22],[23] and aromatic [24],[25],[26] amines, polyamides and acid anhydrides [27],[28],[29],[30],[31] are commonly used co-reactive curing agents.

The scheme below illustrates the reaction of a primary amine with a mono epoxide.

![Reaction Scheme](image)

Figure 1.8. Simplified mechanism of a mono epoxy resin being cured by a primary amine.
Schechter et al. [32] along with Kakurai et al. [33] showed that the presence of hydroxyl species accelerates the cure by partially protonating the oxygen in the epoxide group, thus making it more susceptible to nucleophilic attack, as shown figure 1.8. There are a number of species that can protonate the epoxy ring, for example, water, the [1:1] and [2:1] adducts formed in the above example and also the amine (auto catalysis).

The most commonly used aromatic amines are $m$-phenylenediamine (MPD) [34], 4,4'-diaminodiphenylsulphone (DDS) [35] and 4,4'-diaminodiphenylmethane (DDM) [36]:

![Chemical structures](image)

These tetrafunctional curing agents are usually reacted with BADGE to form an amorphous intractable cross-linked system, illustrated schematically in figure 1.9. The overall structure of such systems is extremely complicated and are virtually impossible to analyse and characterise fully.
1.3.5. Other Possible Reactions

There are three further reactions which require consideration, etherification, homopolymerisation and cyclisation. The former two reactions involve the reaction of the hydroxyl groups on the polymer chain with epoxy groups to form an ether link. The difference between them is the reaction mechanism which is discussed below.

1.3.5.1. Etherification

A general scheme for the etherification reaction is shown below. Here the epoxy group reacts with hydroxyl groups present in the epoxy resin.
This reaction is only significant when the temperature is above 150°C [37],[38] or when the reaction reaches the later stages of a stoichiometric reaction [39]. It has been demonstrated that excess epoxide [40] and impurities [41],[42] increase the likelihood of etherification.

1.3.5.2. Homopolymerization

This reaction involves the opening of the epoxide ring by means of a catalyst, figure 1.11). The mechanism for this reaction is still disputed [43], but the overall result is shown below

\[
\begin{align*}
R' - O & \quad \text{CAT} \\
\text{R-CH-CH}_2 & \\
\text{R-CH-CH}_2 :\text{CAT} + & \quad \text{R-CH-CH}_2 :\text{CAT}+ \\
\text{R-O-CH}_2 - & \quad \text{R-O-CH}_2 - \\
\end{align*}
\]

Figure 1.11. Example of a Lewis Base (R₃N-) catalysed homopolymerisation.

This catalyst (:CAT) can either be Lewis acids or Lewis bases as previously mentioned in section 1.2.4.1, the above mechanism is for a Lewis base. The mechanism for a Lewis acid is somewhat different to the above.

1.3.5.3. Cyclisation

The formation of cyclisation products occurs during the cure of an epoxy system and affects the rheology during cure and the crosslink density of the resulting network. Formation is dependent on structure (steric factors), electronic factors, stoichiometry, temperature and catalysis. Johncock et al. [44] and Attias et al. [45] have studied a range of intramolecular cyclisation reactions by way of the
etherification and amine cure reaction. Examples of the types of cyclisation products investigated by Johncock et al. and Hörhold et al. \cite{46} are represented by structures (I) and (II) respectively.

![Chemical structures (I) and (II)](image)

Figure 1.12. Example of (I) intramolecular and (II) amine cure cyclisation.

1.3.6. Properties and Application of Epoxy Resins

The properties of epoxy resins can be varied depending on the curing agent and the type of epoxy used. The properties that are of commercial importance are the reactivity, pot life, viscosity, toxicity, chemical, physical and mechanical properties.

The reactivity of a curing agent is important when large quantities are mixed, for the reaction mixture could become hot causing autoinitiation before it is properly applied. Pot life is of importance when the mixing of components and the application is conducted in different locations. Therefore it is important for the resin system to remain stable and not cure prematurely. Viscosity plays a significant role when considering how the epoxy system has to be applied. In some applications the epoxy system may have to be sprayable, brushable, be used as a filler or coating. The toxicity of a material is obviously of commercial importance; aliphatic and aromatic amines tend to be very toxic and carcinogenic. The chemical properties, which encompass chemical attack, abrasion properties and heat deformation are also dependent on the chemical composition of the cure agent. Finally, the mechanical and physical properties of the bulk system are very much dependent on the curing agent selected.
The following table summarises the types of cure agents commercially available, their advantages, disadvantages and applications.

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulphides</td>
<td>Moisture insensitive, Quick set time, Flexible</td>
<td>Odour, Poor elevated temperature performance</td>
<td>Adhesives, sealants</td>
</tr>
<tr>
<td>Aliphatic amines</td>
<td>Convenience, Room temperature cure, Low viscosity, Low formulation cost</td>
<td>Critical mix ratios, Strong skin irritant, High vapour pressure, Blushes</td>
<td>Civil engineering, adhesives, grouts, casting and electrical encapsulation</td>
</tr>
<tr>
<td>Polymides</td>
<td>Convenience, Room temperature cure, Low toxicity, Good flexibility or resilience, Good toughness</td>
<td>High viscosity, Low heat resistance, Low vapour pressure, Some incompatibility with epoxy resins</td>
<td>Civil engineering, adhesives, grouts, castings, coatings</td>
</tr>
<tr>
<td>Amidoximes</td>
<td>Reduced volatility, Convenient mix ratios, Good toughness</td>
<td>Poor elevated temperature performance</td>
<td>Construction adhesives, concrete bonding, troweling compounds</td>
</tr>
<tr>
<td>Aromatic amines</td>
<td>Moderate heat resistance, Good chemical resistance</td>
<td>Solids at room temperature, Long, elevated temperature, cure schedules, Carcinogenic</td>
<td>Filament wound pipe, electrical encapsulation, adhesive</td>
</tr>
<tr>
<td>Dicyandiamide</td>
<td>Latent cure, Good elevated temperature properties, Good electrical properties</td>
<td>Long, elevated temperature cure, Insoluble in resins</td>
<td>Powder coatings, electrical laminates, one-component adhesives</td>
</tr>
<tr>
<td>Catalytic</td>
<td>Extremely long pot life, High heat resistance</td>
<td>Long, elevated temperature cure schedules, Poor moisture resistance</td>
<td>Adhesives, electrical, encapsulation, powder coatings, electrical laminates</td>
</tr>
<tr>
<td>Anhydrides</td>
<td>Good heat resistance, Good chemical resistance</td>
<td>Long elevated temperature cure schedules, Critical mix ratios</td>
<td>Filament wound pipe, electrical encapsulation and adhesives</td>
</tr>
<tr>
<td>Melamine formaldehyde</td>
<td>Good hardness and flexibility, One-package stability, Solvent-free systems</td>
<td>Elevated temperature cure</td>
<td>Waterborne coatings, container and deco finishes</td>
</tr>
<tr>
<td>Urea formaldehyde</td>
<td>Good film colour, One-package stability, Good intercoat adhesions</td>
<td>Elevated temperature cure</td>
<td>Fast bake enamels, primers and topcoats</td>
</tr>
<tr>
<td>Phenol formaldehyde</td>
<td>Good elevated temperature properties, Good chemical resistance, Good hardness and flexibility</td>
<td>Solid, Poor weatherability</td>
<td>Powder coatings, moulding compounds</td>
</tr>
</tbody>
</table>

Table 1.4. Summary of types of curing agents used, together with advantages, disadvantages and application.
It can clearly be seen that there are many variable factors [47] that can be changed to obtain the desired commercial property. To cover all these variables is beyond the scope of this work, but there is a wealth of literature [48], [49] that covers these points.

1.4. Introduction to Molecular Modelling of Polymers

Owing to the complex structure of amorphous polymers, modelling and computer simulation studies of polymers have only recently become readily feasible with increased computer power and availability. If the development of polymer modelling is compared with that of protein and nucleic acid modelling [50], where there is a wealth of structural information (from X-ray diffraction studies), or even with metals, ceramics and crystal structures, the area of polymer modelling has lagged behind. To obtain reliable and sensible macroscopic property results (i.e. observed results) from microscopic data (i.e. atomistic co-ordinates and momentum), large representative models are required along with sufficient computing time to simulate the necessary equilibrium or even non-equilibrium processes. (The determination of macroscopic properties from microscopic information will be discussed in greater detail in chapter 3.) Significant progress has been made in the field of molecular modelling of polymers as computer hardware has developed. This has allowed complicated and time consuming calculations to be performed within a reasonable time period.

Classical molecular modelling of polymers is primarily used to understand the atomistic behaviour and properties of the materials, with the ultimate aim of being able to predict the behaviour and properties of materials that have not been synthesised. Such possibilities are commercially very attractive, with potentially large savings in the development of new materials. This is exemplified in the pharmaceutical industry, where stringent preclinical trials, which take many years are required. In many cases it takes up to 10 years from discovery of a potential drug to production, costing tens of millions of pounds. If a potential drug is abandoned toward the later stages of its development, considerable effort is commercially lost. To maximise the chance of success, biological molecular modelling is employed to rationally design and screen potential drugs at the early stages of development, before the compound has been synthesised, hence reducing
the effort required in costly laboratory experimentation. It is for this reason that all major pharmaceutical companies employ molecular modelling techniques [51].

Cost is also of great importance to chemical companies, therefore modelling is becoming a more attractive proposition [52]. Today macromolecular modelling is being used to predict with confidence the behaviour of materials not yet prepared under all possible processing conditions.

An exciting aspect of computer modelling is that it bridges the gap between the two fundamental scientific activities: experiment and theory. This bridge can be classified as a third class of scientific activity: computer experiment. This can be represented by the following figure 1.12.

![Figure 1.13. An illustration of how the experiment and theory can be bridged by computer experiments.](image-url)
There are many advantages to conducting computer experiments. Firstly, they allow artificial conditions that cannot be easily implemented experimentally to be tested. Secondly, it allows phenomena that occur quickly or events that are not easily observed experimentally to be studied. The uses of computer experiments are seemingly limitless and can be applied to many scientific disciplines, including physics, engineering, and meteorology.

1.5. Outline of Research

Over the past decade radio HPLC has been used as an analytical tool to determine the kinetics of simple epoxy systems. As previously mentioned the reaction of commercial epoxy-amine systems is very complicated, resulting in an intractable 3-D crosslinked network, this limits the amount of investigative chemistry that can be performed which is required for kinetic studies. To overcome this hurdle the use of model systems was suggested. This entailed reacting a monoepoxy, like phenyl glycidyl ether (PGE) with a monoamine, N-methylanaline or a diamine, aniline. This reaction is illustrated in figure 1.8, with the formation of low molecular weight adducts.

Jones et al. [53],[54],[55] developed and used a method that incorporates a tritium label into the ring of an aromatic amine, by way of a catalytic reaction. This "hot" amine was reacted with the correct stoichiometric amount of "cold" epoxy. Taking aliquots of the reaction and separating the reaction species by HPLC and determining the concentration of each species from the radioactive concentration, it is possible to follow the reaction and calculate the rate constants by modelling the reaction.

Parker et al. [56] investigated the various factors influencing the kinetics of these simple reactions. These factors include, hydrogen bonding, viscosity and hydroxyl concentration, quantifying the effect of these factors on the rate constants using a program written by Buist and Howlin, based on the Runge-Kutta method [57], which modelled the reaction.

The next evolutionary step toward cross-linked commercial systems are linear epoxy polymers. This involves the reaction of a diepoxy and diamine, to form linear chains. These systems are not usually commercially available or viable, but
nonetheless yield interesting kinetic, physical and mechanical properties. The aim of this work is to build an atomistic model based on experimental information and to utilise simulation methodologies and theories to determine the mechanical and physical properties of a linear epoxy polymer. The atomistic behaviour of the polymer will be studied during the property determining simulations, in an attempt to gain fundamental atomistic information.

The kinetics study which involves the development of a kinetic model to determine the rate constants for the formation of each individual species formed, using radio-HPLC is being investigated by Aspin et al. [58]. The development of a kinetic model is no trivial task considering there are some fifty-two rate constants for the first ten species formed in a linear epoxy polymer reaction.

The flow diagram figure 1.13 illustrates how the work was planned. The thesis is divided into four sections, experimental, simulation, empirical and a comparative section, based on figure 1.12.

Figure 1.14. Illustration of research plan.
The linear epoxy polymer was characterised by spectroscopic and chromatographic methods, as described in chapter 2, physical and mechanical property tests were also conducted. By coupling the structural information with the property, it was possible to quantify the relationship between property and the degree of cure.

The concept of molecular modelling is introduced and discussed in greater detail, in chapter 3. To demonstrate the modelling techniques used, the mechanical properties of simple polyethylene-like models were studied and compared with experimental data.

In chapter 4, representative atomistic models were built, based on the structural information from chapter 2. Additional crystallographic data was used to validate the force field parameters, justify the motions of the molecular chain, and study the response of these linear chains to stress and temperature.

The simulation and empirical calculations for the determination of both physical and mechanical properties are calculated and discussed in chapter 5. Comparisons are made among all three techniques; experimental, computer experiment and theory, showing that good correlation could be seen.

Finally, in chapter 6, a brief summary is given of the results in the preceding chapters, with further discussion on the implications of these results and suggestions on possible areas of future work.
1.6. References

Chapter 1 Introduction

23 Strother S. W. US. Patent 3,303,144. (1967)
30 May C. A., Tanaka Y., Epoxy Resin Chemistry & Technology, N.Y., (1973)
36 Bandaruk W., Plas. World, 16, (1957)
44 Johncock P., Tudgey G.F., Structural features in epoxy networks from N-diglycidyl epoxies and amines: 1. Dominant intramolecular cyclisation
reactions of N,N-diglycidylaniline with aniline and substituted anilines. 
Polymer 32, 323, (1991)
46 Hörhold H-H., Klee J., and Bellstedt K., Hochmolekulare Lineare Epoxid- 
Amin-Additionspolymere. Z. Chem. 22, 166, (1982)
47 Gould R. F., Epoxy Resins, Advanced in Chemistry Series 92, American 
48 Lee H., Neville K., Handbook of epoxy resins, MacGraw-Hill, New York, 
(1967)
51 Blaney F., Molecular Modelling in the Pharmaceutical Industry, Chemistry & 
52 Case F., Winter J., Bott D., Molecular Modelling in the Pharmaceutical 
Industry, Chemistry & Industry., 23, 784, (1990)
53 Buist G. B., Hagger A.J, Jones J R., Barton J.M., Wright W.W., Relative 
reactivity of primary and secondary aromatic amines in the reaction with 
phenyl glycidyl ether. Polymer Communications 29, 5, (1988)
54 Jones J.R., Wright W.W., Poncipe C., Barton J.M. A radiochemical study of 
the kinetics of epoxide cure: Reaction of phenyl glycidyl ether and other 
model epoxides with various imidazoles. Polymer 28, 1358, (1987)
55 Buist G.J., Hagger A.J., Howlin B.J., Jones J.R., Parker M.J., Barton J.M., 
Wright W.W., Chemical modelling studies of amine-epoxide reactions. 
Polymer communications 31 : 265, (1990)
57 Walker R. D. Numerical Methods for Engineers and Scientists, Practical 
Applications Using the IBM PC, p. 232. TAB books Inc., Blue Ridge Summit, 
Pa. (1987)
58 Aspin I., Barton J.M., Buist G.J., Deazle A.S., Hamerton I, Howlin B.J., Jones 
I.R., J. Material Science in press
Characterisation of a Linear Epoxy Polymer by Experiment

2.1. Introduction

2.2. Spectroscopic Characterisation

2.2.1. Nuclear Magnetic Resonance (N.M.R) Spectroscopy

2.2.1.1. Introduction

2.2.1.2. Principles of NMR Spectroscopy

2.2.1.3. Instrumentation

2.2.1.4. 1H spectrum of BADGE

2.2.1.5. 1H spectrum of DAE

2.2.1.6. 1H spectrum of the linear epoxy polymer

2.2.1.7. DEPT 135 experiment on the linear epoxy polymer

2.2.1.8. 1H-13C correlation of the linear epoxy polymer

2.2.1.9. 1H NMR Kinetics of the Linear Epoxy Polymer

2.2.2. Ultra Violet Spectroscopy of components of the Polymer

2.3. Chromatographic Characterisation

2.3.1. Introduction to Gel Permeation Chromatography

2.3.2. Experimental Section

2.3.2.1. Materials

2.3.2.2. Polystyrene Standards

2.3.2.3. Epoxy Standards

2.3.2.4. Sample Preparation

2.3.2.5. Apparatus and Conditions

2.3.2.6. GPC and HPLC experiments

2.3.3. GPC and HPLC results

2.4. Physical Property Determination

2.4.1. Thermal Analysis

2.4.1.1. Principles of Differential Scanning Calorimetry

2.4.1.2. DSC Measurements

2.4.1.3. Thermomechanical analysis

2.4.1.4. TMA Sample Preparation

2.4.1.5. TMA Calibration
2.1. Introduction

This chapter describes the spectroscopic and chromatographic techniques that were used in characterising the linear epoxy polymer. The starting materials were initially characterised along with the resulting molecular chains. The physical and mechanical properties were then determined and related to the degree of cure.

2.2. Spectroscopic Characterisation

2.2.1. Nuclear Magnetic Resonance (N.M.R) Spectroscopy

2.2.1.1. Introduction

$^1$H NMR was used to characterise and confirm the structure of the starting materials, bisphenol-A diglycidyl ether (BADGE) and 1,2dianilinoethane (DAE). Owing to the complicated $^1$H NMR spectrum obtained for the linear epoxy system a $^{13}$C-$^1$H correlation plot in conjunction with a DEPT (Distortionless Enhancement by Polarisation Transfer) experiment were used to determine the structure. These experiments confirmed that neither homopolymerisation nor etherification played a part in the reaction. The initial stages of epoxy consumption were studied and compared with the same system followed by HPLC.

2.2.1.2. Principles of NMR Spectroscopy

Nuclear magnetic resonance spectroscopy deals with the interaction between the magnetic moments of atomic nuclei and magnetic fields. This magnetic moment is related to the nuclear spin $I$.

The nuclei of interest, $^1$H and $^{13}$C both have a nuclei spin of $\frac{1}{2}$. The nuclei can orientate themselves in $2I+1$ ways, therefore alignment of these nuclei in an applied magnetic field $B_0$ is either parallel or antiparallel. These orientations correspond to low $\alpha$ and high $\beta$ energy states respectively, where the population of the $\alpha$ state is greater than the $\beta$ state ($N_\alpha > N_\beta$). The population of the states can be determined by the Boltzmann distribution.

When a radio frequency signal is applied to the system as a single powerful pulse, there is a change in the population distribution from the $\alpha$ state to $\beta$ state. A time is chosen so that the net magnetisation of the system is perturbed by $90^\circ$ when a
radio impulse is applied. The net magnetisation is initially parallel to the applied magnetic field because the population of this state is very large. Removal of the impulse results in the relaxation of the individual nuclei, through interaction with local fluctuating magnetic fields, back to their equilibrium states. This is called the free induction decay (FID). Owing to the complexity of the FID, Fourier transformation (FT) has to be used to convert the signal into a spectrum.

DEPT is a technique which allows the identification of quaternary, methine, methylene and methyl carbons, while a $^1$H-$^{13}$C correlation spectrum assigns each proton to the carbon to which it is bonded.

2.2.1.3. Instrumentation

All the following spectra were collected on Bruker WM300 and AC300 spectrometers with Aspect 2000 and 3000 data systems. The data was analysed using Bruker software.

2.2.1.4. $^1$H spectrum of BADGE

The $^1$H NMR spectrum was run in deuterated chloroform at 298K, see figure 2.2. Tetramethylsilane (TMS) was used as an internal reference standard. The epoxide ring methylene and methine groups are multiples centred at 2.65ppm and 3.3ppm respectively, while the ether methylene group multiplet resides at 4.0ppm. The sharp singlet at 1.6ppm can be assigned to the isopropylidene methyl group, while the para substituted double doublet is centred at 7.0ppm. The integrals are shown to highlight the number of protons assigned to each peak. It clearly shows that there are undetectable amounts of high oligomeric forms of BADGE present, where $n>0$, see figure 2.1. The spectrum shows no spurious residual peaks demonstrating the purity of the BADGE. The exact purity of the BADGE was determined by HPLC.
Figure 2.1. Illustrates the formula for higher molecular weight epoxies which can exist. No broad complex bands at 3.65ppm are seen on the NMR spectrum in figure 2.2. This is indicative of the presence of hydroxy groups. Therefore for our system $n = 0$.

Figure 2.2. A $^1$H NMR spectrum of BADGE

2.2.1.5. $^1$H spectrum of DAE

The DAE was recrystallised from chloroform before use. The $^1$H NMR spectrum was run in deuterated chloroform at 298K, see figure 2.3. TMS was used as an internal reference standard. The ethylene group shows a sharp singlet near 3.35ppm, while the secondary amine proton singlet typically [1] resides in the amine 1-5ppm range at 3.8ppm. The monosubstituted phenyl rings show the characteristic phenyl splitting pattern at 7ppm. There were no detectable impurities present in the spectrum and the integrals show no peculiarities in the ratio of protons present. HPLC was used to determine the exact purity of the DAE.
2.2.1.6. $^1$H spectrum of the linear epoxy polymer

The linear epoxy system was prepared by mixing a 1:1 molar ratio of BADGE and DAE and heating it at 100°C for 5hrs. The resulting mixture was analysed using $^1$H and $^{13}$C NMR spectroscopy.

The initial $^1$H spectrum of the linear epoxy system showed line broadening at 2.8ppm and 3.2ppm, corresponding to the hydrogen bonding resonance positions of the -OH and -NH protons. To remove these broad peaks a drop of D$_2$O was added to the deuterated chloroform and a $^1$H spectrum was re-run at 298K, using TMS as the internal reference standard, see figure 2.4. The opening of the epoxy ring produces a broad complex band at 3.65ppm with the DAE ethylene protons falling within this region making peak assignment difficult. The remaining peaks correspond to the monomer peaks shown in figure 2.2 and 2.3. The spectrum characteristically [2] shows a loss of absorption in the 2.5-3.5ppm region but an increase in intensity at 4.0ppm. The proton ratio cannot be usefully interpreted from the integrals, due to a large number of different oligomers present, see figure 2.4.
Figure 2.4. $^1$H spectrum of the linear epoxy system at 298K. See figure 2.2 and 2.3 for notation.

2.2.1.7. DEPT 135 experiment on the linear epoxy polymer

The linear epoxy sample prepared in the previous experiment was dissolved in deuterated chloroform and the $^{13}$C spectrum was run at 298K. The upper spectrum (a) in figure 2.5 shows the -CH$_3$ and CH groups in the upward position while -CH$_2$ groups are in the downward position. The difference in the number of peaks in the lower spectrum (b), and the upper spectrum (a) highlight the quaternary carbons.
Figure 2.5. A DEPT 135 spectrum of the linear epoxy polymer.

2.2.1.8. $^1H-^{13}C$ correlation of the linear epoxy polymer

The sample used for the DEPT 135 experiment was re-run at 298K. Figure 2.6 shows the $^1H-^{13}C$ correlation plot. The peaks have been assigned to their corresponding protons and carbons, using the proton spectra of each monomer and also from the $^{13}C$ spectra of similar linear epoxy polymers measured by Hörhold et al. [3].
Figure 2.6 A $^1\text{H}$-$^{13}\text{C}$ correlation plot of the linear epoxy polymer.
2.2.1.9. $^1$H NMR Kinetics of the Linear Epoxy Polymer

A (1:1) molar ratio of BADGE and DAE were mixed at 50°C without solvent. The reaction was followed by $^1$H NMR at 373K for 3hrs.

The temperature was calibrated using 80% ethylene glycol in D$_6$-DMSO. This gave a value of 7.80(24)ppm, corresponding to a temperature of 373K. Forty scans were made every 10mins.

The epoxy consumption was followed by measuring the integral of the epoxy methylene group at 2.8ppm, while using the integral of the methyl group at 1.6ppm as an internal reference which remains constant during the reaction, see figure 2.2. The following formula was used to calculate the epoxy concentration at each time interval,

$$[\text{Epoxy}] = \frac{I_{\text{epoxy H}}}{I_{\text{methyl H}}} \cdot \frac{\text{No. of methyl protons}}{\text{No. of epoxy protons}}$$  \hspace{1cm} \text{eqn. 2.1}

where $I$ is the integral of the epoxy methylene and isopropylidene methyl groups. Figure 2.7. shows the progression of the reaction in the 1.6-4.2ppm region over a 2.5hrs period. The peaks after this period become increasingly broader as the viscosity of the linear polymer increases.

Figure 2.7. A $^1$H NMR stack plot of the reaction between BADGE and DAE at 100°C
The total epoxy concentration calculated above was compared with that determined from HPLC. The results will be discussed in section 2.6.1.

2.2.2. Ultra Violet Spectroscopy of components of the Polymer

As UV analysis was used to measure the different species separated and eluted by GPC, it was important to optimise the absorption associated with each oligomeric species, hence the correct wavelength used was determined.

UV spectroscopy is used to measure the transition of electrons between electronic energy levels. The wavelength at which absorption occurs is a measure of the separation between these electronic energy levels. These transitions are usually from a bonding (p-, d-, π-) or lone-pair orbitals to an unfilled non-bonding or anti-bonding orbital. The absorption (A) is proportional to the concentration (c) of molecules present (Beer's law), while the intensities of the incident (I₀) and transmitted (I) light are independent of each other (Lambert's Law). The absorption A = \log_{10}(I₀/I), therefore the molar extinction coefficient [1] \( \epsilon \) through a path length l is

\[
\epsilon = \frac{A}{l.c} \tag{eqn. 2.2}
\]

Low concentrations of BADGE and DAE were made up separately in methanol. Data from the UV spectrum are outlined in table 2.1 BADGE has a lower extinction coefficient than the aromatic amine, so to optimise the absorption of the epoxide its \( \lambda_{\text{max}} \) was taken as the detection wavelength.
<table>
<thead>
<tr>
<th></th>
<th>concentration</th>
<th>Absorption</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BADGE</td>
<td>7.058x10^{-4}</td>
<td>1.1</td>
<td>276.3</td>
<td>1564</td>
</tr>
<tr>
<td>DAE</td>
<td>6.604x10^{-4}</td>
<td>2.7</td>
<td>262.9</td>
<td>4057</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.5</td>
<td>276.3</td>
<td>2271</td>
</tr>
</tbody>
</table>

Table 2.1 Results from UV experiment. The UV cut-off for methanol and chloroform are 210 and 245nm respectively.

2.3. Chromatographic Characterisation

2.3.1. Introduction to Gel Permeation Chromatography

The main object of the gel permeation chromatography (GPC) work was to determine the statistical molecular weights of the linear epoxy polymer. Full characterisation by weight of the system allowed the correct molecular weights to be assigned to each determined physical and mechanical property values. The kinetics of the system will be outlined but due to the complexity of the system no individual rate constants were calculated. Comparisons were made briefly between the NMR and HPLC kinetic data.

Gel permeation chromatography is used to determine weight variations by separating the oligomeric components in a polymeric material. A solid sample is first dissolved in a suitable solvent, allowing individual chains to uncoil. The solution is then injected into a column containing a porous gel material which separates the molecular species according to their hydrodynamic volumes (i.e. effective sizes in solution). The gel is usually a highly cross-linked non-ionic stationary phase such as polystyrene or macro porous silica particles. The larger molecular species cannot permeate through the pores material and are eluted first. However, the smaller molecules penetrate through the pores and are retained for a longer period.

The relationship between the molecular weight and the retention time decreases logarithmically with increasing time. A calibration of retention time versus
molecular weight can be obtained by injection of known polystyrene standard molecular weight distributions. The concentration of the separated species can be measured by using a number of techniques such as refractive index, U.V., radiodetection, etc.

The resulting chromatogram is a molecular weight distribution plot of individual species present in the sample. From this plot it is possible to calculate various molecular weight averages. These include the number average molecular weight ($M_n$), the weight average molecular weight ($M_w$), the $z$-average molecular weight ($M_z$) and if the Mark Houwink ($\alpha$) is known the intrinsic viscosity ($\mu$) can be calculated. Their relative positions are shown below in figure 2.8.

![Molecular Weight Distribution Plot](image)

**Figure 2.8.** A schematic of a high molecular weight polymer containing oligomers.

### 2.3.2. Experimental Section

#### 2.3.2.1. Materials

The linear epoxy formulation consisted of 1,2-dianilinoethane (DAE) (99.5%, Aldrich) and diglycidyl ether of bisphenol A (BADGE) (99.5%, Shell Chemical Company, [EPON® resin 825]). 1,2-epoxy-3-phenoxypropane (99%, Aldrich) commonly known as phenylglycidylether (PGE) was also used with the aromatic amine to prepare standards. The purity of each material was validated using HPLC and melting point determinations.
2.3.2.2. Polystyrene Standards

A series of standard polystyrene calibrants, from Polymer Labs, were used to calibrate the GPC apparatus. Each standard contained a known distribution of polystyrene weights, as shown below in table 2.2., and shared a reference point with another standard.

<table>
<thead>
<tr>
<th>Polystyrene Standards</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>196000 22000 3250 580</td>
</tr>
<tr>
<td>PS2</td>
<td>111000 22000 5050 1060</td>
</tr>
<tr>
<td>PS3</td>
<td>111000 11600 2450 580</td>
</tr>
</tbody>
</table>

Table 2.2. The weight values correspond to a maximum value for a known weight distribution.

The molecular structure and composition of the polystyrene calibrants and linear epoxy system are different, therefore it was necessary to restandardize the standards with known epoxy systems.

2.3.2.3. Epoxy Standards

A 2:1 molar mixture of PGE and DAE were mixed and heated for 5 hours at 90°C. This produced a mixture containing the starting materials, 1:1 adduct and 2:1 adduct as shown in figure 2.9.
2.3.2.4. Sample Preparation

Equimolar quantities of BADGE and DAE were stirred using a magnetic follower for 1 hour at 70-80°C to produce an homogenous mixture. It was essential that all the aromatic amine has dissolved. Once this was accomplished sampling could commence. Using a glass pipette samples were placed into 20 x 2cm³ plastic eppendorfs over a five minute period. These eppendorfs were then placed in a preheated silicone oil bath set at 100°C. At half hour intervals an eppendorf was removed and quenched in liquid nitrogen and then placed in a freezer for storage. The procedure was repeated three times, over a 10 hour period. The sampling became more viscous over this period, as seen from the viscosity measurements in section 2.4.2, therefore normal sampling procedures could not be used.
2.3.2.5. Apparatus and Conditions

Two sets of apparatus were used. The GPC types and the conditions used are outlined below in table 2.3. GPC-I was used to follow the initial stages of the reaction. The column used had a separation range of 0-30,000 molecular weight. The reaction was also followed in HPLC mode to calculate the percentage concentration of each species, described above. In addition to the column mentioned above, GPC-II had a second column in series, which had a separation range of 10,000-100,000 molecular weight, the later stages of the reaction were followed using this apparatus.

<table>
<thead>
<tr>
<th></th>
<th>HPLC/GPC-I</th>
<th>GPC-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection/pump system</td>
<td>Waters Model 510</td>
<td>Waters Model 510</td>
</tr>
<tr>
<td>UV detector</td>
<td>Cecil Instruments</td>
<td>Waters Model 450</td>
</tr>
<tr>
<td>Data Modules</td>
<td>Waters Model 730</td>
<td>Waters Model 730</td>
</tr>
<tr>
<td>Column (1)</td>
<td>PLgel 3m Mixed-E</td>
<td>PLgel 3μ Mixed-E</td>
</tr>
<tr>
<td>Column (2)</td>
<td>µSTYRAGEL 10^4Å</td>
<td></td>
</tr>
<tr>
<td>flow rate</td>
<td>1ml/min</td>
<td>1ml/min</td>
</tr>
<tr>
<td>solvent</td>
<td>CH₂Cl₂/Methanol (95:5)</td>
<td>CH₂Cl₂/Methanol (95:5)</td>
</tr>
<tr>
<td>λ_{(max)} (epoxy system)</td>
<td>276nm</td>
<td>276nm</td>
</tr>
<tr>
<td>λ_{(max)} (polystyrene)</td>
<td>254nm</td>
<td>254nm</td>
</tr>
</tbody>
</table>

Table 2.3. Summary of GPC and HPLC conditions used to study the reaction between BADGE and DAE at 100°C.

2.3.2.6. GPC and HPLC experiments

Solid samples weighing ~1mg were dissolved in ~2cm³ of dichloromethane:methanol (95:5), (HPLC grade, BDH and May & Baker respectively). The same solvent composition was used as the GPC and HPLC mobile phase. The samples once dissolved were passed over a filter (Millipore, 0.45μm). Between 30-100μl were injected into the GPC and HPLC depending on the sample concentration.
Whilst the apparatus was in HPLC mode the concentrations of the BADGE, DAE, and the resulting species that formed were calculated by measuring the individual peak areas and expressing the concentration as a percentage of the total peak areas on the chromatograms, see figure 2.10. The HPLC mode was only used for the first 2.5hrs of the reaction as a comparison with the NMR spectra. The GPC mode was the main technique for determination of the molecular weight distribution, $M_n$, $M_w$ and $M_z$.

2.3.3. GPC and HPLC results

The first four species formed by the BADGE and DAE were analysed by HPLC. The results are shown in figure 2.10.

![Plot of % concentration of oligomers formed from BADGE and DAE, at 100°C, over a 2.5hr period. (A) represents DAE, (E) - BADGE. $(AE)_2$ indicates species of greater molecular weight than $(AE)_2$.](image)

The retention time (RT) associated with peaks of high oligomer weights i.e. $(AE)_2$ were measured but peaks were not well resolved, so the relative concentrations of these higher oligomers could not be readily determined. From the GPC calibration a calibration curve was obtained. This relates molecular weight to retention times and will be referred to as the measured molecular weight.
Using the calibration curve value from the GPC and the HPLC retention times each peak was identified by its calculated molecular weight. Each calculated molecular weight was corrected by the factor 0.64825 determined from the epoxy calibration curve.

All the molecular weights present in the epoxy calibration standards were below the lower limits of the polystyrene standard at 580. Therefore the correction factor for the epoxy standards gave an approximate value. Using this value it is possible to assign the corrected weights of each species to the actual weights.

The standard deviation value for the correction factor determined from the epoxy standards shows that for a corrected weight of 10,594 the standard deviation is 552, i.e. one repeat unit. To improve this value the correction factor has to be refined. This was accomplished by taking the species AEA → (AE)₃ which had been assigned a peak. These were chosen because they gave distinguishable peaks and are above the lower molecular weight limit of the polystyrene standards. A new correction factor was calculated for each species from the 'measured' and actual molecular weight. These values were then averaged to give a new correction factor and corresponding standard deviation. The corrected molecular weights were recalculated from the measured molecular weights. More accurate weights were calculated and the standard deviation was lower than the previous value. For a deviation of 552, i.e. one repeat unit, the corrected weight value would have to be 66,544. This value is within the upper limits of polystyrene standards and well above the epoxy molecular weights which will be analysed. The table 2.4 shows an example of the calculated weights and the likely species associated with each retention time.

Using the correction factor a more realistic weight can be assigned to $\overline{M}_n$ and $\overline{M}_w$ determined by GPC. The figure 2.11 below shows how each of the molecular weight distributions vary with time.
Figure 2.11. Plot of $M_n$ and $M_w$ variation as system is cured at 100°C
<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Species</th>
<th>Actual Weight</th>
<th>Measured Molecular Weight</th>
<th>Corrected Weight†</th>
<th>Standard Deviation†</th>
<th>Corrected Weight‡</th>
<th>Standard Deviation‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.51</td>
<td>A</td>
<td>212</td>
<td>264</td>
<td>171</td>
<td>14</td>
<td>162</td>
<td>1</td>
</tr>
<tr>
<td>18.01</td>
<td>E</td>
<td>340</td>
<td>649</td>
<td>420</td>
<td>34</td>
<td>399</td>
<td>3</td>
</tr>
<tr>
<td>17.35</td>
<td>AE</td>
<td>552</td>
<td>956</td>
<td>619</td>
<td>50</td>
<td>587</td>
<td>5</td>
</tr>
<tr>
<td>16.85</td>
<td>AEA</td>
<td>764</td>
<td>1237</td>
<td>802</td>
<td>64</td>
<td>760</td>
<td>6</td>
</tr>
<tr>
<td>16.41</td>
<td>EAE</td>
<td>892</td>
<td>1565</td>
<td>1015</td>
<td>82</td>
<td>961</td>
<td>8</td>
</tr>
<tr>
<td>16.11</td>
<td>(AE)$_2$</td>
<td>1104</td>
<td>1837</td>
<td>1191</td>
<td>96</td>
<td>1128</td>
<td>9</td>
</tr>
<tr>
<td>15.88</td>
<td>(AE)$_2$A</td>
<td>1316</td>
<td>2079</td>
<td>1347</td>
<td>108</td>
<td>1277</td>
<td>10</td>
</tr>
<tr>
<td>15.61</td>
<td>(AE)$_2$E</td>
<td>1444</td>
<td>2407</td>
<td>1560</td>
<td>125</td>
<td>1479</td>
<td>12</td>
</tr>
<tr>
<td>15.45</td>
<td>(AE)$_3$</td>
<td>1616</td>
<td>2627</td>
<td>1703</td>
<td>137</td>
<td>1614</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 2.4. (†) Epoxy correction factor 0.64825±0.052105, calculated from the epoxy standards. (‡) Oligomer correction factor 0.61425±0.008265, calculated from the oligomers AE to (AE)$_3$. 
2.4. Physical Property Determination

In this section thermal analysis will be used to calculate the $T_g$ and thermal expansion coefficient values for the linear epoxy polymer. The viscosity and density will also be determined. Each of these properties will then be discussed in relation to the degree of cure.

2.4.1. Thermal Analysis

Thermal analysis may be defined as 'the measure of changes in the physical properties of a substance, as a function of temperature, whilst the substance is subjected to a controlled temperature programme' [4].

2.4.1.1. Principles of Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) utilises heat capacity as a measure of the changes that can occur in physical properties as the temperature is increased. A typical DSC instrument cell is illustrated schematically in figure 2.12 below.

Identical aluminium pans are placed on separate heaters, one of the pans containing the sample, the other being a reference pan remaining empty. Nitrogen is purged through the sample holder assembly throughout the temperature program. The temperature is varied over the required range. The DuPont DSC used in this study
measures $\Delta T$ for small samples and is calibrated to convert $\Delta T$ to heat flow $(\frac{dq}{dt})$, the temperature change being proportional to heat flow. Changes in the heat capacity of a sample result from exothermic and endothermic displacements.

In order to quantify the heat capacity of a material, a standard is required to calculate the calibration factor $B$. The relationship $C_p = \frac{hB}{\phi m}$ was used, where $\phi$ is heating rate, $h$ is the enthalpy and $m$, the mass.

Variations in the baseline always occur after a state transition (e.g. solid $\rightarrow$ liquid) and for polymers, many important transitions such as $T_m$, $T_g$, heat of crystallisation, heat of melting, can be observed. The melting and crystallisation temperatures are characterised by maxima in the plot of heat flow against time/temperature, whereas at the glass transition temperatures there is merely a discontinuity in the baseline i.e. $\Delta H=0$. $T_g$ is a second-order thermodynamic response and is discussed in further detail in chapter 1. On the molecular level the $T_g$ is the point when the polymer achieves main chain motion permitting a change in free volume, hence the inflection in the heat flow-temperature plot. The measurements provide both qualitative and quantitative data about physical or chemical changes of the material involving endothermic or exothermic processes.

Figure 2.13 illustrates the physical property $T_g$ and how it was measured.

![Figure 2.13](image_url)

Figure 2.13. Illustration of the type of plot obtained for the linear epoxy system.

The exact determination of $T_g$ from a plot like figure 2.13 is still disputed. There are many ways [5] of extracting the $T_g$ value from such a plot. The method used
here was to extrapolate two straight lines at the point of the first inflection, as shown in the figure.

2.4.1.2. DSC Measurements

The samples used for the average molecular weight determination were used also for \( T_g \) determination using the DSC apparatus, 5-10 mg of the sample were placed in an unsealed aluminium pan. The oligomeric samples which have a low \( T_g \) were initially cooled to -20°C, before ramping the temperature at 10°C/min to 120°C. Samples which had a high average molecular weight value were cooled to room temperature (20°C) before initiating the same temperature control programme. The results are discussed at the end of this chapter.

2.4.1.3. Thermomechanical analysis

Thermomechanical analysis (TMA) uses changes in linear dimension of a solid material as a measure of physical property changes that occur with variation in temperature. This can be described [6] as follows:

\[
L_2 = L_1 (1 + \int_{T_1}^{T_2} \alpha dT)
\]

eqn. 2.3

where \( L_1 \) is the length at temperature \( T_1 \) and \( L_2 \) the length at temperature \( T_2 \), and \( \alpha \) is the linear expansion coefficient. As a material is heated so it expands in a linear fashion. If a transition from one state to another occurs (e.g. \( T_g, T_m \)) there is a change in the gradient of the slope. This is demonstrated in figure 2.14 for an amorphous polymer.
Figure 2.14. Illustration of how $T_g$ and the linear expansion coefficients $\alpha$ can be determined from a TMA plot. $\alpha_g$ and $\alpha_l$ are the linear expansion coefficients in the glassy and liquid regions respectively.

The measuring probe illustrated in figure 2.15, is lowered onto the sample platform and electronically zeroed. The probe is raised and a sample with parallel faces is placed on the sample platform and the probe is lowered again onto the surface. To improve the sample contact a light weight is placed on the probe and removed. If there is no significant change in the measured sample thickness, the contact is deemed good. The heating programme is activated and is controlled via the thermocouple while changes in the sample dimension are measured electronically.

Figure 2.15. A cross section of a typical Thermal Mechanical Analyser cell (TMA).
2.4.1.4. TMA Sample Preparation

An equimolar amount of BADGE and DAE were dissolved in chloroform. The excess solvent was removed from the sample by rotatory evaporation with any residual solvent being removed in a vacuum oven set at 100°C for 1 hour. The solution was poured into circular rubber moulds, 1 cm in diameter and ~2 mm deep. Glass plates were covered in pink melonex which were held down by silicon grease. The moulds were glued to a glass plate, using silicon rubber. Six moulds were placed in a preheated oven set at 100°C, each containing two circular impressions. The moulds were removed approximately every two hours over a twelve hour period. The surfaces of the linear epoxy discs were sanded until they were parallel and then cut in half for testing.

2.4.1.5. TMA Calibration

The TMA was calibrated using an aluminium disc. The temperature was ramped from 20-100°C at a rate of 2 K/min., \( \alpha_{\text{expt.}} = 19.11 \times 10^{-6} \degree \text{C}^{-1} \), \( \alpha_{\text{lit.}} = 23.8 \times 10^{-6} \degree \text{C}^{-1} \), where \( \alpha \) is the linear expansion coefficient.

2.4.1.6. TMA Measurements

The same heating program used for the calibration was used to measure the \( T_g \) and linear expansion coefficient of the linear epoxy samples. The thickness of each sample was initially measured using an electronic micrometer before being mounted onto the TMA platform. The results will be discussed at the end of this chapter.

2.4.2. Viscosity Measurements

A Brookfield Digital Viscometer (RV/LV) was used to measure the viscosity of an equimolar mixture of BADGE and DAE. The reactants were thoroughly mixed at \( \sim 50°C \) and poured into a cylindrical metal container. A Brookfield Model 64 temperature controller regulated the heating jacket temperature at 100±1°C. The metal container was placed into the heating jacket were the viscosity being measured using a no.6 spindle (suitable for the viscosity range 10\( \rightarrow \)199000 mPa.s). The results were recorded on a chart recorder. The viscometer was calibrated (using 480, 950 and 11800 mPa.s standards), prior to each run at room
Chapter 2 Characterisation of a Linear Epoxy Polymer by Experiment

temperature using purchased Brookfield calibrants. Figure 2.16 shows how the viscosity increased as the BADGE/DAE reaction proceeded at 100°C.

\[ \rho_T = \frac{W_{(\text{air})}}{W_{(\text{air})} - W_{(\text{H}_2\text{O})}} \cdot \rho_{(\text{H}_2\text{O})} \]

where \( \rho_T \) is the density of the sample at temperature T, \( W_{(\text{air})} \) is the weight of the sample in air, \( W_{(\text{H}_2\text{O})} \) is weight of the sample in distilled water at temperature T, and \( \rho_{(\text{H}_2\text{O})} \) is the density of distilled water at temperature T. The density of water at these various temperatures were obtained from literature values [8]. The results of the density measurements are listed in table 2.7. The implications of these measurements will be discussed in section 2.6.
2.5. Mechanical Property Determination

In this section the following elastic constants will be calculated: Young's modulus, bulk modulus, shear modulus, Lamé constants and Poisson's ratio. The sample preparations and the experimental procedures will be documented here.

2.5.1. Preparation of Epoxy Sheets

Equimolar mixtures of BADGE (EPON®825) and DAE (Aldrich) were dissolved in chloroform. The resulting solution was then filtered though a sinter funnel and the bulk of the solvent was removed using a rotary evaporator at a temperature of ~50°C. The solution was then transferred to a vacuum oven set at 100°C for an hour. Over this period all chloroform was removed. Total removal of the solvent was determined by NMR, for which chloroform has a characteristic proton signal at δ 7.25ppm.

The sample was transferred by syringe into a mould, fig 2.17 and subsequently cured in a normal oven at 100°C for a twelve hour period. The sample was allowed to cool overnight before being removed from the mould.

![Figure 2.17. Schematic of mould used in making epoxy resin sheets for mechanical property testing.](image)
The mould used to make the mechanical test pieces, see figure 2.17, was made by applying silicon grease evenly over one side of two glass plates. A strip of melonex was cut and placed over the greased surface and a metal stripe covered in tissue paper was used to remove air bubbles from the melonex surface. Metal separators were used to maintain the required 3mm distance between the glass plates when clamped, while a silicon rubber tube, (from BDH-Merck [inner diameter 1.6mm, outer diameter 4.9mm, tube size 14]) was used as the mould. Pink melonex was used, because it has a fine coating of silicon which prevents adhesion of the resin to the melonex surface.

2.5.2. Preparation of Mechanical Test Pieces

The cured epoxy plates were cut into strips (width 8mm, thickness 3mm) using a water cooled diamond wheel. The strips were lightly sanded to remove ripples on the surface and any residual silicon coating from the melonex, while the dust was wiped off with a cloth dampened with aqueous methanol.

Aluminium tabs were cut (8mm wide, 12mm long, 1½ thickness) and lightly abraded on both sides. The surface was then wiped with a damp cloth dipped in aqueous methanol. To one side of the tabs and the test sample a coating of cyanoacrylate adhesive (super-glue) was applied. The two surfaces were placed together and a weight placed on top to assist adhesion, see figure 2.18. Typically the distance between the tabs was ~40-60mm. All samples were left a minimum of 24hrs to harden, under the load, before testing commenced.

![Figure 2.18. Illustration of the dimensions of the epoxy sheet and the positioning of the tabs.](image)
2.5.3. Mechanical Property Tests

Young's Modulus and Poisson's ratio were chosen as the elastic constants to be measured. From these results the remaining elastic constants of interest could be determined. Two 5mm strain gauges (Tokyo Sokki Kenkyujo Co. Ltd) were placed, one parallel to the length of the sample to measure Young's modulus, while the other was placed perpendicular to the applied force to measure Poisson's ratio. The strain gauges were stuck to the resin using cyanacrylate adhesive (super-glue) along with the "Dog Bone Tag's" (connecting terminals) which attach the strain gauges to the strain meters, see figure 2.19.

![Strain Gauges and Terminals](image)

**Figure 2.19.** Illustration of sample used for mechanical property testing.

2.5.4. The Instron Universal Testing Apparatus

All samples were tested on a Instron Universal Testing Apparatus (model 1175) testing apparatus incorporating a highly sensitive electronic Force Measuring system with load cell strain gauges for detecting the load applied to a specimen under tension or compression. The Force Measuring system is electronically calibrated eliminating the need for calibration weights.

The Instron conditions used to measure these elastic constants are tabulated in table 2.5.
Chapter 2 Characterisation of a Linear Epoxy Polymer by Experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area $\text{mm}^2$</th>
<th>Crosshead Speed mm/min</th>
<th>Young's Modulus GPa</th>
<th>Standard Deviation</th>
<th>Poisson's Ratio</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.85</td>
<td>0.5</td>
<td>4.092</td>
<td></td>
<td>0.375</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>25.33</td>
<td>0.2</td>
<td>3.605</td>
<td></td>
<td>0.354</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>24.44</td>
<td>0.2</td>
<td>3.500</td>
<td></td>
<td>0.345</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>23.98</td>
<td>0.2</td>
<td>4.175</td>
<td></td>
<td>0.366</td>
<td></td>
</tr>
</tbody>
</table>

$3.843 \pm 0.340 \quad 0.361 \pm 0.013$

Table 2.5. The confidence levels at 95% are $\pm 0.33$ and $\pm 0.013$ for Young's Modulus and Poisson's Ratio respectively.

The other elastic constants can be derived from the Young's Modulus $E$ and Poisson's Ratio $\nu$, using equations 5.25 and 5.26., see table below.

<table>
<thead>
<tr>
<th>Elastic Constants (Experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus $E$ (GPa)</td>
</tr>
<tr>
<td>Bulk Modulus $B$ (GPa)</td>
</tr>
<tr>
<td>Poisson Ratio $\nu$</td>
</tr>
<tr>
<td>Lame constant $\mu.$ (GPa)</td>
</tr>
<tr>
<td>Lame constant $\lambda.$ (GPa)</td>
</tr>
</tbody>
</table>

Table 2.6. List of experimentally derived elastic constants.
2.6. Discussion

All the experimental results are discussed here to give a coherent and comprehensive account of the mechanical and physical properties of this linear epoxy polymer and how the properties are affected by the degree of cure.

2.6.1. Structure Characterisation

The purity of DAE by HPLC was >99% giving a single eluent peak. The chromatogram obtained from the BADGE showed a very small satellite peak just after the main peak. The area integrated also indicates a purity of >99%. The melting point of BADGE and DAE were respectively measured at 42-43°C and 65-67°C. This compared well with literature values of 41-42°C [9] and 65-67°C [10].

The reaction between DAE and BADGE is a simple addition reaction forming a linear epoxy thermoplastic but side reactions like etherification and cyclisation can also occur. Here it is necessary to quantify these side reactions, if they take place at all, and use this information to determine the likely structure of the epoxy system for molecular modelling.

The epoxy consumption as measured by HPLC and NMR are comparable, see figure 2.20. The NMR validates the information obtained from the chromatography analysis. The figure shows the initial stages of the typical [11],[12],[14] S-shape of reaction as it is sometimes called. The NMR kinetic study could not be taken further due to a marked increase in viscosity of the sample. The resultant NMR lines broaden causing the merging of peaks, therefore satisfactory integration of these broad bands was not possible.
Figure 2.20. Comparison of the degree of epoxy consumption measured by HPLC and NMR at 100°C for a stoichiometric reaction (BADGE:DAE).

2.6.1.1. Etherification

Impurities such as water, alcohols, glycols, solvent, etc. can greatly accelerate the epoxy-amine reaction. Abúin et al. [13] have quantified the effects of these impurities. Such impurities can also result in the acceleration of etherification [9] reaction. To reduce the esterification reaction [14] the temperature must also be below 150°C therefore all experiments where conducted at 100°C. The initial reaction, shown in figure 2.10, shows no evidence of etherification, i.e. the amine and epoxy are being consumed equally. Matejka and Dusek [15] demonstrated that for linear epoxy polymers, stoichiometric mixtures showed no initial etherification but this side reaction became more pronounced toward the later stages of the cure. The spectrum for the DEPT experiment, shown in figure 2.5, has an extra \( \text{-CH}_2 \) which can be attributed to the etherification reaction. This NMR sample was taken after 5 hours at 100°C for a stoichiometric mixture.

The effects of etherification on the mechanical properties would not be expected to be appreciable [16], but the physical properties such as \( T_g \), thermal expansion coefficient, etc. would be affected. These properties are characterised as a function of cure later in this discussion.
2.6.1.2. Cyclisation

Many of the cyclic products formed are via the etherification reaction [15],[17],[18]. Johncock et al. [18] obtained cyclic products via the etherification reaction to form stable seven membered rings. In this system the lowest membered ring possible would be a seventeen membered ring, produced from an (AE) oligomer, where (A) is the DAE and (E) the BADGE. The epoxide group of the (AE) reacts with the hydroxide group forming a ring. The other form of ring which can potentially be made is produced also from the (AE) oligomer. The epoxy group can react with the amine group to form a "head-tail" 21 membered ring. The HPLC results in figure 2.10 shows that the concentration of (AE) gradually decreases with time. If cyclic products were present a plateau would result as cyclic species, when formed, cannot react further. (AE)_2 is the next species which can potentially cyclise, but unfortunately the time period chosen of 2.5 hours was not long enough to see the progression of this species. However, the likelihood of cyclisation occurring as the reaction proceeds becomes increasingly remote. The cyclisation reaction takes place mainly in highly diluted solutions [3], therefore it can be concluded that cyclisation is negligible in this reaction system.

2.6.2. Physical Property Characterisation

2.6.2.1. Glass Transition Temperature

The average molecular weight was compared with the \( T_g \) measured by DSC and TMA. The \( T_g \) determined from DSC measurements were plotted against log\( M_w \), in figure 2.21. As can be seen there are three distinct regions [19]. In region I the \( T_g^m \) has been reached. Here the molecular chains are sufficiently long enough not to incur further changes to the \( T_g \). In region II the \( T_g \) is dependent on the molecular weight of the chains. This is the start of the polymeric region. Region III is the oligomeric region and shows a dramatic decline in the \( T_g \) with a corresponding decrease in the average molecular weight. This is due to the proportionately higher number of chain ends in region III with respect to region II. The chain ends explore a greater free volume [20] than the central region of the chain, therefore as the molecular weights decrease so the thermal energy required to be able to rotate the chain ends decreases.
Figure 2.21. Plot showing the three regions between the $T_g$ and $\log M_n$ determined by DSC and GPC respectively.

$T_g$'s measured by TMA and DSC are comparable but are not exactly the same. Table 2.7. shows the $T_g$ values measured by the two methods. The results are not expected to be the same for two main reasons:

1. Different physical properties are measured, DSC detects heat flow while TMA measures changes in linear dimensions.

2. The rates of heating used in both methods were different. $T_g$ is strictly not only a second order thermodynamic process but has a kinetic element to its behaviour, as discussed in chapter 1. Therefore it has a dependence on the heating rate. As would be expected the $T_g$'s from TMA and DSC follow the same trend when plotted against $\log M_w$, as in figure 2.21.

Linear epoxy systems typically [21] have a $T_g^{\infty}$ between 40 - 100°C. By using the Ueberreiter-Kanig equation [22], as shown below, the $T_g^{\infty}$ can be calculated.

$$\frac{1}{T_g^{\infty}} = \frac{1}{T_g} + KM_n^{-1}$$  

\[ \text{eqn. 2.5} \]
Figure 2.22 shows a plot of equation 2.5. The $T_g^\infty$ value is $358K$ ($85^\circ$C) at 10 °K/min. Day et al. [22] corrected their $T_g$ value to zero heating rate. This resulted in the corrected value being 2.5%, lower than the measured value. Owing to the apparent small correction value it was felt that there was little need to correct the DSC results.

![Figure 2.22. Ueberreiter-Kanig plot of glass transition temperature (K) against number average molecular weight for fractions of linear epoxy polymer.](image)

2.6.2.2. Thermal Expansion Coefficient

Equation 2.3 shows that TMA gives a measure of the linear coefficient of thermal expansion $\alpha$. The thermal expansion coefficient $\beta$ and linear coefficient of thermal expansion $\alpha$ have the following relationship: $\beta = 3\alpha$. The values of the thermal expansion coefficient above ($\alpha_l$) and below ($\alpha_g$) the glass transition temperature are tabulated in table 2.7, for the liquid (or rubber) and glassy states respectively. As can be clearly seen $\alpha_l > \alpha_g$. Figure 2.23 shows the relationship of $\alpha_l$ and $\alpha_g$ with the average molecular weight $M_w$. The thermal expansion coefficient below the glass transition temperature shows very little change as the linear epoxy is polymerised. This behaviour is expected, due to the fact that at low temperatures the molecular chains do not have enough thermal energy to explore the free volume. The energy barriers which the molecular chains must surmount are
independent of chain length and are only dependent on the nature of the molecular chain linkages i.e. functional groups along the back bone of the chain. As the molecular weight initially increases so there is a marked fall in the thermal expansion coefficient above the glass transition temperature. As previously mentioned, the initial $\alpha_i$ is greater than that of $\alpha_l$ after a period of curing because of the higher number of initial molecular chain ends. The chain ends are believed to explore a great free volume space. Two readings depart markedly from this hypothesis but the trend appears nevertheless downwards. Palmese et al. [20] investigated the effect of epoxy-amine stoichiometry on the thermal expansion coefficient $\alpha_g$ and $\alpha_l$ for fully cured systems. Here it was shown that $\alpha_g$ was independent of varying amine concentration while $\alpha_l$ showed a minimum value at stoichiometric composition. The same trend was also demonstrated by Gupta et al. [23].

![Figure 2.23](image)

Figure 2.23 Relation of thermal expansion coefficient with average molecular weight.

A relationship between the two coefficients has been quantified by Simha and Boyer [24]. This relationship was described as follows:

$$ (\alpha_i - \alpha_g) = \phi_c \frac{1}{T_s} $$

eqn. 2.7
where \( \phi_e \) is the fractional excess volume and is equal to \( V_{(S-B)}/V_{Tg} \), where \( V_{(S-B)} \) is the Simha-Boyer free volume and \( V_{Tg} \) the specific volume at \( T_g \). \( \phi_e \) is a constant which is based on a large number of polymer studies and has a value of 0.113. When \( (\alpha_1-\alpha_g) \) is plotted versus \( 1/T_g \), good linearity is obtained with a least squares slope of 0.113, which is very good agreement with the Simha-Boyer value.

![Figure 2.24 A Simha-Boyer Universal plot. Slope \( \phi_e = 0.113 \).](image-url)
<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$\alpha_1/R_1$ x10$^{-4}$ $\rho$/gcm$^{-2}$K</th>
<th>$\alpha_2/R_2$ x10$^{-4}$</th>
<th>$T_g$/K</th>
<th>$T_g$/K</th>
<th>$T_g$ (unc)</th>
<th>$T_g$ (unc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
<td>535</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>534</td>
<td>794</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>599</td>
<td>912</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>1156</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>948</td>
<td>1538</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1394</td>
<td>2191</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>956</td>
<td>2070</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1437</td>
<td>2932</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1795</td>
<td>3882</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2347</td>
<td>3232</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>2280</td>
<td>3282</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>6106</td>
<td>6890</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>5988</td>
<td>7917</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>3067</td>
<td>7544</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

continued
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\overline{M}_n$</th>
<th>$\overline{M}_w$</th>
<th>dispersity</th>
<th>$n$</th>
<th>$T_g / K_{(DSC)}$</th>
<th>$T_g / K_{(TMA)}$</th>
<th>$\alpha_p / K^{-1} \times 10^{-4}$</th>
<th>$\alpha_t / K^{-1} \times 10^{-4}$</th>
<th>$\rho / \text{gcm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3116</td>
<td>7860</td>
<td>2.52</td>
<td>5.64</td>
<td>344</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.17</td>
</tr>
<tr>
<td>16</td>
<td>3344</td>
<td>8640</td>
<td>2.58</td>
<td>6.06</td>
<td>346</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.15</td>
</tr>
<tr>
<td>17</td>
<td>7180</td>
<td>24851</td>
<td>3.46</td>
<td>13.01</td>
<td>353</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.19</td>
</tr>
<tr>
<td>18</td>
<td>8065</td>
<td>31952</td>
<td>3.96</td>
<td>14.61</td>
<td>354</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.17</td>
</tr>
<tr>
<td>19</td>
<td>5943</td>
<td>27641</td>
<td>4.65</td>
<td>10.77</td>
<td>351</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.18</td>
</tr>
<tr>
<td>20</td>
<td>6943</td>
<td>34891</td>
<td>5.03</td>
<td>12.58</td>
<td>351</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.16</td>
</tr>
<tr>
<td>21</td>
<td>750</td>
<td>1100</td>
<td>1.47</td>
<td>1.36</td>
<td>288</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.17</td>
</tr>
<tr>
<td>22</td>
<td>1256</td>
<td>2130</td>
<td>1.70</td>
<td>2.28</td>
<td>318</td>
<td>318</td>
<td>0.52</td>
<td>3.75</td>
<td>1.18</td>
</tr>
<tr>
<td>23</td>
<td>1799</td>
<td>3430</td>
<td>1.91</td>
<td>3.26</td>
<td>327</td>
<td>325</td>
<td>0.68</td>
<td>2.84</td>
<td>1.15</td>
</tr>
<tr>
<td>24</td>
<td>3173</td>
<td>6523</td>
<td>2.06</td>
<td>5.75</td>
<td>339</td>
<td>330</td>
<td>0.60</td>
<td>1.62</td>
<td>1.19</td>
</tr>
<tr>
<td>25</td>
<td>4316</td>
<td>12889</td>
<td>2.99</td>
<td>7.82</td>
<td>342</td>
<td>329</td>
<td>0.95</td>
<td>1.94</td>
<td>1.18</td>
</tr>
<tr>
<td>26</td>
<td>3472</td>
<td>9057</td>
<td>2.61</td>
<td>6.29</td>
<td>333</td>
<td>335</td>
<td>1.24</td>
<td>3.21</td>
<td>1.18</td>
</tr>
<tr>
<td>27</td>
<td>4123</td>
<td>14711</td>
<td>3.57</td>
<td>7.47</td>
<td>348</td>
<td>-</td>
<td>0.81</td>
<td>1.07</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 2.7. Sample code, number molecular weight, average molecular weight, dispersity, repeat unit based on $\overline{M}_n$, glass transition temperature determined by DSC and TMA respectively, expansion coefficient for glass and rubber states respectively, density at 293K.
2.6.3. Characterisation of Volume and Molecular Packing

At high temperatures above the $T_g$ volume changes are dependent on P-V-T relationships. For amorphous systems the rate of cooling is usually independent of volume changes. As a sample is cooled and the $T_g$ is passed, the material reaches a quasi-equilibrium state where the resulting irreversible morphology is dependent on the thermal and mechanical history of a sample.

The expansion coefficient below $T_g$ is independent of molecular weight while above the $T_g$ the expansion coefficient increases with decreasing molecular weight. Lower molecular weight chains have a greater number of chain ends than their higher molecular weight chain counterparts. Chain ends are more flexible than the bulk of the chain and for a given temperature it will explore a larger volume.

It is still not totally clear why $\alpha_l$ fluctuates so markedly in figure 2.23, even when great care was taken in making and measuring the samples. Similar experiments will be repeated for the simulation experiments, in chapter 5, with the view to finding a plausible explanation for these experimental observations.

2.6.4. Elastic Constant Determination

Adams et al. [25] have shown that the elastic constants, Young's Modulus and Poisson's ratio do not vary significantly when the loading rate is changed. The loads applied to this system were essentially static for two main reasons. Firstly, due to the very brittle nature of the sample, high load rates would result in premature breaking. Secondly, techniques were used which would closely resemble computer simulation methodologies.

The value for Young's Modulus is dependent on the cure schedule, (degree of cure [26], type of epoxy and hardener used [27]), therefore it cannot be readily compared with other neat epoxy resin elastic constant values. Nevertheless work by Adams et al. gave Young's modulus values in the same region as this work. Poisson's ratio however has a characteristic value [28] for epoxy resins of 0.34, for which our value is in good agreement at 0.36.
2.6.5. Viscosity Determination

Figure 2.16 shows the typical viscosity response of a polymer melt as the reaction proceeds at 100°C. The shear behaviour of this epoxy system is Newtonian, the shear rate being proportional to the shear stress over the shear range measured. Viscosity measurements are very sensitive to changes in chain length and are used to characterise the chain molecular weight as it increases with time. The following relationship [29] between the Newtonian viscosity $\eta_0$ and $M_w$ can be expressed as follows,

$$\log \eta_0 = n \log M_w + C$$

where $C$ is a constant dependent on the polymer and the temperature, while $n=3.4$. This relationship applies to systems that have a molecular weight above a critical value in the case $M_{cr}$, where $M_w < M_{cr}$ the value of $n \neq 1$. Figure 2.25 highlights the relationship between viscosity and average molecular weight;

![Figure 2.25. Plot of $\log \eta$ against $\log M_w$. The slope = 5.8 and $n=3.6$.](image)

$n$ has an observed value of 3.6 which is in good agreement with the literature value [30]. From figure 2.25 it can be seen that $M_w > M_{cr}$; $M_{cr}$ cannot be determined exactly from this plot but can be seen to be less than 794. $M_{cr}$ depends on the
molecular structure of the polymer and therefore large variations in $M_{cr}$ are seen in a number of polymers. This $M_{cr}$ value is smaller than those cited by van Krevelen [30] (2,000 to 60,000), which may be due to the ability of this system to form hydrogen bonds between chains thus increasing chain association and hence viscosity. Therefore a lower $M_{cr}$ value would be expected.

2.7. Summary

The overall conclusion from the chromatographic and spectroscopic studies is that for the first 2.5 hours cyclisation and etherification are negligible, therefore the epoxy chains are linear during this period. It follows that representative models can now be built for the simulation experiment. The physical properties have been successfully related to the degree of cure (i.e. average molecular weight), therefore, comparisons can be made between experimental and simulation results. Finally the mechanical properties have also been determined but have not been related to the degree of cure; this will be taken into account in the simulation experiments.

The next stage is to give a more detailed account of the theory behind molecular modelling.
2.8. References

10. Aldrich Catalogue - 1,2-dianilinoethane, 99% (N,N'-diphenylethylenediamine, Wanzlick's Reagent for aldehydes), Formula weight 212.30, mp 65-67°C.


3.1. Introduction

This chapter is predominately concerned with introducing the concept of molecular modelling in the context of polymer science. All the simulation techniques used in determining the properties for the linear epoxy are discussed here. A series of simulation studies were also conducted on crystalline polyethylene models in an attempt to validate these techniques.

3.2. Molecular Modelling

The use of computational chemistry as a tool to aid our understanding and to predict unknown quantities has increased over the years. Models of interest are built and properties are calculated and compared with experimental data. These results are used to validate the model.

Commercial epoxy resins are complex, crossed-linked, inhomogeneous, amorphous systems which, unlike the gas phase or solid crystalline phase, have many degrees of freedom. To accurately describe the properties of such systems a statistical ensemble of the system is required, which will bridge the gap between the microscopic behaviour of the atoms and the macroscopic properties of the bulk polymer.

Computationally, such macromolecules are not trivial to simulate and require powerful workstations, mini-supercomputers or even supercomputers to determine the structure and stability or even the free energy change of a transition between states. Over the past decade the development in computing power has been astounding making it now feasible to simulate numerically the behaviour of macromolecules. To correctly sample statistically the configuration space of a macromolecule for property determination, depending on the property of interest, the model can be approximated, in terms of its electrons, atoms, solvents, etc. For example, finding the possible reaction site of a molecule will require quantum mechanics, which uses fundamental approximations to solve the Schrödinger equation. On the other hand if some macroscopic phenomena are of interest then atoms can be treated as groups rather than individual atoms. Accuracy in predicting properties are solely dependent on the quality of the inter- and intramolecular force field. It is also important at each stage to compare calculated data
3.2.1. The Aims of Computer Simulation.

The aim of this work was to compare experimental data with calculated data using a linear epoxy system as a model system. The objectives are outlined below:

1) To gain a fundamental understanding of the relationship between macroscopic phenomena and microscopic structural behaviour.

2) To gain an understanding of quantities inaccessible by experiment.

3) To gain fundamental information for modelling more complex cross-linked epoxy resin systems.

4) Eventually to design new polymers or curing agents tailored to required properties.

3.2.2. The Force Fields

The next area described is the classical methodologies used in simulating macromolecular systems. Atoms can be treated simply as spheres that are bonded together by springs to form molecules. Any perturbation of the molecule will result in intermolecular and intramolecular changes (i.e. bond length, bond angle, dihedral angle, inversion angle; electrostatic, van der Waals and hydrogen bonding), which can be considered to be a function of any associated energy changes. The mathematical functions linking the changes in geometry with the corresponding changes in energy are described by the potential energy functions. The bonding forms of potential energy functions for bond stretching, angle bending, torsion and inversion for this system are given as follows;

\[ E_b = \frac{1}{2} K_b (R - R_0)^2 \]  

\[ E_a = \frac{1}{2} K_a (\theta - \theta_0)^2 \]
where $K_b$ and $K_a$ are the force constants for bond stretching and angle bending, $R_0$ and $\theta_0$ are the equilibrium bond length and angle respectively. In equation 3.3, $E_{\theta}$ represents the dihedral angle torsion interaction potential between two bonds $ij$ and $kl$ connected through a common bond, $jk$. The angle between planes $ijk$ and $jkl$ is the torsional angle $\phi$. $V_{jk}$ is the rotational barrier, $n_\theta$ is the multiplicity and $\phi_\theta$ is the equilibrium value of the dihedral angle. Throughout this thesis the trans configuration corresponds to $\Phi=180^\circ$. The equation 3.4, is the energy function for the inversion angle, where $k_\omega=C\sin^2\omega$ is the force constant and $\omega$ is the angle of an atom that is out of plane. This can be readily depicted by three atoms $j$, $k$, $l$ connected to a common atom $i$. When all the atoms lie flat on a plane $\omega=0$, and then if the atom $j$, for example, moves out of the plane, $\omega$ is the angle between the plane and the new bond position $ij$. The bonding interactions are illustrated below in figure 3.1.

Figure 3.1. Illustration of (I) bond, (II) angle, (III) torsional and (IV) inversion angles.
The van der Waals interaction is represented through a 12-6 Lennard-Jones potential,

\[ E_{vdw}(R) = D_o \left\{ \left[ \frac{R_o}{R} \right]^{12} - 2 \left[ \frac{R_o}{R} \right]^6 \right\} \]  

\text{eqn. 3.5}

where \( D_o \) is the bond strength (well depth), at distance \( R_o \) in Å and \( R \) is the separation between atom pairs in Å. In calculating the non-bonding interactions, a cut-off distance of 9Å was used along with a switching function. The Lennard-Jones 12-6 interaction potential is depicted below.

![Illustration of the 12-6 Lennard-Jones potential as a function of atom separation R.](image)

The hydrogen bonding function is the modified Lennard-Jones 12-10 potential, which is described below:

\[ E_{hb} = (D_o) \left\{ 5 \left[ \frac{(R_o)}{R} \right]^{12} - 6 \left[ \frac{(R_o)}{R} \right]^{10} \right\} \]  

\text{eqn. 3.6}

where \( D_o \) is the hydrogen bond strength (well depth), \( R \) is the distance (in Å) between the donor and acceptor atom, while \( R_o \) is the equilibrium length in Å. There is a switching function which smoothly cuts off the interaction, using the on-distance at 8Å and off-distance at 8.5Å. In the next equation (3.7), \( E_{elec} \) is the
electrostatic energy between two bodies with a charge \( q_i \) and \( q_j \), which are separated by a distance \( R_{ij} \), and \( \varepsilon \) is the dielectric constant and \( K \) is a conversion factor.

\[
E_{\text{elec}} = \frac{Kq_i q_j}{\varepsilon R_{ij}}
\]  

\text{eqn. 3.7}

### 3.2.3. Parameter sets

A parameter set contains atom types, force constants, etc. which are required by the force field terms. Parameters are determined from a series of experimental data \([1],[2],[3],[4]\) or from ab-initio quantum mechanics calculations of small representative molecules. Other values have also been derived using semi-empirical techniques \([5]\). The experimental data is determined from techniques such as Raman and infra-red spectroscopy for force constants, while X-ray crystallography and microwave spectroscopy are used for equilibrium geometries. The parameters for the van der Waals interactions are frequently derived from thermodynamical data, such as heats of fusion and vaporisation.

Choosing the correct parameters to fit the system of interest is important. The following force fields and parameter sets; AMBER \([6]\), GROMOS \([7]\) and CHARMM \([8]\) are ideal descriptors of amino acids, peptides and polypeptides, while MM2 \([9]\) is commonly used for small organic molecules. The Dreiding-II parameter set \([10]\), is a generic force field and was used in simulating the atomic behaviour of the linear epoxy polymer.

### 3.3. Simulation Techniques

This section describes the simulation techniques used in calculating the properties of the polymer.

#### 3.3.1. Molecular Mechanics.

Molecular mechanics \([11]\) (MM) treats the molecule as an array of atoms governed by a set of classical-mechanical potential functions while the force field defines the mechanical model to represent the molecule. The general concept behind MM, is the search for the energy minimum based on this mechanical model. The conformation a molecule adopts can be represented by a potential energy surface
that contains hills and valleys. The lowest valley is representative of the *global* minimum while valleys in general are *local* minima. Finding the *global* minimum as opposed to the *local* minima of a system becomes increasingly more difficult as the size of the system increases. This is due to the existence of many more potential conformations, i.e. hills and valleys. Therefore, the algorithm is likely to reside in a valley near to its original conformation and not explore the total conformational space. It may be a stroke of luck if the *global* minimum is found for large systems.

There are many programs that optimise the structure of a molecule and each having their own explicit analytical method of optimisation. Methods can be classified into two groups, depending on how the optimisation is calculated; first order calculations \( \frac{dE}{dr} \) use the finite-difference method to determine the curve gradient, while, second order \( \frac{d^2E}{dr^2} \) derive the second order derivative analytically. The following MM algorithms outlined below use these methods.

### 3.3.1.1. Steepest-Descent Method

This simple method [12] is recommended for energy-minimising structures with poor geometry. It adjusts the co-ordinates towards a region of low energy conformation. Each iteration step is dependent on the energy gradient (first derivative method), so that as the energy falls rapidly, the step size increases and vice versa.

### 3.3.1.3. Conjugate-Gradient Method

This procedure uses a combination of techniques [13]. Firstly, each iteration step taken depends on the energy gradient. Secondly, the history of the first derivative is implicitly used to gather second derivative information to allow conjugate directions to be searched. Although this method converges rapidly it can only be used successfully on systems with a reasonable starting energy, i.e. already near a (the) minimum.

### 3.3.1.2. Fletcher-Powell Method

The method of finite differences [14] is used to generate a second order derivative matrix. There is a limit to the number of atoms, \( N \), which can be used by this method due to the computational time that increases with the number of atoms by a factor of \( N^3 \).
3.3.2. The Molecular Dynamics Algorithm

In nature molecules are in a constant state of motion, a state which computer simulation can represent. The motion of atoms or particles can be treated using classical Newton equations and molecular mechanics force fields. In molecular dynamics (MD) [15],[16] each atom within the system is first given a random velocity. This translational motion is calculated using Newton's second law:

\[ F = m \left( \frac{d^2r_i}{dt^2} \right) \quad \text{eqn. 3.8} \]

where \( F \) is the force on the atom, \( m \) the mass of the atom and \( r_i \) are the Cartesian co-ordinates of atom \( i \). The bolded text represents summed quantities. From molecular mechanical principles the energy of the molecule can be derived and the force, \( F \), can be expressed as the negative of the derivative of this potential energy, \( E \), with respect to distance.

\[ F = \frac{-dE}{dr_i} \quad \text{eqn. 3.9} \]

therefore :-

\[ \frac{-dE}{dr_i} = m \left( \frac{d^2r_i}{dt^2} \right) \quad \text{eqn. 3.10} \]

The energy, \( E \), and the mass, \( m \), are known, therefore the acceleration \( \alpha \) can be calculated. Using the following Newtonian equations the velocity and the position of each atom can be predicted.

\[ v = u + at \quad \text{eqn. 3.11} \]

\[ r = ut + \frac{1}{2}at^2 \quad \text{eqn. 3.12} \]

where \( u \) and \( v \) are the initial and new velocities respectively, \( r \) is the change in position and \( a \) is the acceleration.
To obtain the new velocities small time steps ($\delta t$) are required. The size of the time step needs to be small compared with the highest frequency motion of the molecule, namely the bond stretch of a covalent hydrogen bond, therefore ($\delta t$) is around 1.0 femtosecond ($10^{-15}$s). The integration scheme, based on a 3rd order Taylor expansion, is as follows:

\begin{align*}
\mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{1}{2}\mathbf{a}_i(t)\delta t^2 + \ldots \quad \text{eqn. 3.13} \\
\mathbf{r}_i(t - \delta t) &= \mathbf{r}_i(t) - \mathbf{v}_i(t)\delta t + \frac{1}{2}\mathbf{a}_i(t)\delta t^2 - \ldots \quad \text{eqn. 3.14}
\end{align*}

By adding equation 3.13 and 3.14 gives:

\begin{equation}
\mathbf{r}_i(t + \delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \mathbf{a}_i(t)\delta t^2 \quad \text{eqn. 3.15}
\end{equation}

This is the basis of the Verlet algorithm [17], which is one of the most stable algorithms for the iteration of thecentre of mass motion for a diffusing molecule. Currently the improved summed-Verlet algorithm [18] or leap-frog [16] is being used. This tends to be less sensitive to numerical error and more efficient when velocities are to be adjusted. This involves defining the velocities at half time steps giving the predicted position and velocity as:

\begin{align*}
\mathbf{v}_i(t + \frac{1}{2}\delta t) &= \mathbf{v}_i(t - \frac{1}{2}\delta t) + \mathbf{a}_i(t)\delta t \quad \text{eqn. 3.16} \\
\mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t + \frac{1}{2}\delta t)\delta t \quad \text{eqn. 3.17}
\end{align*}

Other algorithms that can be used are the less accurate Runge-Kutta [14] and Gear [19] methods.

The random velocities assigned to the atoms are consistent with the initial input temperature, which is related as shown below:

\begin{equation}
\sum m_i v_i^2 = 3Nk_B T \quad \text{eqn. 3.18}
\end{equation}

where $N$ is the number of atoms, $k_B$ is the Boltzmann constant and temperature $T$ in Kelvin. Controlling the temperature of a system is dependent on the ensemble used. The types of ensembles will be discussed in the next section. For isothermal
experiments, namely isothermal (TVN) or isobaric-isothermal (TPN) ensembles the
temperature is simply held constant. However, for microcanonical ensembles
(EVN), the temperature is controlled as a function of the total (potential and
kinetic) energy. As shown in equation 3.18 it is the kinetic energy not the potential
energy that determines the temperature of the system. To control the temperature
an "ad-hoc" temperature scaling method is used. Since the kinetic energy is
dependent on the velocity of the atoms, the velocity can be scaled accordingly.

\[
\beta = \sqrt{\frac{\text{target temperature}}{\text{actual temperature}}} \quad \text{eqn. 3.19}
\]

The scaling value \( \beta \) is then applied to the velocities and the corresponding
coordinate updates are made. For an EVN ensemble, energy is a constant
parameter, not temperature therefore, the target and actual temperatures are never
identical but are nevertheless very close.

All the interesting properties can be derived from the atom positions and their
corresponding velocities. This trajectory information can be stored at regular time
intervals and can be used to determine static and dynamic properties of the system.
The types of properties that can be calculated are outlined in section 3.3.4.

3.3.3. Thermodynamic Ensembles

There are a few types of molecular dynamic methods that are used to simulate
different thermodynamic ensembles. It is important to use the appropriate
ensemble when performing simulation studies to obtain the correct second order
properties such as specific heat, thermal expansion, bulk modulus, etc., because
their values differ from one method to another, unlike first order properties (e.g.
potential energy, kinetic energy, pressure, volume). Each method will be briefly
described below.

The properties measured experimentally are macroscopic properties. In this
simulation work microscopic properties, such as atomistic position and momentum
are calculated. To convert this microscopic information into macroscopic
properties a set of boundary conditions need to be chosen - 'an ensemble', this
thermodynamically represents the system of interest. The temperature \( T \), pressure
\( P \), energy, \( E \), and number of molecules \( N \), are be used as variables for
thermodynamic ensembles. By selecting which variables are to remain constant the correct second order properties can be calculated. The first order thermodynamic properties such as density, volume, stress, strain, internal energy and pressure can be calculated by averaging, an instantaneous microscopic dynamic variable \( A \) (for example this could be potential energy), over the length of the trajectory.

\[
\bar{A} = \frac{1}{NT} \sum_{1}^{NT} A(t_n)
\]

where \( N \) is the value at time \( t_n \), and \( T \) is the total number. Although an infinite time would be preferable, a long finite time is satisfactory, to reach thermodynamic equilibrium. The key point to note is that sufficient phase space is explored by the trajectory, to allow consistent thermodynamic properties to be calculated irrespective of the internal conditions (atom position and momentum) of the system. The following section describes the various forms of ensembles used in molecular dynamics, and highlights the types of second order thermodynamic properties that can be calculated. These ensembles are all closed systems, except the grand canonical ensemble.

The ensemble with constant temperature, volume and number of atoms (TVN) is an isothermic ensemble and is commonly called the canonical ensemble. For this ensemble the following second order thermodynamic properties can be calculated: specific heat at constant volume, \( C_V \), the thermal coefficient of pressure, \( \gamma_V \), the thermal coefficient of stress, \( \gamma_j^V \), and the isothermal bulk modulus, \( B_T \).

The isobaric-isothermal ensemble (TPN) is an extension of the previous canonical ensemble. The following second order thermodynamic properties can be calculated: specific heat at constant pressure \( C_p \), thermal expansion coefficient, \( \alpha_p \), the temperature coefficient of strain, \( \alpha_{ji} \), the isothermal compressibility, \( k_T \), and the isothermal compliance constants, \( S_{ij}^T \).

The classical microcanonical ensemble (EVN) is an adiabatic thermodynamic ensemble. The second order thermodynamic properties that can be calculated are \( C_V \), \( \gamma_V \) and the adiabatic compressibility \( \beta_s \). The adiabatic EPN ensemble also has
its corresponding second order thermodynamic properties which are analogues to the TPN ensemble.

Another type of ensemble, which is not used in simulations, is the Grand canonical ensemble ($\mu$VE) or ($\mu$PE), where $\mu$ is the chemical potential. Unlike the other ensembles described above the number of molecules in the system is not constant.

3.3.4. Properties Determined from Molecular Dynamics Calculations

A number of macroscopic properties can be determined from a trajectory, which contains the velocities and atomistic co-ordinates. The accuracy of the calculated macroscopic property is dependent on the amount of phase space the trajectory has explored. Dynamic (time-dependent) and static (time-independent) properties can be calculated from the trajectory. The static properties can be calculated from the sum of the properties of the individual molecules at any time step or every time step. For all our MD simulation calculations, averages were made after every 100 steps (each step was 1 femtosecond). The following properties can be determined from such averages.

The potential energy $V$ is defined as

$$V = \langle \sum_{i} \phi_{i} \rangle$$

where $N$ is the number of molecules in the system and $\phi_{i}$ the potential energy of a molecule $i$ which is the sum of the internal and nonbonding energies and $\langle \rangle$ denotes the ensemble average.

The translational kinetic energy and its respective temperature are determined from

$$K_{\text{trans}} = \langle \frac{1}{2} \sum_{i} m v_{i}^2 \rangle$$

and

$$T_{\text{trans}} = \frac{K_{\text{trans}}}{(3/2) N k_{B}}$$

where $v_{i}$ is the velocity of molecule $i$, $m$ is the mass of molecule $i$, and $k_{B}$ is the Boltzmann constant.
The rotational kinetic energy and temperature are similarly defined. The total kinetic energy is the sum of the rotational and translational kinetic energies and the temperature $T$ is the average of the translational and rotational temperatures.

For systems with a periodic boundary condition the pressure can be calculated from the virial theorem. This term consists of two parts, firstly a kinetic term that takes into account the thermal motion of the molecules and secondly, the potential (or virial) term that accounts for the effect of intermolecular interactions.

$$P = \frac{1}{V} (Nk_b T + W) \quad \text{eqn. 3.24}$$

where the virial $W$ of the system is

$$W = -\frac{1}{3} \left< \sum_i r_i \frac{\partial}{\partial r_i} \Phi_i \right> \quad \text{eqn. 3.25}$$

The heat capacity $C_V$ (constant volume) can be determined from the fluctuation in the kinetic or potential energies,

$$C_V = 2 \left( \frac{3}{2} \frac{K}{n} \right) \left( \frac{N}{2} k_b T^2 \right)^{-1} \quad \text{eqn. 3.26}$$

where $n$ is the degrees of freedom per particle and $K$ is the total kinetic energy.

The radial distribution function, $g(r)$, is the probability of finding an atom $i$ at a distance $r$ away from an atom $j$. The shape of the plot can include a number of peaks and troughs as a function of $r$. The peaks relate to co-ordinated or near neighbour atoms, while troughs indicate voids or excluded volumes. This value is usually normalised and values of unity for $g(r)$ indicate an entirely uniform distribution of molecules or atoms. The resulting $g(r)$ plot can be related to X-ray and neutron scattering data,

$$g(r) = \frac{\rho_r}{\rho} = \frac{N_r V}{N (4\pi r^2) dr} \quad \text{eqn. 3.27}$$
where $\rho_r$ is the number of atoms in the volume element, $\rho$ is the overall density, $N_r$ and $N$ are the number atoms in the shell and system respectively, while $V$ is defined as the volume.

A number of interesting macroscopic dynamic properties can be calculated from the trajectories, these are listed below.

- Velocity auto correlation function $C_{\nu\nu}(t)$ - this is a measure of how the velocity of a molecule has been influenced by past velocities of that molecule. A positive correlation means that the initial velocities relate to present velocities, while a negative correlation shows that the velocities have reversed and zero correlation means that the velocities are totally unrelated.

- Self diffusion coefficient $D$ - is a measure of the translational mobility of a molecule and is derived from the velocity auto-correlation function. The corresponding rotational mobility can also be determined.

- The dielectric constant can also be related to fluctuations in the dipole moment of the system.

Information derived from these studies can be used to compare with experimental data. These correlation functions decay exponentially with time and can be readily compared with the relaxation times in infra red band shapes [20] and NMR relaxation times [21].

3.3.5. Conformational Analysis

This process, was one of the first applications of computer modelling [22], and is a way of systematically searching conformational space in pursuit of low energy conformations of molecules. The amount of computer time required for this process can be fairly high. To overcome this problem numerous techniques have been developed to reduce the computer processing time required. Only the techniques used by us will be discussed during this work.

Two adjacent dihedral angles are set at $0^\circ$, e.g. $\Phi_1$ and $\Phi_2$. $\Phi_1$ is fixed while $\Phi_2$ is stepped about a specified angle (i.e. $10^\circ$). At each step the potential energy of the molecule is minimised while the pair of dihedral angle of interest are held constant.
This is known as a "soft" conformational search. After $\Phi_2$ has moved through $360^\circ$, $\Phi_1$ is allowed to move one step (i.e. $10^\circ$) and the process is repeated until each dihedral pair has explored all possible conformational space. A "hard" conformational search skips the minimisation step.

### 3.3.6. Monte Carlo Technique

A complete search for low energy conformations of large molecular systems that contain many degrees of freedom is virtually impossible. The Monte Carlo algorithm is a random search technique that searches conformational space and is outlined below.

Firstly a starting conformation is chosen. From this initial conformation a new conformation is generated randomly. The dihedral angles are perturbed within a small window. Secondly, the energy is calculated for this newly generated structure. The acceptance or rejection of this molecule is made by calculating the Boltzmann factor, $\exp(-\Delta E/RT)$, and comparing this factor to a random number between 0 and 1. If the Boltzmann factor is greater than the randomly generated number then the structure is accepted, if not the structure is rejected. The acceptance of a structure results in the new structure being the starting point for new perturbations. Rejection of a structure means returning to the initial structure.

This process produces a Boltzmann ensemble that has the computational advantage of exploring only the low energy conformations and not wasting time on irrelevant high energy configurations. The main disadvantage with this technique is that it cannot deal with time-dependent properties.

### 3.3.7. Periodic Boundary Conditions (PBC)

To simulate bulk effects and minimise edge effects the periodic boundary was introduced by Metropolis et al. [23] in 1953. The molecule is placed in a simulation box, usually a cube. This cube is surrounded by identical boxes in the $x$, $y$, $z$-directions, totalling $3^3=27$. Atoms within the simulation box can interact with image atoms within a cutoff radius. Translation of atoms or molecules out of the box results in identical atoms or molecules entering at the same velocity and trajectory at the opposite side of the box, see figure 3.3.
The calculation of forces between atoms has to be reconsidered for this infinite system. A cut-off is used to limit the short range interactions with atoms within this cut-off radius being considered as pairwise-additive interactions. Long range interactions such as charge-charge and dipole-dipole interactions between an ion and all its surrounding periodic images are effectively handled by using the Ewald sum, which will be discussed next.

Problems can be encountered when calculating correlation functions such as radial distribution function. Care must be taken to include the correct image in the calculation, there will be apparent long range ordering that is in fact an artefact of the periodic boundary but not of the system.

3.3.8. Ewald Sum

The charge-charge interaction comes under the category of long range forces and is one of the largest forces in nature. Its influence penetrates a range far greater than half the box length for a typical computational (i.e. ~ 500 molecules). By simply truncating the nonbonding force at the periodic boundary, is a crude and unsatisfactory method of dealing with long range interactions, causing discontinuity
in the forces and a resultant loss of conservation of energy in MD calculations. The Ewald sum technique [24],[25], developed by Ewald [26], is a way of summing the long range interactions of a system, and its periodic images, that are generated by the PBC. The convergence of a summation like this, tends to be slow and dependent on the order in which the terms are added (i.e. convergence). This problem is overcome by replacing the original point charge lattice by one in which Gaussian charge distribution of the opposite sign to the point charges, are superimposed on the original lattice. Partial cancellation of these two charges results in the interactions now being more short-ranged. By adjusting the width of the Gaussian the interactions from this composite lattice system can be truncated within the MD cell, along with all the other short-range interactions. In order to cancel the potential from these Gaussian's, the potential arising from another lattice has to be added. This is formed out of the previous Gaussian lattice, but with an opposite sign, this time summed in reciprocal space. By adjusting the width of Gaussian, these two series can be made to converge relatively rapidly. The resulting potential includes the interaction of the cancelling distribution centred at \( r_1 \) with itself; this self term is then subtracted from the total. The magnitudes of the charge-charge interactions are dependent on the relative permittivity of the medium surrounding the molecules, which therefore must be specified (see equation 3.7). The use of the Ewald sum results in stable dynamics and greater accuracy of thermodynamic and structural properties.

3.3.9. Calculation of Charges

Charges can be determined from ab-initio, semi-empirical or empirical calculations. Two methods were considered for the epoxy polymer, semi-empirical (MNDO) and empirical (Gasteiger). These methods will be discussed below. Ab-initio, using the wave function, is the most rigorous method for atomistic charge determination. This method is computationally demanding and has a low atom number limit.

Electron distribution is an important factor on the physical properties of molecules. In real systems, where molecules are in a state of motion, the atomistic charges fluctuate due to collisions, etc. Such fluctuations can be calculated from the computationally expensive ab initio or semi-empirical calculations. Ideally simulation studies should represent these atomistic charge distribution changes, but
in order to save computational time the Gasteiger method was used and the results were compared with MNDO, see appendix 1.

3.3.9.1. Semi-Empirical Method

MOPAC is one of the most popular semi-empirical program packages currently used. It contains a suite of semi-empirical methods of which one will be discussed here. MNDO [27], an acronym for modified neglect of diatomic overlap combines empirical data and quantum mechanical calculations and hence is a semi-empirical method. The empirical data contain numerical parameters that can be adjusted to fit experimental data resulting in a method that is less computationally expensive than ab initio methods. MNDO can be used to calculate a number of properties, in addition to partial charges, namely geometry optimisation, ionisation energies, dipole moments and heats of formation.

3.3.9.2. Gasteiger Method

This method, developed by Gasteiger et al. [28], is an empirical method that rapidly calculates the charges of atoms in $\sigma$-bonded and nonconjugated $\pi$ systems. In the calculations only the topology of the atom is considered not the topography. Each atom is characterised by its orbital electronegativity, thus giving a partial charge value that can be used in MM & MD calculations.

3.3.10. Building Amorphous Models

To simulate the amorphous state of a single chain, the structure can be built using the rotational isomeric state (RIS) or random methodology. Flory [29],[30] developed the concept of RIS approximation. It determines the likely state a torsional angle resides in based on its conformational energy. The temperature and the density are initially specified and are the main specifications for the generation of an amorphous cell. The method used is the random method that uses the Monte Carlo (MC) technique which assigns random values to all the dihedral angles. Systematically at each dihedral a new dihedral angle position $\tau_{i+1}$ is proposed. Its acceptance or rejection is determined by the change in energy, $\Delta \Phi$, resulting from the new interactions caused by this dihedral change. To prevent the generation of high energy conformations a 'bump checking' method is used, which rejects any resulting conformation with atomic overlap. The energy is added to the dihedral angle's energy, $\Phi(\alpha)$. The Boltzmann factor of this energy change, $\exp(-\Delta \Phi/k_B T)$
is compared to another random number between 1 and 0. Acceptance results when the random number is less than the Boltzmann factor otherwise it is rejected if greater than this value. This process is repeated up to ten times and if there is no acceptance of a structure then the accepted dihedral angle position $r_i$ is reconsidered. If the chain can not find a suitable conformation then the dihedral position $r_{i-1}$ will have to be reconsidered. This is continued until all $N$ monomers have been generated to form the amorphous model. To increase the chances of acceptance, only 30% of the vdw radius is considered on construction of the amorphous cell, but the vdw values are fully restored on completion of the amorphous cell.

There are essentially two problems with this technique, firstly as the monomers are added at each stage the later monomers do not experience the same effective volume as the initial monomers. This biases the dihedral values toward the later stages. Secondly these generated structures are in a highly energetic state, which results from the reduced van der Waals forces during the amorphous cell generation. These two problems are eliminated once the chain is allowed to relax dynamically using a series of molecular mechanics and dynamic routines.

3.4. Modelling Hardware and Software

The molecular modelling studies of polymers were performed using a three-dimensional graphics program called POLYGRAF (version 2.2) produced by Molecular Simulation Inc. The software was installed on a Stardent TITAN II graphics mini-supercomputer and on a CONVEX C3840 at the University of London Computing Centre (ULCC). The CONVEX was used as a workhorse machine while the TITAN was primarily used for the sole purpose of visualisation and analysis. MOPAC (version 5.00) calculations were also run on the TITAN and the Cambridge Data Base (CDB) was searched on a DEC microvax II. For some calculations Professional POLYGRAF (version 3.2) was used at BP (Sunbury) and Queen Mary & Westfield College (London).

3.5. Introduction to Polymer Modelling

As an introduction to polymer modelling it was felt that the study of a very simple polymer in its most stable conformation and configuration would be necessary. Such a study would validate the methods and algorithms used for calculating the
mechanical and physical properties of more complicated systems such as amorphous polymers. An ideal candidate for such a study was crystalline polyethylene. This system is very simple with a wealth of parameterisation information \[31\],\[32\],\[33\]. The crystal structure of polyethylene is well documented and the mechanical properties are available from the literature. Three simple studies were performed on the polyethylene model. Firstly, the modulus of a single polyethylene chain was determined. This was compared with a second experiment that determined the modulus of crystalline polyethylene at absolute zero and thirdly at room temperature (i.e. 300K).

3.5.1. Modulus of a single Polyethylene chain at absolute zero

A single chain of polyethylene was constructed using two ethane molecules from the POLYGRAF monomer library. The two ethane molecules were joined and minimised until the change in potential energy between steps (\(\Delta E\)) was less than 0.001 kcal/mol. The resulting butane molecule was duplicated six times and bonded together to form a long straight chain. A box was placed around the resulting structure and the chain was again minimised until \(\Delta E < 0.001\) kcal/mol, forming a perfectly linear chain. The chain was then subjected to a series of individually applied stresses along the z-axis (i.e. chain length) and the corresponding length variation of the box along the z-axis was used as a measure of the strain. The xy, xz, yz planes were fixed, so that determining the Young's modulus from the box distortion was in the z-axis only. The atom positions in the box were scaled on application of the force. This means, for example, that as the box is compressed the molecules also experience a compressive force and move with the box. This is equivalent to fixing one end of the molecule while compressing or expanding the other end. Energy minimisation was used to determine the modulus and in this case the Fletcher-Powell method was used. Figure 3.4 shows the results from the series of applied stresses. The zz stress tensor was used as a measure of the applied stress, while, the dimension of the unit cell in the direction of the applied force was utilised as a measure of the resulting strain.
Figure 3.4. Stress-strain plot of a single polyethylene chain, where \( n = 12 \). Young's Modulus 268 GPa.

### 3.5.2. Modulus of Crystalline Polyethylene at zero Kelvin

For the next series of experiments it was necessary to construct a crystalline polyethylene lattice. The atomic co-ordinates for the crystal were obtained from the literature [34].

The coordinates were expressed in non-standard form, i.e. P\(_{\text{nam}}\) [acb]. POLYGRAF does not accept these values unless it is in standard form P\(_{\text{nma}}\) [abc]. The unit cell parameters are as follows:

\[
P_{\text{nma}} \quad a = 7.388 \quad b = 2.539 \quad c = 4.929
\]

<table>
<thead>
<tr>
<th>( \text{C}_1 )</th>
<th>( x )</th>
<th>0.25</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_{11} )</td>
<td>( x + 0.143 )</td>
<td>0.25</td>
<td>( z - 0.02 )</td>
</tr>
<tr>
<td>( \text{H}_{20} )</td>
<td>( x - 0.030 )</td>
<td>0.25</td>
<td>( z + 0.21 )</td>
</tr>
</tbody>
</table>

where \( x = 0.041 \) and \( z = 0.060 \)
Figure 3.5 shows a projection of the generated unit cell after entering the coordinates into POLYGRAF.

Figure 3.5 The large filled spheres represent carbon atoms, while the smaller open spheres are hydrogen atoms.

From this unit cell a 3x7x3 (abc) lattice was constructed using the crystal builder in POLYGRAF. All the chains were lined up in a symmetrical manner as illustrated in figure 3.6a.
Figure 3.6. An illustration of the crystalline polyethylene lattice before a) and after b) the application of an external stress along the length of the polyethylene chain.

A series of stresses were applied to the lattice along the y-axis of the unit cell (this is along the chain length shown in figure 3.6). The same conditions in the previous section were used, but a larger range of stresses were applied. Figure 3.7 shows the results from this experiment.
3.5.3. Modulus of Crystalline Polyethylene at 300K.

Molecular dynamics was used to determine the Young's modulus of polyethylene at room temperature. Since this technique is computationally more time-consuming than molecular mechanics a 3x3x1 (abc) lattice was constructed from the polyethylene unit cell. The temperature was set to 300K and the experimental time period was 0.05ps with time steps of 0.001ps. Large stresses were applied so that a noticeable variation in the strain could be exhibited in this relatively short time period. The results from this experiment are shown in figure 3.8.
3.6. Discussion

The experimental Young's modulus of crystalline polyethylene, which was determined from Raman Spectroscopy, Neutron and X-ray experiments, is very high at 210-360GPa. This is because 100% crystalline polyethylene has no amorphous regions within the system that can reduce the overall modulus. Such a system is ideal and commercially available polyethylenes have moduli that are some fraction of this ideal value.

The results obtained from the three experiments are all within the range of the literature values for crystalline polyethylene. This is partly because the Dreiding-II force field associated with valence angles in POLYGRAF is particularly good. Deformation of the polyethylene involves mainly changes in the valence angles. Bond angle bending was largely responsible for the changes in energy that occurred with the applied stress. Bond stretching also occurs, but is less significant. There is no change in the dihedral angles, due to the initial zigzag conformation of crystalline polyethylene.

Although the results are satisfactory, there is enough variation in the individual results to warrant further comment. The lattice structure which was used to
determine the modulus illustrates effectively how important these structural factors are. Take experiment 2 for example, which shows the highest modulus, at 360 GPa. This is due to intermolecular forces that operate between the chains. In figure 3.6a the chains are symmetrically aligned, but as a stress is applied along the axis of the chains, chain slippage takes place and they move into an asymmetric environment figure 3.6b. The hydrogen atoms on neighbouring chains become very close and repel each other, hence a larger force is required to overcome this repulsive force. This results in an increase in the modulus.

Experiment 3 has a smaller lattice structure than that in experiment 2 although this structural difference is not expected to play a part in the reduced modulus, of 306 GPa, because of the periodic nature of this crystalline system. Temperature is the important factor in this simulation. At higher temperatures such as 300 K the chains have greater K.E energy and can overcome the repulsive force encountered by close van der Waal interactions. The chains are able to slide over each other more readily, resulting in a reduced modulus. The model used in experiment 1 is a single chain that is not in a lattice environment. Hence the packing force in a crystal which is present in experiment 2 and 3 is absent, therefore there is an overall reduction in the modulus.

By using low-frequency Raman scattering spectroscopy Shaufele et al. [35] have determined the Young's modulus of infinite polyethylene chains from the longitudinal acoustical accordion mode. This gave a value of 358 ± 25 GPa at 300 K for a series of hydrocarbons C_8-C_94. Barham et al. [36] used a dynamic mechanical thermal analyser as a means of measuring the modulus of drawn high-molecular weight polyethylene in xylene and found it to be ≈ 324 GPa at 0 K. At 300 K Holliday et al. [37] have cited the following Young's modulus values: X-ray 240 GPa, Raman 340 - 358 GPa and neutron 329 GPa. Karasawa et al. [33] have summarised the Young's moduli from the various techniques and estimate the results to be in the range of 341 ± 9 GPa at 0 K and 322 ± 9 GPa at 300 K. These simulation results are in good agreement and show a similar trend to Karasawa's et al. experimental results. The aim of this work was not to obtain precise values for the modulus, but to demonstrate an appreciation for the techniques used in modelling polymers.
3.7. References

1 Burkert U., Allinger N.L., Molecular Mechanics (ACS Monogr) 177, (1982)
11 Chemical calculations 19.


Characterisation of a Linear Epoxy Polymer by Simulation

4.1. Introduction ........................................................................................................................... 105
4.2. Conformational Analysis ...................................................................................................... 105
  4.2.1. Simulation I .................................................................................................................. 105
  4.2.2. Conformational Analysis Results .................................................................................. 105
4.3. Crystal Data Search ............................................................................................................. 115
  4.3.1. Introduction .................................................................................................................. 115
  4.3.2. Models used in Search ............................................................................................... 115
  4.3.3. Results from CDB search ........................................................................................... 117
4.4. Stress and Temperature Analysis by Boltzmann Distribution .......................................... 126
  4.4.1. Simulation Techniques ............................................................................................... 126
    4.4.1.1. Simulation I (Temperature Analysis) ..................................................................... 126
    4.4.1.2. Simulation II (Stress Analysis) .............................................................................. 126
  4.4.2. Temperature and Stress Distribution Results ............................................................... 128
4.5. Discussion ........................................................................................................................... 137
  4.5.1. Virtual bonding ............................................................................................................ 143
  4.5.2. Chain Mobility ............................................................................................................. 146
4.6. Conclusion ............................................................................................................................ 150
4.7. References ............................................................................................................................ 152
4.1. Introduction

This chapter deals with the characterisation of the linear epoxy polymer, in an attempt to increase our understanding of the microscopic behaviour in relation to macroscopic influences. Since the torsional angles are the main contributors to polymer motion, their perturbation will be investigated under varying stress and temperature conditions. The states in which each torsional angle resides are compared initially with conformational analysis plots and crystal data.

4.2. Conformational Analysis

These series of computer experiments generate the likely energy minimum conformation between 1,2-torsional pairs. The torsional angles considered in this study are indicated in figure 4.1.

![Figure 4.1. Structure of the model used in the conformational analysis study. The torsional pairs of interest have been highlighted. N is the repeat unit.]

4.2.1. Simulation I

A conformational search between all adjacent torsional angle pairs was calculated. A pair of torsional angles were stepped from -180° to 170° (through 0°) at 10° intervals. After each iteration the pair of torsional angles were held stationary while the remainder of the molecule was minimised to energy convergence, see figures 4.2-4.10.

4.2.2. Conformational Analysis Results
Figure 4.2. Conformational energy map for rotations about $\Phi_1$ and $\Phi_2$, showing minima near $\pm 90^\circ$ and $\pm 180^\circ$, for $\Phi_1$ and $\Phi_2$ respectively. The legend energy values are in kcal/mol.
Figure 4.3. Conformational energy map for rotations about $\Phi_2$ and $\Phi_3$, showing minima near $\pm 180^\circ$, for both $\Phi_2$ and $\Phi_3$. The legend energy values are in kcal/mol.
Figure 4.4. Conformational energy map for rotations about $\Phi_3$ and $\Phi_4$, showing minima near $\pm 180^\circ$ and $-60^\circ$, for $\Phi_3$ and $\Phi_4$ respectively. The legend energy values are in kcal/mol.
Figure 4.5. Conformational energy map for rotations about $\Phi_4$ and $\Phi_5$, showing minima near -60° and 120°, for $\Phi_4$ and $\Phi_5$ respectively. The legend energy values are in kcal/mol.
Figure 4.6. Conformational energy map for rotations about $\Phi_2$ and $\Phi_6$, showing minima near $120^\circ$ and $120^\circ, -60^\circ$, for $\Phi_2$ and $\Phi_6$ respectively. The legend energy values are in kcal/mol.
Figure 4.7. Conformational energy map for rotations about $\Phi_5$ and $\Phi_9$, showing minima near $-50^\circ$ and $120^\circ$, for $\Phi_5$ and $\Phi_9$ respectively. The legend energy values are in kcal/mol.
Figure 4.8. Conformational energy map for rotations about $\Phi_6$ and $\Phi_9$, showing minima near $-50^\circ$, $-70^\circ$, $140^\circ$ and $130^\circ$, for $\Phi_6$ and $\Phi_9$ respectively. The legend energy values are in kcal/mol.
Figure 4.9. Conformational energy map for rotations about $\Phi_7$ and $\Phi_8$ showing minima near $\pm 60^\circ$ and $\pm 120^\circ$ for both $\Phi_7$ and $\Phi_8$ respectively. The legend energy values are in kcal/mol.
Figure 4.10. Conformational energy map for rotations about \( \Phi_9 \) and \( \Phi_{10} \) showing minima near -70° and -170°, for \( \Phi_9 \) and \( \Phi_{10} \) respectively. The legend energy values are in kcal/mol.
4.3. Crystal Data Search

4.3.1. Introduction

There are no direct experimental methods for determining the likely conformation of an amorphous polymer. In an attempt to validate the computer generated conformational analysis plots, which determine the likely minima positions, the results were compared with analogous crystal structures from the Cambridge Structural Database (CSD).

4.3.2. Models used in Search

The linear epoxy polymer had to be broken into segments, each of which contained a torsional angle of interest. The segments used in the CSD search are shown in the table 4.1.
Table 4.1. List of segment structures used in CDB search. The arrows indicate the torsional angle(s) searched.
### 4.3.3. Results from CDB search

<table>
<thead>
<tr>
<th>Reference Codes</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_4$</th>
<th>$\phi_5$</th>
<th>$\phi_6$</th>
<th>$\phi_7$</th>
<th>$\phi_8$</th>
<th>$\phi_9$</th>
<th>$\phi_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACBUOL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56.37</td>
</tr>
<tr>
<td>ASCIIQT</td>
<td>-80.40</td>
<td>-172.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-77.52</td>
</tr>
<tr>
<td>ALPROL</td>
<td>-78.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-68.17</td>
</tr>
<tr>
<td>BAMWER</td>
<td>61.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAPCCT</td>
<td>63.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAXIFL</td>
<td>64.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BEMBOK</td>
<td>0.00</td>
<td>-178.00</td>
<td>-173.61</td>
<td>173.00</td>
<td>169.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFINAN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.87</td>
</tr>
<tr>
<td>BOTPAB</td>
<td>-67.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BRUDAG</td>
<td>-176.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BRUDAG</td>
<td>173.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BUFROL</td>
<td>-169.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CABPRO</td>
<td>58.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEGYOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>136.08</td>
</tr>
<tr>
<td>CEGYOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-53.98</td>
</tr>
<tr>
<td>CEGYOC</td>
<td>-119.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48.45</td>
</tr>
<tr>
<td>CEGYOC</td>
<td>-123.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-127.31</td>
</tr>
<tr>
<td>CEGYOC01</td>
<td>-136.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-124.33</td>
</tr>
<tr>
<td>CEGYOC01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>62.45</td>
</tr>
<tr>
<td>CEGYOC01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-136.91</td>
</tr>
<tr>
<td>CEGYOC01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-124.30</td>
</tr>
<tr>
<td>CEGYOC01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52.84</td>
</tr>
<tr>
<td>CERRAS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-62.79</td>
</tr>
<tr>
<td>CIDXIW</td>
<td>-179.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIDXIW</td>
<td>177.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIMUD</td>
<td>167.25</td>
<td>-177.00</td>
<td>60.35</td>
<td>-179.00</td>
<td>-172.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COFDEG10</td>
<td>-6.66</td>
<td>-167.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Chapter 4 Characterisation of a Linear Epoxy Polymer by Simulation

<table>
<thead>
<tr>
<th>Reference Codes</th>
<th>$\Phi_1$</th>
<th>$\Phi_2$</th>
<th>$\Phi_3$</th>
<th>$\Phi_4$</th>
<th>$\Phi_5$</th>
<th>$\Phi_6$</th>
<th>$\Phi_7$</th>
<th>$\Phi_8$</th>
<th>$\Phi_9$</th>
<th>$\Phi_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COWSACI</td>
<td>-177.47</td>
<td>179.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COWSACI</td>
<td>179.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (A) [1]</td>
<td></td>
<td></td>
<td>-6.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (A)</td>
<td></td>
<td></td>
<td>14.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (B) [2]</td>
<td>-68.00</td>
<td>131.00</td>
<td>10.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (B)</td>
<td></td>
<td>71.00</td>
<td>-23.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (C) [3]</td>
<td></td>
<td></td>
<td>-4.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (C)</td>
<td></td>
<td></td>
<td>7.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (D) [4]</td>
<td>-11.00</td>
<td>-102.00</td>
<td>-20.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (D)</td>
<td></td>
<td>12.00</td>
<td>-93.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (E) [5]</td>
<td>-178.00</td>
<td>-72.00</td>
<td>-20.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (F) [6]</td>
<td>-177.47</td>
<td>179.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL (F)</td>
<td></td>
<td></td>
<td>63.96</td>
<td>49.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUDXUU</td>
<td></td>
<td></td>
<td>63.97</td>
<td>49.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUDXUU</td>
<td></td>
<td></td>
<td>132.45</td>
<td>-63.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUDXUUU01</td>
<td></td>
<td></td>
<td>63.97</td>
<td>49.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUDXUUU01</td>
<td></td>
<td></td>
<td>132.41</td>
<td>-63.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUIXEX</td>
<td></td>
<td></td>
<td>174.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUIXEX</td>
<td></td>
<td></td>
<td>174.11</td>
<td>177.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUIXEX01</td>
<td></td>
<td></td>
<td></td>
<td>172.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUIXEX01</td>
<td></td>
<td></td>
<td>-172.84</td>
<td>173.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUZTIA</td>
<td>152.12</td>
<td>-177.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUZTIA</td>
<td></td>
<td>-175.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGBPA10</td>
<td>177.62</td>
<td>-175.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGBPA10</td>
<td>-176.89</td>
<td>-174.78</td>
<td>49.01</td>
<td>64.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Chapter 4 Characterisation of a Linear Epoxy Polymer by Simulation

<table>
<thead>
<tr>
<th>Reference Codes</th>
<th>$\Phi_1$</th>
<th>$\Phi_2$</th>
<th>$\Phi_3$</th>
<th>$\Phi_4$</th>
<th>$\Phi_5$</th>
<th>$\Phi_6$</th>
<th>$\Phi_7$</th>
<th>$\Phi_8$</th>
<th>$\Phi_9$</th>
<th>$\Phi_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DINWOM10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-61.43</td>
<td>-35.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DITLAT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>179.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DL.CARC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>174.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPOXIX</td>
<td>9.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>167.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPOYET</td>
<td>-179.64</td>
<td>171.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPOYET</td>
<td>-179.64</td>
<td>171.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPNBIE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>177.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FALTIV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-63.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FALTIV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>63.33</td>
<td>166.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FASFOU</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-179.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIWMAZ</td>
<td>-169.04</td>
<td>176.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOKOAN</td>
<td>177.90</td>
<td>-177.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOPYUE</td>
<td>-7.03</td>
<td>-170.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FUCVOO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>174.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FUCVOO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>174.03</td>
<td>-169.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GEHJAE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-119.70</td>
<td>-105.09</td>
<td></td>
</tr>
<tr>
<td>GLPCHO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>172.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLPHEA20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>166.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HEXPIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-170.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPALXP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>178.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPALXP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-177.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JAPNIX</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-120.59</td>
<td>57.00</td>
<td></td>
</tr>
<tr>
<td>JECVES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>178.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JENGIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-169.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JENGIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-169.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JEFFFEY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-155.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference Codes</td>
<td>$\Phi_1$</td>
<td>$\Phi_2$</td>
<td>$\Phi_3$</td>
<td>$\Phi_4$</td>
<td>$\Phi_5$</td>
<td>$\Phi_6$</td>
<td>$\Phi_7$</td>
<td>$\Phi_8$</td>
<td>$\Phi_9$</td>
<td>$\Phi_{10}$</td>
</tr>
<tr>
<td>----------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>JEZZIX</td>
<td>171.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JIKJOC</td>
<td></td>
<td>-61.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JIKJOC</td>
<td></td>
<td></td>
<td>169.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JIKJOC</td>
<td></td>
<td></td>
<td>175.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JIKJOC</td>
<td></td>
<td></td>
<td>-57.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JINIBAJ</td>
<td></td>
<td></td>
<td></td>
<td>-173.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KADNIM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-67.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KEHUU</td>
<td></td>
<td>-6.00</td>
<td></td>
<td></td>
<td></td>
<td>178.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KEFBIG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>53.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KEFBOM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-176.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NACOLY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPHOFN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-127.54</td>
<td>-151.59</td>
</tr>
<tr>
<td>PBUMSL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>178.40</td>
</tr>
<tr>
<td>PBUTOL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>176.53</td>
</tr>
<tr>
<td>PBUTOL10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>176.98</td>
</tr>
<tr>
<td>PCHOLB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>172.21</td>
</tr>
<tr>
<td>PCHOLB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>179.30</td>
</tr>
<tr>
<td>FINDOL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>176.05</td>
</tr>
<tr>
<td>PROPDD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-174.60</td>
</tr>
<tr>
<td>PROPDLL10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>58.57</td>
</tr>
<tr>
<td>PROPDLL10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>58.01</td>
</tr>
<tr>
<td>PROPRA10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-68.79</td>
</tr>
<tr>
<td>PXEZSD</td>
<td></td>
<td>-14.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-165.33</td>
</tr>
<tr>
<td>SDODGL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>173.96</td>
</tr>
<tr>
<td>SDODGL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>176.42</td>
</tr>
<tr>
<td>SEWEF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-176.62</td>
</tr>
<tr>
<td>SGLYCP02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-47.63</td>
</tr>
<tr>
<td>SGLYCP02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-175.39</td>
</tr>
</tbody>
</table>
### Table 4.2. Results from Cambridge Data Base search. The structures related to the reference codes are listed in Appendix 1.

To help visualise the results from the CDB search, the search hits are shown for each individual torsional angle.

<table>
<thead>
<tr>
<th>Reference Codes</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_4$</th>
<th>$\phi_5$</th>
<th>$\phi_6$</th>
<th>$\phi_7$</th>
<th>$\phi_8$</th>
<th>$\phi_9$</th>
<th>$\phi_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGLYCPI0</td>
<td>-49.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SGLYCPI0</td>
<td>-174.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIXDOS</td>
<td></td>
<td></td>
<td>112.60</td>
<td>-53.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOGSOW</td>
<td>-175.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOGSOW</td>
<td>177.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOGSUC</td>
<td>-176.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TACHAG</td>
<td></td>
<td></td>
<td>-37.55</td>
<td>105.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIMOLM</td>
<td>-176.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIMOLM</td>
<td>167.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VANKIE</td>
<td>60.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VANKIE</td>
<td>53.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VANKIE</td>
<td>65.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VANKIE</td>
<td>51.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIGWAV</td>
<td>54.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VUXLUV</td>
<td>-50.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VUXLUV</td>
<td>-50.77</td>
<td>-165.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VUXTIR</td>
<td>-169.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZZZPV02</td>
<td>67.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.11. A summary of the $\Phi_1$ results from the CDB search shown in table 4.2.

Figure 4.12. A summary of the $\Phi_2$ results from the CDB search shown in table 4.2.
Figure 4.13. A summary of the $\Phi_3$ results from the CDB search shown in table 4.2.

Figure 4.14. A summary of the $\Phi_4$ results from the CDB search shown in table 4.2.
Figure 4.15. A summary of the $\Phi_5$ results from the CDB search shown in table 4.2.

Figure 4.16. A summary of the $\Phi_6$ results from the CDB search shown in table 4.2.
Figure 4.17. A summary of the $\Phi_7, \Phi_8$ results from the CDB search shown in table 4.2.

Figure 4.18. A summary of the $\Phi_9, \Phi_{10}$ results from the CDB search shown in table 4.2.
4.4. Stress and Temperature Analysis by Boltzmann Distribution

4.4.1. Simulation Techniques

The Boltzmann distribution method is an easy and informative procedure for determining the population shifts that occur between torsional states, under varying temperature and stress conditions. To calculate the torsional population, the torsional values were collected from the trajectories (see next section for experimental details) and rounded to the nearest 10°. From this the percentage plots were generated. An illustration of the type of model used in the following calculations is shown in picture 4.1.

4.4.1.1. Simulation I (Temperature Analysis)

In this study four structures were used, whose conformations had been previously generated by the Monte Carlo technique. The following steps were used to determine the Boltzmann torsional distribution of each torsional angle: step 1, the structures were energy-minimised using the conjugate gradient method, until energy convergence; step 2, the structures were then heated from 0-500K and were held at 500K until the potential energy for each system equilibrated. At this high temperature the time period is typically ~10ps; step 3, the temperature was then lowered by 100K; step 4, the system was then allowed to equilibrate for a further 100ps; step 5, steps 3 and 4 were repeated until 300K was reached. The time step for the molecular dynamics was 1fs and 'snapshots' were taken every 0.1ps during step 4. The values of each torsional angle, shown in figure 4.1 were analysed from the 'snapshots' and are shown as population plots in figures 4.19-4.27.

4.4.1.2. Simulation II (Stress Analysis)

A periodic boundary box was applied to four conformations of the structure which had previously been generated by the Monte Carlo technique. The following steps were applied during this computer experiment: step 1, the molecule only was energy-minimised, using the conjugate-gradient method, until energy convergence was achieved; step 2, the molecule was allowed to equilibrate at 300K at a fixed volume until the potential energy reached equilibrium, using the summed verlet algorithm [7]; step 3, at this point the conformation with the lowest potential energy was extracted; step 4, the structure was subjected to an uniaxial force...
which was applied to the face perpendicular to the axis of the epoxy molecule. Three separate experiments, compressive and tensile stress experiments along with a non-stressed experiment were then applied to each system. The time step for the molecular dynamics was 1fs and 'snapshots' were taken every 0.1ps during steps 2 and 4.

Picture 4.1. Model used in temperature and stress calculations.
4.4.2. Temperature and Stress Distribution Results

Figure 4.19. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.20. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.21. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.22. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.23. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.24. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.25. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.26. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
Figure 4.27. The top figure illustrates the structural motif studied, followed by temperature and stress percentage population plots.
4.5. Discussion

The schematic representation of the epoxy molecule and notation, in figure 4.28 is used to clarify the torsional states of the linear epoxy polymer. In many instances the atoms in question, i.e. O and N, do not form tetrahedral structures, as shown below, nevertheless the schematic is used to illustrate the general theme.

![Schematic representation of notations used to classify torsional states.](image)

The value of the torsional angle $\Phi_1$, determined by the minimum positions in the conformational analysis plot, figure 4.2, deviates significantly from the crystal data, figure 4.11. For a phenol system ab initio calculations [8] indicate that the conformation of the O-C bond is approximately co-planar with the phenyl ring. This conformation maximises the conjugation between the $\pi$ lone pair on the ether oxygen and the $\pi$ electrons of the phenyl ring. Molecular mechanic (MM) calculations reveal that when $\Phi_1 = 0^\circ$ (or 180$^\circ$), there is a 9kcal/mol increase in the van der Waal's energy component. This is due to the close proximity (1.89Å) of the methylene hydrogens and the phenyl hydrogen, see figure 4.29. If however, $\Phi_1 = \pm 90^\circ$ the total potential energy decreases by ~5kcal/mol.
As expected there is close agreement between the conformational analysis plot, figure 4.2, and the populated regions in figure 4.19. The $\Phi_1$ population distribution is bimodal, residing in the $g_i^-$ and $g_i^+$ domains, which correspond to the minimum positions on the $\Phi_1\Phi_2$ plot. At 300K in both the periodic boundary condition (PBC) and non-PBC systems the populations are the same, with a value of about 78% and 75% for the $0\rightarrow180^\circ$ region respectively. The population decreases in the $0\rightarrow180^\circ$ region as the temperature is raised, whereas the population increases for the $0\rightarrow180^\circ$ region under similar conditions. These observations suggest that the $g_i^+$ domain is not a minimum region, but the results from the $\Phi_1\Phi_2$ contradict this. It can be only concluded that molecular unit is being forced to populate the $g_i^+$ region due to external factors. This point will be discussed later in context with hydrogen bonding that occurs further along the chain.

On the application of a compressive stress the $\Phi_1$ shifts to two degenerate states, which are energetically higher. These two degenerate states can be seen in figure 4.2, forming a tetra-modal system that resides in the $t.g_i^+, g_i^+g_i^+$ and symmetry-related domains. The energy difference between the ground and degenerate states is approximately 1kcal/mol with an energy barrier of 3kcal/mol. When the system is expanded there is a population shift from $g_i^- \rightarrow t.g_i^-$ along with its symmetrically related region to form a bimodal system. Again it must be noted that under both stress conditions the population in the $0\rightarrow180^\circ$ region predominates over the $0\rightarrow$
180° domain. This is due to the effects of hydrogen bonding at Φ₃, and will be discussed later in this section.

The majority of the Φ₂ values from the CDB search are at ±180°, see figure 4.12, which compares favourably with the minimum regions seen in the conformational energy plots Φ₁Φ₂ and Φ₂Φ₃ (figure 4.2 and 4.3 respectively). However, from all the molecular dynamic's runs Φ₃ appears to be a tri-modal system with degenerate states at g⁻ and g⁺, while the energy minimum resides at t₁t₄. From the results of the conformational analysis the degenerate state has an energy barrier of 3kcal/mol, and energy difference of 1kcal/mol, shown in figure 4.2. In figure 4.3 the position of the degenerate states corresponds to high energy states, in the region of 2-5kcal/mol. As the temperature increases so the population shifts, g⁻→t₁ and g⁺→t₄ while the g⁺ population domain increases at the expense of the g⁻ population. What is strange about this torsional angle is that from the conformational energy plots Φ₁Φ₂ and Φ₂Φ₃ one would expect the population at g⁻ to be lower at 300K than that at t₁t₄, due to the higher energy of these states, but the reverse is observed. It appears that hydrogen bonding stabilises this conformation. The effects of this will be discussed with Φ₃. When the system is under expansive stress the t₁t₄ domain is highly populated, with respect to the degenerate states at g⁻ and g⁺. Under a compressive stress a population shift takes place and the high population of the g⁺ domain diminishes as the population of its symmetry-related domain increases. From the Φ₂Φ₃ and Φ₃Φ₄ plots the population shifts appear to move to states that have a high energy value of 2-4kcal/mol.

Figure 4.21 shows that Φ₃ is essentially a tri-modal system, with population regions at t₁t₄, g⁻g⁺ and g⁺g⁻. The crystal data (figure 4.13) and the conformational analysis plots (figure 4.3 and 4.4), agree with the positions of these populated regions, however the population magnitudes warrant further discussion. Under non-stress conditions the region at g⁺ is highly populated compared with other states. This is not only due to the minima regions (0-1kcal/mol) that are found at these points from conformational plots Φ₂Φ₃ and Φ₃Φ₄, but is largely due to the intramolecular hydrogen bonding taking place, (between the hydroxyl hydrogen and ether group at this minimum site for Φ₃). For the temperature experiments, the total population in the t₁t₄ region remains fairly constant at approximately 24%. As the temperature increases there is a shift in population...
from the highly populated, low energy region $g_+^+g_+^+$, to the sparsely populated, high energy region $g_-^+g_-^-$. This reduces the overall hydrogen bonding energy, as would be expected with increased temperature. As external stresses are applied so shifts in the population from one low energy region to another are observed. On the application of a tensile stress the population almost completely shifts away from $g_-^+g_-^-\rightarrow g_+^+g_+^+$ to populate predominately the $t_-t_+$ region and the $g_+^+g_+^+$ domain. When the molecular chain is compressed the population of the $g_-^+g_-^-\rightarrow g_+^+g_+^+$ region predominates at the expense of the $g_-^+g_-^-\rightarrow g_+^+g_+^+$ region. The hydrogen bonding energy under both stress conditions is reduced due to the perturbing forces.

The torsional angle values which appear in the crystal data for $\Phi_4$ (figure 4.14), compare favourably with the results from the conformational analysis plots, (figure 4.4 and 4.5) and molecular dynamics experiments in figure 4.22. The $\Phi_3\Phi_4$ conformational analysis plot, shows that there is only one region on the plot that is below 1 kcal/mol. This single mode is situated in $g_-^+g_-^-\rightarrow g_+^+g_+^+$ domain, a position where intramolecular hydrogen bonding, between the hydroxyl and the ether group is observed. The population in the $t_-t_+$ region was found to be very high considering the energy is almost 3 kcal/mol higher than the minima, in both energy plots, $\Phi_3\Phi_4$ and $\Phi_4\Phi_3$. The reason for this is because the hydrogen bonding, as discussed above, is very prevalent in the $g_-^+g_-^-\rightarrow g_+^+g_+^+$ region for $\Phi_3$ (see figure 4.3). This forces the $\Phi_4$ to adopt a conformation which is energetically higher, with respect to $\Phi_3$ (see $\Phi_3\Phi_4$). As the temperature increases the effectiveness of the hydrogen bond is reduced, resulting in a reduction in population in the $t_-t_+$ region, for the more energetically favourable $g_-^+g_-^-\rightarrow g_+^+g_+^+$. Figure 4.22 shows how for $\Phi_4$ the $0\rightarrow 120^\circ$ region predominates, when a tensile force is applied. On the application of a compressive force the $g_-^+g_-^-\rightarrow g_+^+g_+^+$ domain predominates.

The energy contour maps $\Phi_4\Phi_5$, (figure 4.5), $\Phi_3\Phi_6$ (figure 4.6) and $\Phi_5\Phi_6$ (figure 4.7) show minima values over a wide range. The crystal data also shows a large distribution for $\Phi_4$ in figure 4.15. Despite this the crystal data 'hits' and energy plot minima values coincide. The large population distribution is because $\Phi_5$ is surrounded by three other torsional bonds producing complex torsional distributions. In figure 4.23a, there appears to be very little consistency or readily interpretable trends in the results. For example, in the $0\rightarrow 180^\circ$ region the total population of $\Phi_5$ is 98.9% at 300K, whereas at 500K, the population reduces to 66.9%. An intermediary population at 400K would be expected, but a population
of 64.2% is observed. However, the population shifts can be explained in terms of neighbouring torsional motions. This is demonstrated with the aforementioned example. At 300K, the intramolecular hydrogen bonding is greatest and as mentioned in the previous section, it forces $\Phi_4$ into the $t_1 t_4$ domain. From $\Phi_3 \Phi_5$, it can therefore be seen that a region 1-3 kcal/mol is populated. This corresponds to the $g_1^+ g_1^-$ and $g_2^+ g_2^-$ domain in figure 4.23. In the non-PBC system at 300K, one of the regions is highly populated while in the PBC system both these regions are equally populated. The reason for the discrepancy between the 300K population distributions may be due to the lack of phase space searched (non-statistical results) and the fact that the neighbouring phenyl group will experience a varying environment in the bulk. When $\Phi_2$ is subjected to a compressive stress the majority of peaks reside in the negative region, see figure 4.23b. This relates to the compression population shifts that occur in $\Phi_4, \Phi_6$ and $\Phi_9$. When the molecule is expanded the highest population distribution peak for $\Phi_3$ is in the $g_3^-$ domain, with a broad distribution between $g_3^+ \leftrightarrow g_3^-$ (see figure 4.23). These distributions correspond to all the minima regions in the conformational analysis plots and relate very strongly to the population expansion values of $\Phi_4, \Phi_6$ and $\Phi_9$.

The conformational energy plot for $\Phi_6$, figure 4.6, contains four minima regions at $\pm 120^\circ$ and $\pm 60^\circ$, while $\Phi_3 \Phi_5$ (figure 4.8) has two deep minima wells at $-50^\circ$ and $-70^\circ$. The crystal data, figure 4.16, shows 'hits' in the vicinity of these minima values. Figure 4.24 shows the overall population distribution of $\Phi_6$ to be a tetra-modal system. In the previous section it was seen that $\Phi_6$ resides in the $g_3^+ g_3^-$ domain, at 300K. From $\Phi_3 \Phi_5$, it can be concluded that because of this the $\Phi_6$ population would be a maximum at $g_3^- g_3^-$ and $t_1 g_3^+$. This trend is clearly seen in figure 4.24. To simplify the description of changes that occur in the population shift, when stress is applied to $\Phi_6$, the population distribution is split into two regions, $g_3^- \rightarrow t_1$ and $g_3^+ \rightarrow t_4$. The total population for each region is 50%, under a compressive, tensile stress and even at 300K for both non-PBC and PBC systems. The fact that the population remains fairly constant, with fluctuations of $\pm 2.5\%$, as the temperature is varied, demonstrates that the net $\Phi_6$ population is unaffected by temperature and stress, and that localised motions are due to the influence of neighbouring torsional angles.

The energy contour map, in figure 4.9., clearly illustrates these torsions as degenerate tetra-modal systems, with minima values in the $t_2 g_3^-, g_3^- g_3^-$ and
corresponding symmetry related energy domains. The energy barriers between the minima regions is 12.5kcal/mol, which is in very good agreement with literature value [9] of 11.7kcal/mol. Owing to the steepness of the energy minima well, the population of the region is dependent on the starting conformation and will surmount this barrier at high temperatures and stresses. Taking the distribution of $\Phi_\gamma \Phi_\delta$ as a whole in figure 4.25, all the regions are occupied. The regions occupied by the modes do not change under the application of stress or temperature, but there appears to be a broadening in the population distribution. The crystal data [10] values for $\Phi_\gamma$ and $\Phi_\delta$ are 64.301° and 49.01°, which are in good agreement with the conformational analysis plot and crystal plot (figure 4.17). Other studies [11] using molecular mechanics also show excellent agreement with these values.

The low energy regions on the energy contour map $\Phi_9 \Phi_{10}$ are very broad, in the $g^+$ and $g^-$ domain (figure 4.10), whereas the minima positions in $\Phi_9 \Phi_9$ and $\Phi_8 \Phi_9$ are confined to the $t_+g^+$ domain. The torsional angle $\Phi_9$ like $\Phi_5$ has three neighbouring torsional angles which affect the torsional angle population distribution. The population between the non-PBC and bulk systems both have values of ~74%, in the $t_+g^+$ region, at 300K. This corresponds to a minima in the $\Phi_9 \Phi_{10}$, which is at the point where $\Phi_{10} = -50^\circ$. As the temperature increases there is a population migration from $t_+g^+ \rightarrow g^+$ and $g^+$; these transitions also show corresponding minima positions in the conformational energy plots. To simplify the discussion about the influence of stress on the $\Phi_9$ population distribution, figure 4.26, will be divided into two regions $g^- \rightarrow t_-$ and $g^+ \rightarrow t_+$. On expansion the torsional $\Phi_9$ population in the $g^+ \rightarrow t_+$ region accounts for 58.4% of the total population, whereas under compression the population falls to 46.7%.

The contour map for $\Phi_9 \Phi_{10}$ shows minima positions in the $g^-g^+$, $g^-g^+$ and $t_+t_+$ domain making $\Phi_{10}$ a non-degenerate tri-modal system. The population distribution plot (figure 4.27), shows a very highly populated region at 300K, in the $g^-g^+$. This corresponds to the minima position in $\Phi_9 \Phi_{10}$, which has been discussed in the previous paragraph. As the temperature increases the shifts in population follow a logical trend, for example $t_+t_+$ domain population increases incrementally with respect to temperature at the expense of the $g^-g^+$ region. As a tensile stress is applied there is an increase in the population in the $g^+g^+$ region at the expense of the $g^+g^-$ domain, while the reverse occurs when a tensile force is applied. The $t_+t_+$ region remains fairly constant under both conditions.
At 300K the epoxy molecule adopts a conformation which preserves the hydrogen bonding between the hydroxy hydrogen and ether bond. Above this temperature the effectiveness of the bond is greatly reduced and this is seen by the large reduction in the $\Phi_{10}$ population at $g^7$ in figure 4.27. Since hydrogen bonding appears to influence the conformation, its effect on physical properties will be investigated in the next chapter.

4.5.1. Virtual bonding

The lengths $(N_1N_2, N_2C_\alpha, N_3C_\alpha, N_3N_4)$ and angle $(N_2C_\alpha N_3)$, shown in figure 4.1 and 4.30, are dependent on all the torsional angles, the exception being $\Phi_6$ which adopts a conformation with respect to neighbouring torsions $\Phi_3$ and $\Phi_9$.

![Figure 4.30](image)

**Figure 4.30.** Illustrates virtual bonding of the epoxy link system. See figure 4.1 for the respective atom positions.

The effect of stress on the virtual bonds will be discussed in context with the type and direction of force applied to the system. Since the direction in which the force is applied influences the response of the molecule, to simplify the discussion the forces were applied parallel to the axial length of the epoxy link.

Figure 4.31 shows the average and respective standard deviations of each virtual bond length in Å, when subjected to various conditions. The structural pairs $N_1N_2$, $N_3N_4$ and $N_2C_\alpha$, $N_3C_\alpha$, as seen in figure 4.30, are structurally synonymous, therefore are averaged as pairs for the plot.
Chapter 4 Characterisation of a Linear Epoxy Polymer by Simulation

Figure 4.31 The geometry changes that occur in the above structural motifs.

On the application of stress the $N_1N_2/N_3N_4$ structural units show very little deviation away from the mean values, which are themselves relatively constant at 3.38Å. This is consistent with the fact that $\Phi_9$ and $\Phi_{10}$ populations show equal and opposite torsional values under both stress conditions. The result is no net change in the virtual bond lengths under both stress conditions.

However, the $N_2C_\alpha$ and $N_3C_\alpha$ distances result in a noticeable increase in virtual bond length when a tensile stress is applied, which suggests a net torsional angle population shift from $90^\circ \rightarrow 180^\circ$ for $\Phi_9 - \Phi_5$. Closer inspection of the $\Phi_9 - \Phi_5$ population plots in figure 4.19-4.23, show this to be the case, the only exception being $\Phi_4$, where the population for the compressive stress experiment dominates the $\ell_{\ell_\varphi}$ domain. When a compressive stress is applied the net population shift for the remaining torsions is reversed.

Lovell et al. [11] calculated the average distance of NC_\alpha using MM. Their value of 9.5Å was the maximum length obtained for an energy-minimised structure. From figure 4.31 it is seen that our average distance is ~8.5Å. The reason for the discrepancy in these results, is that when using MD at 300K the torsional angles
have sufficient thermal energy to explore the energetically higher $0\rightarrow90^\circ$ regions. This results in a fall in the overall virtual bond length.

The $N_2N_3$ distance was also analysed and as seen in figure 4.31, its stress response is as expected, with an increase and decrease with respective tensile and compressive stresses. The large standard deviation of $N_2N_3$ is 2.4Å, at 300K, an indicator that subtle shifts in torsional angles values can result in large deviations away from the mean value. The compressive and expansive stresses are large enough for the torsional angles not to explore as much phase space, resulting in lower standard deviations as the structural motif is forced into a high energy configuration.

The response of $N_2C_\alpha N_3$ corresponds to the stresses applied to the link molecule, see figure 4.32. The population distribution of $N_2C_\alpha N_3$ is a bimodal system, with maxima at $60^\circ$ and $120^\circ$. At 300K the population in each mode is approximately equal. However, when a tensile stress is applied the equilibrium is disturbed and there is a population shift to the $120^\circ$ region. The population in this domain is 76.8%, but when the epoxy link is compressed the population falls to 57.6%. Lovell et al also determined the $N_2C_\alpha N_3$ angle from MM, giving a value of $110^\circ$, which is close to one of the bimodal regions.
4.5.2. Chain Mobility

The mobility of chains in the condensed state can be characterised by the autocorrelation function of the rotation of torsional angles $\phi$. The mobility of a chain is dependent on the temperature, i.e., the thermal energy the chains have to overcome the rotational energy barriers, and also the density, i.e., the free volume available for the chain to occupy. The autocorrelation function for each torsional angle $\phi$ is defined as

$$R_\phi = \frac{\langle \cos(\phi(t))\cos(\phi(0)) \rangle - \langle \cos(\phi(0)) \rangle^2}{\langle \cos^2(\phi(0)) \rangle - \langle \cos(\phi(0)) \rangle^2}$$  \hspace{1cm} \text{eqn 4.1}

The Fourier transform of this function gives the frequency at which the rotations and vibrations of the torsional angles occur. However, the frequency spectrum is dependent on the intervals of the 'snapshots', which in our case was 0.1ps. Such a time interval is too large to observe molecular vibrations [12], which are measured by infra-red ($10^{12}$ to $3\times10^{14}$Hz) but is more akin to the lower frequency molecular
rotations situated between $10^{10}$ and $10^{12}$ Hz (microwave spectroscopy). A typical autocorrelation function plot of one of the torsional angles is shown below. The irregularity of the plot is due to the inadequate sampling time.

![Autocorrelation plot](image)

Figure 4.33. Autocorrelation of $\Phi_1\Phi_1$ torsional pair under compression at 300K.

To obtain the frequency at which the torsional pairs interact the autocorrelation plots were Fourier transformed (FT). This gave plots similar to that shown below.
Figure 4.34. Fourier transform of the $\Phi_1 \Phi_1$ autocorrelation plot.

The peak at the beginning of figure 4.34, is an artefact of the FT cut-off point. All the torsional angles in a given experiment have the same frequencies, these values are listed in the following table.

<table>
<thead>
<tr>
<th>Compressive stress</th>
<th>Non-stress system</th>
<th>Tensile stress</th>
<th>Non-PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega \times 10^{12}$ s$^{-1}$</td>
<td>30.9</td>
<td>30.9</td>
<td>30.4</td>
</tr>
<tr>
<td>$\lambda$ cm$^{-1}$</td>
<td>1031</td>
<td>1031</td>
<td>1015</td>
</tr>
</tbody>
</table>

Table 4.3. Frequency and wavenumber results from fourier transformed autocorrelation functions.

When a tensile load is applied to the molecule the frequency shifts to a lower value. As the density decreases so the free volume increases and the intramolecular bonds become more 'flexible' because of the reduced steric effect of the surrounding chains, therefore the molecular chain can explore more phase space. This is seen in the tensile population plot for $\Phi_5$ see figure 4.23. No comments can be made
concerning the magnitude of the observed frequency because no serious attempt was made to take into account the anharmonicity of the molecular chain in the force fields. The only comment that can be made concerns the change in the frequency that occurs when a tensile stress is applied. In this system there was a 16 cm⁻¹ fall in frequency, the magnitude of which compares with that found in crystalline polyoxymethylene [13]. The frequency for the equilibrium system (i.e. non-stress system) and the compressive stress system show no observed change. Usually a hydrostatic pressure is applied to the polymer experimentally, in order to measure the response of the frequencies to compressive stresses. In our simulation a uniaxial stress was applied which appears not to have been of significant magnitude to observe a change in the rotational torsional frequency. However, it is quite possible that some other unmeasured skeletal mode (i.e. bond or angle) may have absorbed the strain energy. Experimental frequencies show a marked increase in the frequency when a hydrostatic pressure is applied. The reason for this is that in the condensed state the structure is dominated by excluded volume packing constraints. As the free volume decreases the molecules are in closer proximity, therefore the frequency increases due to greater steric effects.

When the molecule is in the isolated state (i.e. non-PBC system) intramolecular hydrogen bonding plays an important role in the configuration of the chain. It was observed that the chain curls up on itself, therefore enhancing the likelihood and the effectiveness of hydrogen bonding, see picture 4.2. This locks the structure in a given configuration, which is equivalent to increased steric factors, therefore the rotational frequency increases.

The changes in frequency and corresponding free volume changes can be associated with the changes in population that occur. It is observed, from the population plots, that when the system is compressed and the frequency increases the population in general forms a higher and narrower peak than its tensile stress counterpart.
4.6. Conclusion

This study demonstrates how each torsional angle in a linear epoxy system varies with the application of stress. They all demonstrate population migration from lower energy states to a higher energy state on the application of an external stress, except $\Phi_7$ and $\Phi_8$. The $\Phi_6$ torsional angle is the only one not directly forming the main chain of the link molecule and it can be concluded that its motion is due to the motions of $\Phi_5$ and $\Phi_6$. Subtle changes in torsional angle value can result in large changes in virtual bond lengths $N_2C_\alpha$ and $N_3C_\alpha$. This is due to the many energy minima sites which each torsional angle possesses. The response of angles $N_1N_2C_\alpha$ and $N_4N_3C_\alpha$ is due to the orientation of the torsional angles.
between N\textsubscript{2}C\textalpha{} and N\textsubscript{3}C\textalpha{}. N\textsubscript{2}C\textalpha{}N\textsubscript{3} shows a clear and positive response to the type of external stress applied, increasing and decreasing on the application of respective tensile and compressive stresses.

At 300K, the conformation appears to be dictated by the presence of hydrogen bonding, causing the torsional angles to reside in regions which are not the energy minima positions. In 1957 Bernal [14] noted this observation and stated that wherever hydrogen bonding occurs it appears to be mainly responsible for the configuration of the polymer molecule, that is for their so-called secondary structure. As the temperature increases the epoxy link has enough thermal energy to break these bonds and explore more phase space. Owing to the importance of this bond, its effect will be studied in response to the calculated mechanical and physical properties of the polymer in the next chapter.

Finally, the frequencies calculated from the torsional angle autocorrelation function show a strong correlation with the applied stress. Quantifying the response of this non-equilibrium process is very difficult, therefore to simplify the problem the torsional autocorrelation functions would have to be calculated during an equilibrium period. This means that the volume would remain fixed while the molecule equilibrates, only after this period would 'snapshots' be collected. In order to measure the response of the torsional angles to density changes, a fixed strain should be applied and the molecule should then be allowed to equilibrate. Again, only when equilibrium has been reached should 'snapshots' be collected every 1-10fs. The controlled method should yield results that could be compared with experimental data, but it should be noted that refinements to the force fields would be required if comparable results with spectroscopic techniques are to be obtained.
4.7. References

Simulation & Theoretical Study of a Linear Epoxy Polymer

5.1. Introduction ....................................................................................................................... 154
5.2. Theoretical Calculations of Properties ............................................................................. 154
  5.2.1. Physical Property ................................................................................................. 154
      5.2.1.1. Density ......................................................................................................... 154
      5.2.1.2. Cohesive Energy ......................................................................................... 156
      5.2.1.3. The Hildebrand Solubility Parameter ......................................................... 157
  5.2.2. Mechanical Properties ......................................................................................... 157
      5.2.2.1. Bulk Modulus ............................................................................................. 158
      5.2.2.2. Other Elastic Constants ............................................................................... 159
5.3. Theory of Mechanical Properties ............................................................................... 160
  5.3.1. Theory of Stress and Strain ..................................................................................... 160
      5.3.1.1. Bulk modulus (B) ......................................................................................... 163
      5.3.1.2. Young's Modulus (E) .................................................................................. 164
      5.3.1.3. Shear Modulus (G) ...................................................................................... 165
      5.3.1.4. Poisson's Ratio (ν) ....................................................................................... 166
      5.3.1.5. Lamé Constants (λ, μ) ................................................................................ 167
      5.3.1.6. Other Properties ............................................................................................ 167
      5.3.1.7. Relationship between Elastic Constants ..................................................... 168
5.4. Simulation Calculations of Mechanical Properties ......................................................... 168
  5.4.1. Simulation Method .................................................................................................. 168
5.5. Simulation Calculations of Physical Properties ............................................................ 171
  5.5.1. Simulation Method ................................................................................................ 171
5.6. Discussion ..................................................................................................................... 172
  5.6.1. Mechanical Properties ......................................................................................... 172
  5.6.2. Physical properties .............................................................................................. 173
      5.6.2.1. Glass Transition Temperature ..................................................................... 174
      5.6.2.2. Thermal expansion coefficients .................................................................... 180
      5.6.2.3. Density .......................................................................................................... 184
      5.6.2.4. Cohesive Energy .......................................................................................... 186
      5.6.2.5. Hildebrand Solubility Parameter ................................................................. 187
      5.6.2.6. Hydrogen bonding ......................................................................................... 188
5.7. Conclusion ...................................................................................................................... 192
5.8. References ...................................................................................................................... 193
5.1. Introduction

This chapter is divided into two sections, theoretical and computer simulation. The main objective is to determine the physical and mechanical properties of the linear epoxy polymer using these two techniques. In the discussion the results will be compared with the experimental data collected in chapter 2.

5.2. Theoretical Calculations of Properties

This section describes how all the mechanical and physical properties are calculated from empirical group additive values based on van Krevelen's property estimation which is correlated with chemical structure.

5.2.1. Physical Property

The following physical properties will be calculated: density, cohesive energy and Hildebrand's solubility parameter.

5.2.1.1. Density

The density, which is the reciprocal of specific volume, can be readily determined experimentally (chapter 2). Density and specific volume have certain characteristic values for certain families of polymers. The specific volume \( v \) is the volume per unit weight shown below:

\[
\nu = \frac{1}{\rho} \quad [\text{cm}^3\cdot\text{g}^{-1}] \quad \text{eqn. 5.1}
\]

The molar volume \( V \) is related to density as shown in equation 5.2. Despite it being one of the first physical properties to be derived by group contributions, the values of \( V \) do vary slightly between authors. These deviations accumulate as the values are added, giving relatively large variations in density values. The following table lists the molar volume values recommended by van Krevelen, but as will be demonstrated discrepancies arise between rubbery and glassy state densities.
Table 5.1 Contains group contribution values for the determination of density at 298K. †This value is derived from atomic contributions where the values of C, H, O are 10.00, 3.20 and 6.40 respectively. ‡There are no values for N in the rubbery state therefore the V_g value was used.

The density can be calculated from the following equation:

$$\rho_{298K} = \frac{M}{V}$$  \hspace{1cm} \text{eqn. 5.2}$$

where $M=552$, being the molecular mass of the repeat unit. The density of the linear epoxy polymer in the glassy and rubbery state was calculated from equation 5.2 to be 1.12 g/cm³ and 1.16 g/cm³ respectively. The latter value is too high due to the small molar volume value. It should be noted that under normal circumstances the density in the rubbery state is lower than that in the glassy, this is due to the greater molar volume $V$ a molecule occupies when in the rubbery state. The molar volume values estimated by Traube [1] and Malone et al. [2] are also too small resulting in very high densities.
5.2.1.2. Cohesive Energy

The cohesive energy $E_{\text{cohesive}}$ is defined [3] as 'the increase in the internal energy $U$ per mole of substance if all the intermolecular forces are eliminated'. The $E_{\text{cohesive}}$ can be calculated directly from heat of evaporation experiments, but due to their high molecular weight, polymers do not evaporate. Therefore it is necessary to use other methods to determine $E_{\text{cohesive}}$, such as, comparative swelling or dissolution experiments in various liquids of known cohesive energy density.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Number of Groups</th>
<th>$E_{\text{cohesive}}$</th>
<th>$\sum E_{\text{cohesive}}$</th>
<th>$V_m$</th>
<th>$\sum V_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\text{CH}_3$</td>
<td>2</td>
<td>4710</td>
<td>9420</td>
<td>33.5</td>
<td>67</td>
</tr>
<tr>
<td>$-\text{CH}_2$</td>
<td>6</td>
<td>4940</td>
<td>29640</td>
<td>16.1</td>
<td>96.6</td>
</tr>
<tr>
<td>$-\text{CH}$</td>
<td>2</td>
<td>3430</td>
<td>6860</td>
<td>-1.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>$-\text{O}$</td>
<td>1</td>
<td>1470</td>
<td>1470</td>
<td>-19.2</td>
<td>-19.2</td>
</tr>
<tr>
<td>$-\text{OH}$</td>
<td>2</td>
<td>29800</td>
<td>59600</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>$-\text{O}$</td>
<td>2</td>
<td>3350</td>
<td>6700</td>
<td>3.8</td>
<td>7.6</td>
</tr>
<tr>
<td>phenyl</td>
<td>4</td>
<td>31940</td>
<td>127760</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>phenyl</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>71.4</td>
<td>142.8</td>
</tr>
<tr>
<td>phenylene $(o,m,p)$</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>52.4</td>
<td>104.8</td>
</tr>
<tr>
<td>$-\text{N}$</td>
<td>2</td>
<td>4190</td>
<td>8380</td>
<td>4190</td>
<td>8380</td>
</tr>
</tbody>
</table>

$\Sigma$ 249830 399.6

Table 5.2. Group contribution values for the determination of the cohesive energy and Hildebrand solubility parameter.
The cohesive energy determined from table 5.2 is merely the summation of each group contribution. The final value is converted from J/mol to kcal/mol (where 1cal = 4.184J), therefore

\[ E_{\text{cohesive}} = 59.71 \text{ kcal/mol} \]

### 5.2.1.3. The Hildebrand Solubility Parameter

In 1949 Hildebrand [4] introduced the concept of a solubility parameter \( \delta \), as a manner of quantifying the solubility of polymers in solvents. If the solubility parameters of both polymer and solvent equal each other then the polymer will dissolve in the corresponding solvent.

Hildebrand's solubility parameter \( \delta \) can be calculated from the following equation:

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

\text{eqn 5.3}

where \( V_m \) is the molecular volume in cm\(^3\)/mol, the group values of which are listed in table 5.2, therefore,

\( \delta = 12.22 \text{ cal}^{1/2}/\text{cm}^{3/2} \).

### 5.2.2. Mechanical Properties

This section is concerned with calculating the mechanical properties of the linear epoxy polymer. The properties of interest are Young's Modulus, bulk modulus, Poisson's ratio and the Lamé constants \( \mu \) and \( \lambda \). Unfortunately bulk modulus is the only elastic constant that can be calculated from additive properties, but by using equation 5.25 and 5.26, which relate all the elastic constants, it is possible to derive all the other experimentally measurable elastic constants.
5.2.2.1. Bulk Modulus

The definition of bulk modulus will be given in greater detail in section 5.3.1.1. The following table lists the group additive values used in the calculation of bulk modulus.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Number of groups</th>
<th>$U_i$ (cm$^{1/2}$.s$^{-1/2}$,mol$^{-1}$)</th>
<th>$\sum U_i$ (cm$^{1/2}$.s$^{-1/2}$,mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>880</td>
<td>5280</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4650</td>
<td>9300</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>600</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>450</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>400</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4100</td>
<td>8200</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1400</td>
<td>2800</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td></td>
<td>28730</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Group contribution values for the determination of bulk modulus.

The bulk modulus was calculated as follows:
where $V$ is the molar mass, in the glass region, from group contributions in table 5.2, $U$ is from table 5.3 while the calculated density $\rho$ was used from section 5.1.1.1.

### 5.2.2.2. Other Elastic Constants

Epoxy resins have a characteristic [5] Poisson's ratio of 0.34. By using this value and the theoretically calculated bulk modulus, the other elastic constants of interest can be derived using equations 5.25 and 5.26. The results are listed below in table 5.4.

<table>
<thead>
<tr>
<th>Calculated Elastic Constants (Theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus $E$, (GPa)</td>
</tr>
<tr>
<td>Bulk Modulus $B$, (GPa)</td>
</tr>
<tr>
<td>Poisson's Ratio $\nu$</td>
</tr>
<tr>
<td>Lamé constant $\mu$, (GPa)</td>
</tr>
<tr>
<td>Lamé constant $\lambda$, (GPa)</td>
</tr>
</tbody>
</table>

Table 5.4. Calculated elastic constants based on the determination of the bulk modulus and Poisson's ratio.
5.3. Theory of Mechanical Properties

The mechanical properties of a material are concerned with its behaviour under the application of an external force. This force is referred to as the applied stress and is the force \( F \) acting on unit cross-section area \( A \), i.e. \( F/A \). The response by the material is the strain: the extension of the length. So if the extension is \( \varepsilon \) and the original length is \( l \), then the strain is \( \varepsilon/l \). Hook's law is a simple relationship between the stress \( \sigma \) and the strain \( \varepsilon \), for an ideal elastic material. Therefore the ratio of stress/strain is Young's Modulus \( E \).

To keep within the limitation of the simulation work it is only necessary to consider a Newtonian system. Hence the strain is directly proportional to the stress. This normally applies to very small strains. The theory for this will now be discussed and applied to the determination of the elastic constants from simulation calculations.

5.3.1. Theory of Stress and Strain

Consider a cube (figure 3.2) whose sides are parallel to the x, y, z coordinates, and are subjected to external forces, \( F_1 \), \( F_2 \) and \( F_3 \) acting on the yz, xz and xy planes respectively.

![Figure 3.2 The theoretical cube with stress components.](image-url)
Each force can be resolved into six components related to the coordinate axes x, y and z. The normal stress components are $\sigma_{xx}$, $\sigma_{yy}$ and $\sigma_{zz}$, and the shear stress components are $\sigma_{xy}$, $\sigma_{yz}$ and $\sigma_{xz}$, which form the stress tensor $\sigma_{ij}$:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$  \hspace{1cm} \text{eqn. 5.4}$$

In determining the modulus of a material the cubic shape of the motif greatly simplifies the calculation.

The elastic properties of an isotropic polymeric material can be calculated after an initial energy minimisation, followed by a fast second derivative energy minimisation calculation under a small fixed strain. The expression used to calculate the potential energy is shown below:

$$U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j + \text{higher order terms}$$  \hspace{1cm} \text{eqn. 5.5}$$

where $U$ is the total energy, $U_0$ the equilibrium energy and $\varepsilon$ is the strain. The second derivative is used to calculate the stiffness matrix, using the stress method \([6]\). Theodorou \textit{et al.} [7] have demonstrated that the stress method calculates the elastic constants with greater accuracy than the corresponding energy method, (which is not discussed here).

$$C_{ij} = \frac{\left( \frac{\partial U}{\partial \varepsilon_i}, \frac{\partial U}{\partial \varepsilon_j} \right)}{V}$$  \hspace{1cm} \text{eqn. 5.6}$$

$$= \frac{\partial \sigma_i}{\partial \varepsilon_j} \hspace{1cm} \text{eqn. 5.7}$$

$$= \frac{(\sigma_{i+} - \sigma_{i-})}{2\varepsilon_j} \hspace{1cm} \text{eqn. 5.8}$$

where $V$ is the volume of the cell, $\varepsilon_i$ and $\varepsilon_j$ are the components $i$ and $j$ of the strain tensor, and $\sigma_i$ is the $i$th component of the initial stress tensor. The $\sigma_{i+}$ and $\sigma_{i-}$. 
components are associated with the stress tensor under tension and compression, respectively. Very small strains typically 0.05% are applied along the strain components $\pm \varepsilon_1$ to $\pm \varepsilon_6$, i.e. 12 times. Therefore, for every strain applied to the system there is a corresponding change in each component. The existence of a strain-energy function [8] provides the relationships $c_{pq} = c_{qp}$ and $s_{pq} = s_{qp}$. From this the entire stiffness matrix can be generated, while the compliance matrix is simply the inverse of the stiffness matrix ($S = C^{-1}$).

\[
\begin{bmatrix}
  c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
  c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
  c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\
  c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\
  c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\
  c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66}
\end{bmatrix}
\]

\text{eqn. 5.9}

For an ideal isotropic solid [9], the $s_{ij}$ matrix reduces to

\[
\begin{bmatrix}
  s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\
  s_{12} & s_{11} & s_{12} & 0 & 0 & 0 \\
  s_{12} & s_{12} & s_{11} & 0 & 0 & 0 \\
  0 & 0 & 0 & 2(s_{11} - s_{12}) & 0 & 0 \\
  0 & 0 & 0 & 0 & 2(s_{11} - s_{12}) & 0 \\
  0 & 0 & 0 & 0 & 0 & 2(s_{11} - s_{12})
\end{bmatrix}
\]

\text{eqn. 5.10}

From these two matrices numerous elastic properties can be calculated, namely Young's modulus, bulk modulus, shear modulus, volume compressibility, Poisson's ratio, Lamé constants and the velocity of sound in specified directions. The information obtained from the matrices is dependent on the mode of deformation, i.e. uniaxial extension, hydrostatic pressure or simple shear. Each will be discussed in turn.
5.3.1.1. Bulk modulus (B)

By definition bulk modulus is the volume change per unit volume when a hydrostatic pressure is applied.

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

where \( V_0 \) is the original volume and \( V \) is the volume after the deformation force \( F \) has been applied. The force can be expressed as an external pressure \( p \). \( \Delta V \) is the change in volume.

From the compliance matrix

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

eqn. 5.12
5.3.1.2. Young's Modulus (E)

This is the strain per unit length when a force $F$ per unit cross-sectional area $A$ is applied.

\[ E = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta l/l_0} \]  
\[ \text{eqn. 5.13} \]

where $\sigma$ and $\varepsilon$ are the stress and strain respectively. From the compliance matrix

\[ E_x = \frac{1}{s_{11}}, \quad E_y = \frac{1}{s_{22}}, \quad E_z = \frac{1}{s_{33}} \]  
\[ \text{eqn. 5.14} \]

The values are given in the three directions $x$, $y$, $z$, but for an isotropic system $s_{11} = s_{22} = s_{33}$; see the matrix equations 5.9 and 5.10.
5.3.1.3. Shear Modulus (G)

This is the shear per unit distance between shearing surfaces when a shear force $F$ per unit area $A$ is applied.

$$G = \frac{\tau}{\tan \gamma}$$  \hspace{1cm} \text{eqn. 5.15}

where $\tau = F/A$. The shear modulus can be calculated from the compliance matrix as follows:

$$G = \frac{1}{2}(s_{11} - s_{12})$$  \hspace{1cm} \text{eqn. 5.16}

and also from the stiffness matrix

$$G = \frac{1}{3}(c_{44} + c_{55} + c_{66})$$  \hspace{1cm} \text{eqn. 5.17}
5.3.1.4. Poisson's Ratio ($\nu$)

When a uniaxial tensile load is applied to a material there is a change in length per unit length, (i.e. axial strain). There is a corresponding change in width per unit width of the sample, i.e. a lateral contraction.

![Diagram of a uniaxial tensile load on a rectangular sample]

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

**eqn. 5.18**

This is a measure of Poisson's ratio, which can also be determined from the compliance matrix. The elastic constant is expressed in its numerous directional forms.

\[
\begin{align*}
\nu_{xy} &= -\frac{S_{21}}{S_{11}} \quad \nu_{yx} = -\frac{S_{31}}{S_{11}} \\
\nu_{yx} &= -\frac{S_{21}}{S_{22}} \quad \nu_{yx} = -\frac{S_{32}}{S_{22}} \\
\nu_{zx} &= -\frac{S_{31}}{S_{33}} \quad \nu_{yx} = -\frac{S_{32}}{S_{33}} 
\end{align*}
\]  

**eqn. 5.19**
5.3.1.5. Lamé Constants ($\lambda$, $\mu$)

The Lamé constant $\mu$ is related to the more common shear modulus $G$, which has a direct physical interpretation. See section on shear modulus $G$ for further details.

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

eqn. 5.20

The Lamé constant $\lambda$ has no direct physical meaning and applies only to isotropic materials. From the following equation it can be seen that it is the relation between the two strain components perpendicular to the applied axial stress (transverse modulus), i.e. $b_{yy}, b_{zz}$ in relation to $\sigma_{xx}$:

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}$$

eqn. 5.21

From the stiffness matrix its value can be determined as follows:

$$\lambda = \frac{1}{3}(c_{11} + c_{22} + c_{33}) - \frac{2}{3}(c_{44} + c_{55} + c_{66})$$

eqn. 5.22

5.3.1.6. Other Properties

Other physical quantities can be derived from the moduli and compliance matrix. These include the volume compressibility $\beta$ and velocity of sound $v$ respectively. The volume compressibility can be readily calculated from the bulk modulus as follows:

$$\beta = \frac{1}{B}$$

eqn. 5.23

While the velocity of sound through a material can be calculated from eigenvalues that correspond to the stiffness submatrix, $\lambda_{sc}$, and the density $\rho$. The longitudinal and transverse components for the $x$, $y$ and $z$ directions are taken into account. A total of nine components for the velocity of sound are generated.

$$v = \sqrt{\frac{\lambda_{sc}}{\rho}}$$

eqn. 5.24
5.3.1.7. Relationship between Elastic Constants

These moduli are all interrelated as shown by the following equations. In many cases it is sufficient to determine only two elastic constants, experimentally or theoretically and the other elastic constants can be derived.

\[ E = 3B(1 - 2\nu) = 2G(1 + \nu) \]  

or

\[ B = \frac{\lambda + \frac{2}{3}G}{E} \frac{E}{3(1 - 2\nu)} \]  

5.4. Simulation Calculations of Mechanical Properties

5.4.1. Simulation Method

The monomer unit used to build the linear epoxy chain has a repeat number of 2. This value is very low, because of the atom limit of 200 atoms that can be used in the Elastica [10] module. This limit is dependent on the memory limits of the machine. Such a small number of atoms is not representative of our system and as explained in chapter 1, molecular weight affects the mechanical properties of a polymer. To resolve this problem additional modelling techniques were employed which are discussed next.

To simulate the bulk amorphous state the chain was initially built to an experimentally determined density value of 1.17 g/cm\(^3\) at 300K. The amorphous cell was generated using the random Monte Carlo technique in the amorphous builder. Twenty structures were generated, to obtain a representative number of configurations. Ten structures with the "correct" configuration were extended into an infinite chain based on the scheme of Weber et al. [11], to give an 'infinite' molecular weight. This was achieved by extending the PBC and connecting the tail of the chain to the head of the image. These infinite structures are in a highly energetic state, which is due to the high van der Waals energy component. A series of molecular minimisation (MM) and dynamic simulations (MD) are used to remove the near proximity of some of the atoms and to move the molecule out of...
high energy local minima. All the MM routines used in the relaxation process of the chain employed the conjugate-gradient algorithm. The following steps were applied:-

1) The PBC cell was fixed while the molecule was allowed to minimise until $\Delta E \leq 0.1$ kcal/mol.

2) Micro-canonical MD was then used on a fixed cell for 1000 steps, from 600-300K

3) steps 1 and 2 were repeated followed again by step 1.

4) An adiabatic (EPN) MD algorithm was applied from 100-300K. Both the molecule and the cell were allowed to equilibrate. The run continued until the atom and cell temperature reached the equilibrium temperature of 300K.

5) repeat step 1

6) A canonical (TPN) MD algorithm was then applied at 300K to the molecule and the PBC until a steady volume equilibrium state was achieved. This was typically within 15ps.

7) A configuration with the lowest energy was extracted from the resultant trajectory and saved. The conformer must be within the later half of the run to be well removed from the initial structure.

8) To this saved configuration the MM routine was applied to the cell and the chain until energy convergence was reached. This structure was then used for mechanical property testing.

From steps 4-8 the PBC moves from its idealised cubic shape, this is a reflection of the slight anisotropic nature of the molecules used in the simulation. To overcome this distortion a larger model would have to be built, which is not possible due to atom limits in the program.
The results from ten structures were used to compile the data in table 5.5. The implication of these results and comparison with experimental and theoretical data will be discussed later in this chapter.

<table>
<thead>
<tr>
<th>Calculated Elastic Constants (Simulation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus $E$ (GPa)</td>
</tr>
<tr>
<td>Bulk Modulus $B$ (GPa)</td>
</tr>
<tr>
<td>Poisson’s Ratio $\nu$</td>
</tr>
<tr>
<td>Lamé constant $\mu$ (GPa)</td>
</tr>
<tr>
<td>Lamé constant $\lambda$ (GPa)</td>
</tr>
</tbody>
</table>

Table 5.5. List of elastic constants determined from computer experiments.

Picture 5.1. Space filled amorphous $(\text{AE})_2$ model at 1.17 g/cm$^3$. The colours represented are: blue-nitrogen, red-oxygen, grey-carbon and white-hydrogen.
5.5. Simulation Calculations of Physical Properties.

A series of monomer repeat units of DAE and BADGE, as shown in figure 4.1, were used in the simulation. The object of this study was to see the effect of chain length and temperature on the thermal expansion coefficients \( \alpha_g \) and \( \alpha_l \), the glass transition temperature \( T_g \) and the density.

5.5.1. Simulation Method

Using the amorphous builder, (which has been previously described in section 3.2.10), ten amorphous cells were built, for each of the following oligomers and polymer system, \((AE), (A_2E), (AE)_2 \) and \((AE)_m\), where A=amine, E=epoxy. The densities in each case were set to 1.17 g/cm\(^3\), which is the experimental value determined in section 2.3.5. The following procedures were used in this computer experiment: step 1, the oligomer chain was energy-minimised while the periodic boundary cell was fixed until energy convergence; step 2, the oligomer chain was then fixed and the PBC was energy minimised until energy convergence; step 3, the energy of the system was calculated and the system with the lowest potential energy was chosen for further evaluation; step 4, while the cell was fixed the temperature was raised from 0K to 500K over a 10-15 ps period. The temperature was then lowered to 450K; step 5, the volume and the molecule were allowed to reach equilibrium using the EPN ensemble over a 100 - 150 ps period; step 6, the temperature was lowered 10 or 50K depending on the model used, and step 5 was repeated; step 7, repeat step 5 and step 6 until 150K has been reached. The 0 K structures were obtained by extracting a low volume/P.E. conformation for the 150K run and energy-minimising the PBC and molecular structure until energy convergence.

The time step for the summed verlet molecular dynamics was 1fs and "snapshots" were taken every 0.05ps during step 5. The stability of the potential energy and the volume was used as an indicator of equilibrium. Once volume and energy equilibrium had been reached, the last 20ps from the collected "snapshots" were used in the determination of the physical properties.
5.6. Discussion

5.6.1. Mechanical Properties

The elastic constants calculated from theory, simulation and experiment are summarised in table 5.6. All the results are comparable when the standard deviations are taken into account. There are a few factors that need to be considered when comparing these values.

Firstly, temperature plays a significant role in the magnitude of the elastic constants. The experimental and theoretical results show closer agreement because both procedures represent results taken at 298K. The simulation values however were calculated at zero Kelvin, thus giving the elastic constants higher values than expected. The effect of temperature on the elastic constants of crystalline polyethylene was discussed in chapter 3. This system showed a 54 GPa decrease in Young's modulus as the temperature was raised from 0 to 300K. However, such large changes are not expected with amorphous systems. Qian et al. [12] demonstrated this with a 0.12 GPa decrease in Young's modulus with a corresponding 200K increase in temperature for amorphous polyethylene. For Brown et al. [13] there was approximately a 0.3 GPa decrease over the same temperature range for a similar polymer. Hsu et al. [6] and Rutledge et al. [14], who employed a similar simulation method, experienced an identical trend, with simulation results being higher than experimental values. They concluded their results to be in good agreement with experimental values.

Another factor that has to be taken into account is the size of the model used in the simulation experiment. The program has a 200 atom limit and only 10 models were constructed. Ideally, an isotropic model should be built but the probability of building an amorphous model that displays some anisotropic behaviour is quite high, even after relaxing the system using MM and MD algorithms. Therefore, the elastic constants will vary from one model to another depending on the degree of anisotropy. This results in relatively large standard deviations between elastic constant values.

Finally, there is one important factor that has not been accounted for in the model and that is macroscopic defects. This includes voids and structural defects, such as cracks, phase separation, etc. Our model represents an ideal system with ideal...
interactions between atoms and molecules, which means our simulated elastic constants will be higher than the experimental values.

By considering these three factors it can be concluded that the simulation results represent the upper limits of the elastic constants. Taking all these factors into consideration it can be concluded that the simulation results are in good agreement with experimental and theoretical results.

### Mechanical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment (GPa)</th>
<th>Simulation (GPa)</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus $E_y$</td>
<td>$3.84 \pm 0.34$</td>
<td>$5.84 \pm 2.40$</td>
<td>4.15</td>
</tr>
<tr>
<td>Bulk Modulus $B$</td>
<td>$4.61 \pm 0.12$</td>
<td>$5.36 \pm 2.68$</td>
<td>4.32</td>
</tr>
<tr>
<td>Poisson's Ratio $\nu$</td>
<td>$0.36 \pm 0.01$</td>
<td>$0.37 \pm 0.09$</td>
<td>0.34</td>
</tr>
<tr>
<td>Lamé constant $\mu_x$</td>
<td>$1.41 \pm 0.17$</td>
<td>$2.05 \pm 0.91$</td>
<td>1.55</td>
</tr>
<tr>
<td>Lamé constant $\lambda$</td>
<td>$3.67 \pm 0.01$</td>
<td>$6.19 \pm 2.94$</td>
<td>3.29</td>
</tr>
</tbody>
</table>

Table 5.6. Summary of elastic constants from experimental, computer simulation and theoretical studies.

### 5.6.2. Physical properties

A number of interesting physical properties will be discussed in this section and will be compared with experimental data in chapter 2. The accuracy of $\alpha_g$, $\alpha_t$, density and $T_g$ are all dependent on a number of factors that must be considered before any comparisons can be made with experimental values.

Firstly, the approximation of the model is a very important factor. If the "united atom" approach were used, where for example, $\text{CH}_2$ is not expressed as three explicit atoms but as a single unit, with the combined mass of the individual atoms, then the van der Waals interaction would have to be modified [15]. Such a step
would result in the packing between the atoms, not being representative of a real system, therefore lower densities would be calculated [13], [15]. For the linear epoxy polymer all the hydrogen atoms were treated explicitly, due to the potential effects of inter and intramolecular hydrogen bonding. This action however, significantly increases our computational time.

Secondly, the pressure applied to the system has a direct effect on the density (or specific volume). A study by Boyd et al. [16] demonstrates quite clearly the increase in density (decrease in specific volume) with increasing pressure. This in turn affects the glass transition temperature. Therefore, any discrepancies in density result in a deviation in the glass transition temperature. An external pressure was not applied to the epoxy polymer system, but the pressure of the system was constant.

Thirdly, because $T_g$ is not purely a second order thermodynamic property, but has a kinetic element to its behaviour, the difference in cooling rate between experiment and simulation must be noted. Several decades of change in the cooling rate cause variations in the observed $T_g$ of about 20-40K [17].

5.6.2.1. Glass Transition Temperature

Section 1.1.2.1 describes the thermodynamic changes that occur when the temperature of a polymer is increased. In section 2, the experimental section, two thermodynamic relations were used, heat capacity ($C_p$) and volume changes. To be consistent with experiment the determination of $T_g$ will be kept in this context.

The heat capacity was initially used to determine $T_g$. Figure 5.1, shows heat capacity against temperature for the (AE)$_2$ system. This nondescript plot does not indicate the transitions that occur in DSC experiments. This may be because heat capacity is calculated from fluctuations from the appropriate ensemble (section 3.2.4). For the heat capacity to be statistically viable the molecule has to explore a large amount of phase space. In this case the time period used at a particular temperature was 100-150ps, for one molecule. Therefore the heat capacity values are not statistically sound. Sylvester et al. [18] successfully calculated $C_p$ for polyethylene using the Monte Carlo technique. Their results compared well with experimental readings greater than 400K, but unfortunately showed no expected thermodynamic transitions at the $T_g$, which is less than 400K. The determination of
volume, however, is not calculated from fluctuations but is directly dependent on the volume the molecule occupies and the kinetic energy it possesses. This is a more sensitive indicator of thermodynamic changes from a simulation perspective. The specific volume changes for the three oligomers AE, A_2E, (AE)_2 and the polymer (AE)_oo are shown in figure 5.2. In each case there are clear transition points that are comparable with TMA measurements.

![Graph](image)

**Figure 5.1.** Plot of heat capacity (cal/mol) against temperature for the (AE)_2 oligomer.
Figure 5.2. Change in specific volume of the (AE), (A₂E), (AE)₂, and (AE)ₘ oligomers as a function of temperature.

The $T_g$ can be readily determined from the intercepting lines, to within a few degrees ($\pm 2^\circ$). As the chain length increased by one monomer unit an increase in the $T_g$ was observed. The experimental $T_g$ values for these oligomers were extrapolated from the Ueberreiter-Kanig plot, shown in section 2.5.2.1. The experimental and simulation $T_g$ values are given in the following table.
Table 5.7 Glass transition temperature values from experimental observation and simulation calculations.

In spite of the discrepancies that exist between the experimental and simulation $T_g$ results, its relationship with molecular weight is preserved. Figure 5.3 clearly shows how well the changes in molecular weight agree with experimental and simulation $T_g$'s.

Figure 5.3. Ueberreiter-Kaeg plot of (Δ) simulation and (—) experimental data.
Many authors have shown large discrepancies in their $T_g$ simulation values. Fan et al. [6] calculated a $T_g$ of approximately 200K for a polyethersulphone, which is very low considering the $T_g$ is between 460-470K [19]. Takeuchi et al. [20] determined the $T_g$ of a polyethylene like system with varying chain lengths. In their model they used the united atom approach. This was one of the reasons for their very low $T_g$ results. In spite of this, the results of Roe et al. [15] successfully demonstrated the linearity between the reciprocal of $T_g$ and chain length (this is proportional to molecular weight), although this was not illustrated graphically.

In 1984 Anderson et al. [21],[22] used constant pressure MD to quench a fluid system isobarically, for which he observed a simulated $T_g$. It must be noted that volume changes in the epoxy simulation were not due to gradually quenching the linear epoxy system as is done experimentally, but achieved by allowing the model to equilibrate at a specified temperature at constant pressure. It was hoped that this would solve the cooling rate phenomenon that has beleaguered authors such as Roe et al. [15], who had a cooling rate $10^9$ times faster than a typical DSC heating rate of 10 K/min (0.167 K/sec). Sylvester et al. [18] used a methodology similar to that used in simulating the epoxy polymer, in their study of an atactic poly(propylene) polymer. This also resulted in a simulated $T_g$ 24K higher than experimental. In an attempt to explain this discrepancy they noted a 'low pressure' of ± 5 atmosphere in their simulations. However, Allen et al. [23] have shown that by compressing polystyrene while applying normal cooling rates, the resulting polymer had a higher density with a correspondingly higher $T_g$.

If we plot the time-average pressure of the (AE) system over the temperature range and at each specific temperature we see that in figure 5.4, there was a net compressive pressure of -0.00058 GPa. The overall pressure-average for all the MD calculations was ±0.00082 GPa. It appears from these results that the effects of pressure is negligible.
A general review of the literature reveals that authors who have tried to calculate the $T_g$ by simulation are generally within 30°C of the experimental $T_g$ value. In many cases trends are more important than absolutes, and these results do show an excellent simulation and experimental trend with molecular weight. Bearing in mind the three simulation factors that effect the $T_g$: approximation of the atomistic model, pressure and thermal history, our results are in good agreement with experimental data.

By nature of the adiabatic ensemble (EPN) used, the temperature fluctuates with time along with the volume of the system. When looking at the relationship between temperature and volume it is important to take the average temperature value not the initial temperature. In some cases it was found that the temperature reached equilibrium some 5-10K higher than the initially stated value. Plotting the changes in volume with the initial temperature would result in incorrect thermal expansion coefficient values. The potential energy was averaged at each MD run to gauge the equilibrium state of the system. Figure 5.5 shows how the potential energy varies with temperature. Ideally this plot should be a straight line, with any...
deviation from linearity meaning the molecules configuration is not sufficiently equilibrated.

![Graph](image)

**Figure 5.5.** A plot showing how the potential energy of the \((\text{AE})_{\infty}\) oligomer varies with temperature.

### 5.6.2.2. Thermal expansion coefficients

The thermal expansion coefficients, \(\alpha_1\) and \(\alpha_g\) were calculated from the slopes above and below the \(T_g\), respectively, from figure 5.2.

The slope for each curve is given by

\[
\left( \frac{\partial V}{\partial T} \right)_p = e
\]

**eqn 5.27**

where \(e\) is the specific thermal expansivity (cm\(^3\)/g.K). This has the following relation with the thermal expansion coefficient.

\[
\alpha = \frac{\rho e}{3}
\]

**eqn 5.28**
where the original density \( \rho \) was extrapolated at 300K from figure 5.8. The results from the plots in figure 5.2 are listed in the table below.

<table>
<thead>
<tr>
<th>Thermal Expansion Coefficient x10^{-4} K^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
</tr>
<tr>
<td>( \alpha_g )</td>
</tr>
<tr>
<td>(AE)</td>
</tr>
<tr>
<td>(AE)E</td>
</tr>
<tr>
<td>(AE)E</td>
</tr>
<tr>
<td>(AE)E</td>
</tr>
<tr>
<td>(AE)_{1\rightarrow m}</td>
</tr>
</tbody>
</table>

Table 5.8 List of thermal expansion coefficient values from simulation and experiment. The average simulation Simha-Boyer Universal value \( \phi_e = 0.0341 \) was calculated from equation 2.6 and the experimental value was 0.113. \((n)\) signifies the range of experimental thermal expansion coefficient values.

The specific \( \alpha \) values for each oligomer cannot be determined or extrapolated from experimental data, but can be compared with a range of experimental values \([(AE)_{1\rightarrow m}]\). The simulation results show excellent agreement with experimental data. There appears to be a general consistency in the \( \alpha_g \) value in comparison with the \( \alpha_l \) values, which are relatively scattered. Very few workers have made any serious attempt to calculate \( \alpha_g \) and \( \alpha_l \) despite a large interest in calculating the \( T_g \) from volume fluctuations. Closer inspection of authors specific volume or density vs. temperature plots reveals one major error in the calculation of \( \alpha \). Hsu et al. [6] claim to have determined experimentally comparable \( \alpha \) results, but they incorrectly averaged both the \( \alpha_g \) and \( \alpha_l \) values to obtain an apparent experimentally agreeable \( \alpha_g \) value. By estimating the \( \alpha_g \) and \( \alpha_l \) values from a specific volume vs. temperature plot, by Roe et al. [15] and determining \( \phi_e \), a value of 0.188 was calculated, which is in good agreement with the Simha-Boyer value. The model used was a united atom system and the pressure was negligible. This demonstrated
that even if the simulated \( T_g \) was low, the relation between the \( T_g \) and \( \alpha_g/\alpha_1 \) values can satisfy the Simha-Boyer Universal value. Boyd et al. specifically calculated their \( \alpha \) values and were within 18\% of experimental values. Their \( \phi_e \) value was 0.142, which is also in excellent agreement with the Simha-Boyer Universal value.

The Simha-Boyer Universal value \( \phi_e \) has an experimental value of 0.113, calculated using equation 2.6 and by plotting \( (\alpha_1 - \alpha_g) \) against \( 1/T_g \), see figure 5.6. The \( T_g \) values were taken from the simulation results in table 5.7. The \( \phi_e \) value, calculated from the slope was 0.0341, which is slightly low. Gupta et al [24] showed the Simha-Boyer to be inadequate for characterising the free volume of epoxy networks and other authors [25],[26] have cautioned any predictions based on this rule. To explain this discrepancy a closer look at the thermal expansion coefficient values is required.

![Figure 5.6](image)

**Figure 5.6.** A Simha-Boyer Universal plot. Slope \( \phi_e = 0.0341 \)

The thermal expansion coefficient values were compared with experimental trends by plotting \( \alpha \) against increasing molecular weight. This plot is shown in figure 5.7. When this plot is compared with the experimental plot in figure 2.23, there is a
marked similarity in the trends. For example $\alpha_g$ also shows a general consistency in its value while $\alpha_1$ appears to be randomly scattered.

![Figure 5.7](image.png)

**Figure 5.7.** Relationship between thermal expansion coefficients and increasing molecular weight.

The only conclusion that can be drawn about the random nature of $\alpha_1$ in figure 5.7 are the end groups, because all other possible influencing factors are constant. It appears that the amine-amine ended oligomer has a relatively higher $\alpha_1$ value than the amine-epoxy ended oligomers, while the oligomer with no end groups $(AE)_\infty$ has an intermediate value.

The trends displayed in figure 5.7. can be explained in terms of the flexibility and the volume occupied by the aromatic amine and epoxy functional end groups. It is clear that the aromatic amine group, which consists of a phenyl group, occupies a larger volume than the epoxy group. Also the conformational space explored by the amine group is larger. This can be determined from the torsional angle population $\Phi_9$ that controls the motion of the aromatic amine group. The population results in chapter 4 show a broad population distribution for $\Phi_9$, see figure 4.26. The epoxy group's conformational space is determined by $\Phi_3$, see figure 4.21. The population is concentrated in three well-defined regions (i.e. trimodal system). Therefore a combination of a smaller volume and limited
exploration of conformational space means that the epoxy group will have a lower thermal expansion coefficient. This is seen in figure 5.7, where the oligomers with one epoxy terminal group have the lowest thermal expansion coefficient.

The aromatic amine terminated oligomers, however, have relatively high thermal expansion coefficients. To draw further conclusions about these observations would require an investigation of epoxy-epoxy terminated oligomers; unfortunately these oligomers were not studied. In the case of the experimental $\alpha_1$ values the statistically averaged weights correspond to a particular terminated chain. This postulation can not be proved directly because it is not possible for the gel permeation chromatography to differentiate between single monomer changes in a chain at high molecular weights.

Palmese et al. [27] however, investigated the effect of epoxy-amine stoichiometry on the thermal expansion coefficients for fully cured systems. They concluded that $\alpha_g$ was independent of varying amine concentrations while $\alpha_1$ was a minimum when the molar ratio was 1:1 i.e. epoxy-amine ended chains predominate. Figure 5.7, clearly shows that the $\alpha_1$ for epoxy-amine ended chains have the lowest values. From experimental observations by Palmese, where the epoxy or amine is in excess there is an increase in the $\alpha_1$ value, again this is seen for our amine-amine terminated chain.

5.6.2.3. Density

There are a number of authors [28],[29],[30] who have used the density temperature plot to show trends in molecular chain length and position of $T_g$. The density for each oligomer and polymer chain were calculated over a wide temperature range. The trend is the inverse of the specific volume and is shown in figure 5.8. The density was compared with experimental data in chapter 2, at 298K and the results are tabulated in table 5.9.
Figure 5.8. Change in density of the \((\text{AE})\), \((\text{AE})_2\), \((\text{AE})_\infty\) oligomers as a function of temperature.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Experimental</th>
<th>Simulation</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{AE})_\infty)</td>
<td>1.17 ±0.02</td>
<td>1.052 ±0.041</td>
<td>-</td>
</tr>
<tr>
<td>((\text{AE})_\infty)</td>
<td>-</td>
<td>1.090</td>
<td>1.11</td>
</tr>
<tr>
<td>((\text{AE})_2)</td>
<td>-</td>
<td>0.977</td>
<td>-</td>
</tr>
<tr>
<td>((\text{A}_2\text{E}))</td>
<td>-</td>
<td>1.006</td>
<td>-</td>
</tr>
<tr>
<td>((\text{AE}))</td>
<td>-</td>
<td>0.930</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.9. List of densities. The simulation densities were extrapolated at a temperature of 298K from figure 5.8. †These results are from the MD calculations used to determine the elastic constants.

Obtaining the correct density from MD calculations is not simple. These simulation results are within 10% of their respective experimental values at 298K. This is
very good considering no serious attempt was made to apply an isotropic pressure of one atmosphere to the system. Quian et al. [12] used a constant stress molecular dynamics (CSMD) algorithm to apply a 1 atm isotropic pressure to a range of polymers. Their results were also within 10% of experimental values. Ludovice et al. [31] calculated an improved density value only after energy minimisation. The density value after energy-minimisation is 1.153 g/cm³ for (AE)ₙ. Even this value is lower than our average experimental value. In an attempt to explain the low density values we have to consider the thermal history of the sample. Ludovice et al. [31] clearly demonstrated that by initially running a CSMD at different temperatures for a given polymer system and then energy-minimising, marked changes in density values of up to 24% resulted. Such changes also have an effect on the $T_g$. Despite all these influences on the density values, the epoxy polymer results are in good agreement with experimental data for (AE)ₙ.

Without isolating the other oligomers experimentally and determining their density, no direct comparisons can be made for the individual oligomeric simulation results. The only comments which can be made are the trend and relation between values. This has been previously discussed in relation to specific volume.

5.6.2.4. Cohesive Energy

The oligomeric model used in the cohesive energy and Hildebrand solubility parameter calculation was $A_2E$. Ten structures were built and used in the calculation where no PBC was used.

The cohesive energy is readily calculated from computer experiments. This was achieved by using MD at 500K for 5ps and then extracting the conformation with the lowest potential energy. This conformation was then energy-minimised until energy convergence and the potential energy calculated.

$$U_{\text{chain}} = 166.99 \pm 2.72 \text{ kcal/mol}$$

The results from the physical property simulation experiments at 0 K were used to calculate the potential energy in the bulk state, i.e. within a periodic boundary cell, for the $A_2E$ oligomer.

$$U_{\text{bulk}} = 107.18 \pm 2.14 \text{ kcal/mol}$$
Chapter 5 Simulation & Theoretical Study of a Linear Epoxy Polymer

The cohesive energy is calculated from the following equation:

\[ E_{\text{cohesive}} = U_{\text{chain}} - U_{\text{bulk}} \]  

eqn. 5.28

The results are listed in table 5.10.

### 5.6.2.5. Hildebrand Solubility Parameter

This parameter can be calculated from the same series of experiments as described above, and is related to the \( E_{\text{cohesive}} \) in equation 5.3. The molar volume \( V_m \) is an additive quantity and is derived from group contributions in table 5.2. The results are listed in the following table.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesive Energy ( E_{\text{cohesive}} ) (kcal/mol)</td>
<td>59.81 ± 4.86</td>
</tr>
<tr>
<td>Hildebrand Solubility Parameter ( \delta ) (cal ( ^{1/2} )/cm( ^{3/2} ))</td>
<td>12.23 ± 0.11</td>
</tr>
</tbody>
</table>

Table 5.10. List of \( E_{\text{cohesive}} \) and \( \delta \) results from simulation and theoretical studies.

These results are in excellent agreement with the theoretically derived values. The values obtained are largely dependent on the forcefield and respective parameters used. In this case it is seen that the Dreiding-II parameters describe the epoxy model well. Hsu et al.\[32\] also achieved good results for their cohesive energy and Hildebrand Solubility parameter values, when they used the same parameter set. Suter et al. \[33\] used this type of calculation to validate the parameters and forcefields used in their model. From this experiment it is clear which energy contributions affect the overall potential energy of the epoxy polymer. The following table presents an energy decomposition list of the results.
### Table 5.11. Energy decomposition of (A₂E) oligomer in the bulk and single chain state.

<table>
<thead>
<tr>
<th>Energy Components</th>
<th>Bulk (kcal/mol)</th>
<th>Single Chain (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond</td>
<td>18.41 ± 0.44</td>
<td>18.40 ± 0.40</td>
</tr>
<tr>
<td>angle</td>
<td>17.23 ± 1.18</td>
<td>16.55 ± 2.43</td>
</tr>
<tr>
<td>torsion</td>
<td>29.14 ± 0.60</td>
<td>27.17 ± 1.32</td>
</tr>
<tr>
<td>inversion</td>
<td>0.51 ± 0.14</td>
<td>0.22 ± 0.13</td>
</tr>
<tr>
<td>hydrogen bonding</td>
<td>-16.88 ± 3.04</td>
<td>-0.08 ± 0.11</td>
</tr>
<tr>
<td>van der Waals</td>
<td>47.14 ± 1.97</td>
<td>99.50 ± 1.44</td>
</tr>
<tr>
<td>electrostatic</td>
<td>11.64 ± 1.05</td>
<td>5.26 ± 1.22</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>107.18 ± 2.14</strong></td>
<td><strong>166.99 ± 2.72</strong></td>
</tr>
</tbody>
</table>

There is negligible energy difference in the bonding components between the bulk and single chain system. The comparability indicates how well the bulk epoxy system has been energy-minimised, in particular the torsional energy component, which is a very good indication of how well an amorphous system has been relaxed. Before minimisation of the bulk system, the torsional energy component is very high.

The non-bonding energy components show marked changes between the bulk and chain systems. The key points to note here are the van der Waals and hydrogen bonding. Since the hydrogen bonding is very important in this system it will be discussed further.

#### 5.6.2.6. Hydrogen bonding

Hydrogen bonding can occur between hydrogen donating groups; NH and OH and the electronegative atoms oxygen and nitrogen. Table 5.11 shows the dramatic increase in hydrogen bonding when a molecular chain is placed in a bulk environment.
Hydrogen bonding is intrinsically affected by temperature, resulting in greater hydrogen bonding in the solid state than in the liquid state. Therefore a discontinuity would be expected when the polymer changes state as the temperature is lowered. To demonstrate this the hydrogen bonding energy was plotted against temperature for the (AE)$_2$ oligomer. The plot (figure 5.9) shows very little change in the hydrogen bonding energy at low temperatures (0-275K) but there is a sharp decrease as the temperature is raised above 323K. This happens to coincide with the $T_g$ of this system. As the temperature increases and the molecular chains have sufficient thermal energy to change to the liquid state, the greater motion of the molecules causes the hydrogen bonds to break.

![Figure 5.9](image)

**Figure 5.9.** This plot of hydrogen bonding demonstrates its relationship with temperature for the (AE)$_2$ oligomer. The transition point coincides with the $T_g$ (323K).

When the molecule was subjected to tensile and compressive stresses, in chapter 4, changes in the hydrogen bonding energy were also observed. This is illustrated in the figure below, for the $A_2E$ oligomer as it was compressed.
The extent of hydrogen bonding in the solid state is illustrated in the following picture. In picture 5.2, not all the possible hydrogen interactions are shown, for both inter- and intra-molecular hydrogen bonding have been observed. The inter-molecular interactions have been observed as interactions between the real chain and its image, but no attempt was made to quantify the contribution of each of these components to the overall hydrogen bond energy.
Picture 5.2. Linear epoxy polymer in the solid state, showing hydrogen bonding as the dotted blue line.
5.7. Conclusion

The mechanical and physical calculations from the computer experiments and theoretical calculations compared well with experimental values. The theoretical calculations gave a fast and easy method for providing very good first estimates, while the computer experiments give more accurate and detailed estimates from atomistic information.

Although the simulation results are good, there are areas in the simulation methodology that can be improved in order to improve the results. In the mechanical property experiment the calculations were performed at absolute zero, therefore the values were higher than the experimental values. To improve this the simulation should be conducted at the appropriate temperature using constant stress molecular dynamics and the canonical ensemble. This will give temperature related elastic constants which should be more applicable to experimental values.

One of the major shortcomings of the method used in the physical property calculations is that atmospheric pressure was not applied to the system. This resulted in a slightly reduced density and $T_g$ values, while the thermal expansion coefficients, above and below the $T_g$, had a larger value. To overcome this problem atmospheric pressure should be applied to the system by also using constant stress molecular dynamics and the canonical ensemble.

The simulation work has proved very useful in providing trends observed experimentally. In some cases it has allowed plausible explanations to be given to experimental observations not readily explainable, an example of this is the relation of the thermal expansion coefficients with molecular weight.

With computer simulation experiment shedding light on areas that are not readily available to experimental scrutiny, it has been demonstrated that it is a useful investigative tool into the behaviour of the molecular chains. The next chapter discusses the future work that can be conducted in characterising the polymer systems further.
5.8. References

19 Attwood T. E., Cinderey M. B., Rose J. B., Effects of repeat unit structure on the toughness of poly(aryl ether sulphone)s *Polymer*, 34(6), 1322, (1993)
Discussion & Conclusions

6.1. Introduction ....................................................................................................  196
6.2. Initial Aims .......................................................................................................................  196
6.3. What has been achieved? ................................................................................  196
6.4. Future Work ..................................................................................................................  197

6.4.1. Introduction ........................................................................................................  197
6.4.1.1. Thermal History and Volume Fraction .........................................................  198
6.4.1.2. Elastic Constants .........................................................................................  198
6.4.1.3. Conformational Changes .........................................................................  199
6.4.1.4. Molecular Motion ..........................................................................................  199
6.4.1.5. Hydrogen Bonding .....................................................................................  201
6.4.1.6. Cross-linked Polymers ..............................................................................  201

6.5. References .............................................................................................................  204
6.1. Introduction

This final chapter will discuss and draw to a conclusion the results of this study. It will be divided into three areas of discussion, firstly a restatement of the original problem seen in the context of what has been learned, secondly, the goals achieved will be stated and finally, the implications of the results and how they will lead on to future work.

6.2. Initial Aims

The aims of this work were to build a representative atomistic model based on experimental information and to utilise simulation methodologies and theories to determine the mechanical and physical properties of a linear epoxy polymer. The atomistic behaviour of the polymer was also studied during the property determining simulations, in an attempt to gain fundamental atomistic information about its behaviour.

6.3. What has been achieved?

The mechanical and physical properties calculated from computer experiment and theoretical calculations compared extremely well with experimental values. The only exceptions were the computer generated $T_g$, $\alpha_g$ and $\alpha_1$ values, which showed some discrepancy with experimental observations. The reasons for this were discussed in chapter 5. Although in these cases absolute values obtained by different methods did not coincide, the apparent trends were astonishingly similar. The first of these cases were clearly seen in the Ueberreiter-Kanig plot (see figure 5.3), where computer simulation and experimental trends married perfectly. In the second case, figure 2.23 shows the relation between $\alpha_g$ and $\alpha_1$ against increasing average molecular weight, a trend which initially aroused great curiosity. However, when similar trends were seen in figure 5.7, for computer experiments, it was not only possible to deem the experimental trends valid, but plausible explanations could be given for the observations.

In chapter 4, the simulation experiments have shed some light on areas that are not readily available to experimental scrutiny. By using torsional angle values from representative crystal structures it was possible to confirm the minima regions in the conformational analysis results. These results were used in turn to validate the
results from the temperature and stress experiments. For all the torsional angles studied, the crystal data positively confirmed the likely minima states, thus validating the force field and parameter sets used in describing the molecular interactions. The excellent results calculated in chapter 5 for the cohesive energy and Hildebrand's solubility parameter were further confirmation of the suitability of the Dreiding force field for this polymer system.

The simulation values would be meaningless without sound experimental characterisation. Since there is good correlation between experiment, theory and simulation it was assumed that the experimental work in chapter 2 was correctly characterised. The synthesis and property tests were all conducted in relation to simulation constraints and limitations. In many instances molecular modellers have relied on experimental work performed by other researchers and this has raised questions as to how the samples were made and tested, even how these factors influence the final property results. By doing the synthesis, sample preparation, testing, and analysis a greater understanding of the material has been attained.

6.4. Future Work

6.4.1. Introduction

The ultimate aim of this type of work is to model the physical and mechanical properties of cross-linked polymers, and to use the increased atomistic information thereby gained to design new materials in a rational manner. However, before this can be achieved, a greater understanding of polymer systems that are amenable to experimental characterisation is required. The next section will concentrate on the atomistic information that can be verified by numerous techniques. This information can then be used to build representative models of complex cross-linked polymer systems, for which macroscopic properties are obtainable.
6.4.1.1. Thermal History and Volume Fraction

The volume fraction and thermal history are integrally linked; since the \( T_g \) can be expressed in terms of volume fraction its value will be obviously affected by thermal history. As mentioned previously, one of the simulation areas which did not exactly fit the experimental was the \( T_g \) value. Ludovice et al. [1] have clearly demonstrated that computer experiments can be used to simulate the effects of thermal history, i.e. quenching, annealing and minimisation, on a polymer's total energy, density and torsional angle distribution. The following theories relate the \( T_g \) with free volume and have been used to experimentally characterise the free volume in cross-linked polymers [2],[3]: Doolittle free volume [4], Simha-Boyer [5] free volume, Williams-Landel-Ferry [6] (WLF) free volume fraction and the Simha-Somcynsky free volume [7],[8] to name but a few. These theories can be verified experimentally by measuring volume changes as a function of temperature, using a standard dilatometer or thermal mechanical analyser. Because there is no unique definition [9] of free volume, there is some ambiguity as to its determination from simulation. However, Rigby et al. [9],[10] have used the unambiguously defined Voronoi tessellation analysis technique, which proved to be a useful measure of free volume as a function of temperature.

When the free volume distribution of a linear polymer is fully characterised the cross-linked system can be studied with the knowledge of and in relation to linear systems.

6.4.1.2. Elastic Constants

The elastic constants were calculated at absolute zero, thereby neglecting entropy contributions and local volume fluctuations which result in values higher than experimental data measured at room temperature. By using constant stress molecular dynamics (CSMD) [11] estimates of the bulk density and temperature related elastic constants can be calculated. Such results can be readily compared with experimental data. Brown et al. [12] applied a series of constant tensions to an amorphous polyethylene model over a range of temperatures. Although they gave no quantitative results, qualitative comparisons showed that there was strong similarity between similar time scales in both experimental and simulation measurements. Despite the short time of these simulation runs with respect to
experimental times, useful information, such as population shifts, etc. could be determined.

6.4.1.3. Conformational Changes

The population changes that occur during molecular perturbation require further characterisation. In our study of population shifts due to stress, the changes were measured in a non-equilibrium state, i.e. during a transition period, and were compared with an equilibrium system. To correctly characterise the torsional population shift, the population should be measured in an equilibrium state before and after perturbation, with the differences in population being a measure of the polymers response to the applied force. Brown et al. [13] have used this type of method which can be applied to the study of transitions between torsional angle states in epoxy polymer's. This method determines the kinetics of isomerization from which reaction rates can be calculated when the polymer is in an equilibrium state. Auto-correlation [14] and cross-correlation [15] calculations would be a useful measure of firstly, how each torsional angle relaxes in the glassy and liquid states and secondly, whether neighbouring torsional angles, 1-2, 1-3, or even 1-4 are coupled, i.e. if the motion of one torsional angle is coupled (or affected) by the motion of another torsional angle.

Light scattering, small-angle X-ray scattering, and small-angle neutron scattering studies can be used to determine the conformation linear chains adopt, while wide-angle and neutron scattering can give a more detailed insight into the atomistic structure and whether local ordering is present. Such properties have been determined from simulation studies, [16],[17] using \( g(r) \), which is the Fourier transform of the structure factor \( S(r) \) found from X-ray scattering experiments.

6.4.1.4. Molecular Motion

With the recent advent of two-dimensional nuclear magnetic resonance techniques [18],[19] and electron spin resonance [20] the relaxation times of various structural components can be determined. Gillies et al. [21] have successfully used NMR to determine the correlation times of methyl groups in a number of compounds by measuring the 'fast' internal motions within the chains, and the 'slow' tumbling motions of the molecule as a whole. The relaxation time and other informative functions such as the distribution function can be readily determined.
from MD calculations. Roe et al. [14],[22],[23] investigated local chain motions in an amorphous polyethylene-like model, above and at the glass transition temperature. Their studies concentrated on the effects of relaxation times and distribution functions on temperature, the position of the molecular segment within the chain and the packing of the molecular chains. Internal comparisons were made with respect to each other, but no comparisons were drawn from experimental data. An attempt to simulate the experimental values from such a study would be an obvious area for further study.

Another experimental technique that is used to monitor molecular motion is dynamic mechanical thermal analysis (DMTA), see chapter 1 for description. By lowering the temperature below the glass transition temperature it is possible to see local motions freeze out. Because of the large differences in the frequencies used experimentally (0.01-10 Hz) and in simulation calculations ($10^{-9}$-$10^{13}$ Hz) there is no direct way of comparing the relations observed. However Letton [24] and Bicerano et al. [25] used semi-empirical methods and quantum mechanics respectively to help characterise the molecular motions associated with DMTA relaxations.

Polymers that are polarised when an electrical field is applied to them can yield interesting dielectric thermal analysis (DETA) spectra. The technique works by applying an oscillating electrical field, which causes certain functional groups to act as dipoles and align with the field. When the force is released the dipoles relax back to some random orientation. Since the molecular chains are closely packed there is a slight delay in the relaxation of these groups. The response of a polymer to an electric force is analogous to an applied sinusoidal mechanical force (DMTA), with the storage and loss dielectric permittivities being calculated, (see description of DMTA in chapter 1). Since the frequencies are higher for DETA, comparisons can be made with simulation experiments. Tiller et al. [26] in 1992, developed a computational scheme, which utilised molecular dynamics. By determining the Fourier transforms of calculated dipole autocorrelation functions, the frequencies characteristic of motions important to dielectric relaxations can be identified. Although the frequency range ($10^{-9}$-$10^{13}$ Hz) for simulations is higher than experimentally used frequencies, this type of simulation gives a substantial insight into the nature of molecular processes which influence the dielectric relaxation of polymers.
The local bond motions can be characterised experimentally using infra-red and Raman spectroscopy. The various vibrational modes associated with these spectroscopic techniques can be readily determined from simulation studies. Computer programs like Professional POLYGRAF and BIOSYM have specific modules that generate the infra-red and Raman spectra, which can be used to help our understanding of the vibrational modes of the molecules, determine the molecular structure and calculate thermodynamic properties, such as entropy, heat capacity and the free energy of gaseous molecules.

6.4.1.5. Hydrogen Bonding

As discussed in chapter 5, hydrogen bonding plays a vital role in the properties the linear epoxy polymer possess. This area would certainly warrant further work, with infra-red spectroscopy as an experimental method of validating the simulation work. The variation in the intensity of the absorption associated with the hydrogen bond interaction can be investigated as a function of temperature for a cured epoxy polymer or as an isothermal experiment on a curing epoxy system. The latter experiment would yield information on the rate of hydrogen bond formation as the polymer is cured at a constant temperature. Several authors [27],[28] have commented on the importance of hydrogen bonding in amine cured epoxy resins and its effects on densification, but to date no simulation investigation has been conducted.

6.4.1.6. Cross-linked Polymers

Once there is sufficient knowledge on the atomistic behaviour of linear polymers, attempts can be made to predict mechanical and physical properties of cross-linked systems. There are two ways in which to build a representative cross-linked model, depending on the properties of interest, for example, a virtual bond model may suffice when calculating the mechanical properties, while a more detailed atomistic model is obviously required when considering thermal volume changes, due to the importance of the volume the molecule occupies and the interactions between chains.

Termonia et al. [29],[30],[31] have extensively used a model which explicitly takes into account the role of the weak attractive forces between chains as well as chain slippage through entanglement, (based on the Eyring chemical activation theory) to
determine the mechanical properties of polyethylene. In a virtual bond model, information from detailed atomistic data can be used to calculate the force constants and geometry required to model the linear epoxy system, this type of model can then be used in mechanical property calculations.

There is a wealth of experimental techniques and theories, as previously mentioned, that can be used to characterise the molecular packing [2] of epoxy resins, information that can be used in conjunction with spectroscopic techniques to elucidate the possible structure of complex amorphous cross-linked systems.

Figure 6.1 illustrates how the overall work fits together. The initial work would be to experimentally characterise the linear and cross-linked polymer before building representative crosslinked models. Two models could be built: a virtual bond and a fully atomistic model, depending upon the type of properties being investigated. From this point equivalent experiments could be conducted on the models, as well as on the real polymer, so that comparable results could be obtained. The resulting information could mean that further refinement in the models is required, or it could yield enough knowledge to improve or design a new polymer.
Figure 6.1 Illustration of future work on cross-linked polymer systems.
6.5. References


Appendices
A1.1 Experiment

The charges on the epoxy molecule represented in figure A1.1 were calculated using MOPAC. Five models were constructed, each representing a section of the linear epoxy polymer. These structures were initially minimised and the charge calculations were conducted using the conditions stated above. The results from these experiments are listed in the table below. Charges calculated from the Gasteiger method are also listed. The main atoms that are involved in hydrogen bonding are highlighted in the table.

![Figure A1.1 Atom positions with corresponding numbers used in table A1.1](image)

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Atom Type</th>
<th>MOPAC 1</th>
<th>MOPAC 2</th>
<th>MOPAC 3</th>
<th>MOPAC 4</th>
<th>MOPAC 5</th>
<th>Gasteiger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>0.0483</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0595</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>0.0542</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0758</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>0.0520</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0595</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>-0.2586</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.3705</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>-0.0245</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1048</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>0.0683</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0652</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>0.2083</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0818</td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>0.0284</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>-0.0019</td>
<td></td>
<td></td>
<td></td>
<td>0.0600</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>O</td>
<td>-0.2797</td>
<td>-0.2804</td>
<td>-0.2827</td>
<td>-0.2815</td>
<td>-0.2810</td>
<td>-0.3433</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>0.0969</td>
<td>0.0754</td>
<td>0.0767</td>
<td>0.0754</td>
<td>0.0743</td>
<td>0.0751</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>-</td>
<td>-0.0701</td>
<td>-0.0687</td>
<td>-0.0713</td>
<td>-</td>
<td>-0.0315</td>
</tr>
<tr>
<td>13</td>
<td>H</td>
<td>-</td>
<td>0.0667</td>
<td>0.0655</td>
<td>0.0659</td>
<td>-</td>
<td>0.0650</td>
</tr>
<tr>
<td>14</td>
<td>C</td>
<td>-</td>
<td>-0.0279</td>
<td>-0.0283</td>
<td>-0.0267</td>
<td>-</td>
<td>-0.0555</td>
</tr>
<tr>
<td>15</td>
<td>H</td>
<td>-</td>
<td>0.0580</td>
<td>0.0583</td>
<td>0.0588</td>
<td>-</td>
<td>0.0627</td>
</tr>
<tr>
<td>16</td>
<td>C</td>
<td>-</td>
<td>-0.0727</td>
<td>-0.0827</td>
<td>-0.0822</td>
<td>-</td>
<td>-0.0375</td>
</tr>
<tr>
<td>17</td>
<td>C</td>
<td>-</td>
<td>-0.0261</td>
<td>-0.0276</td>
<td>-0.0249</td>
<td>-</td>
<td>-0.0555</td>
</tr>
<tr>
<td>18</td>
<td>H</td>
<td>-</td>
<td>0.0587</td>
<td>0.0582</td>
<td>0.0591</td>
<td>-</td>
<td>0.0627</td>
</tr>
<tr>
<td>19</td>
<td>C</td>
<td>-</td>
<td>-0.0735</td>
<td>-0.0681</td>
<td>-0.0741</td>
<td>-</td>
<td>-0.0315</td>
</tr>
<tr>
<td>20</td>
<td>H</td>
<td>-</td>
<td>0.0622</td>
<td>0.0633</td>
<td>0.0613</td>
<td>-</td>
<td>0.0650</td>
</tr>
<tr>
<td>21</td>
<td>C</td>
<td>-</td>
<td>0.0050</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0146</td>
</tr>
<tr>
<td>22</td>
<td>C</td>
<td>-</td>
<td>0.0502</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.0517</td>
</tr>
<tr>
<td>23</td>
<td>H</td>
<td>-</td>
<td>-0.0037</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>24</td>
<td>H</td>
<td>-</td>
<td>-0.0054</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>25</td>
<td>H</td>
<td>-</td>
<td>-0.0007</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>26</td>
<td>C</td>
<td>-</td>
<td>0.0502</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.0517</td>
</tr>
<tr>
<td>27</td>
<td>H</td>
<td>-</td>
<td>-0.0049</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>28</td>
<td>H</td>
<td>-</td>
<td>-0.0035</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>29</td>
<td>H</td>
<td>-</td>
<td>0.0011</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0243</td>
</tr>
<tr>
<td>30</td>
<td>C</td>
<td>-</td>
<td>-0.0739</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.0378</td>
</tr>
<tr>
<td>31</td>
<td>C</td>
<td>-</td>
<td>-0.0274</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.0555</td>
</tr>
<tr>
<td>32</td>
<td>H</td>
<td>-</td>
<td>0.0576</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0627</td>
</tr>
<tr>
<td>33</td>
<td>C</td>
<td>-</td>
<td>-0.0714</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.0315</td>
</tr>
<tr>
<td>34</td>
<td>H</td>
<td>-</td>
<td>0.0665</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0650</td>
</tr>
<tr>
<td>35</td>
<td>C</td>
<td>-</td>
<td>0.0759</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0751</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>C</td>
<td>-</td>
<td>-0.0715</td>
<td>-</td>
<td>-</td>
<td>-0.0315</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>H</td>
<td>-</td>
<td>0.0628</td>
<td>-</td>
<td>-</td>
<td>0.0650</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>C</td>
<td>-</td>
<td>-0.0525</td>
<td>-</td>
<td>-</td>
<td>-0.0555</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>H</td>
<td>-</td>
<td>0.0595</td>
<td>-</td>
<td>-</td>
<td>0.0627</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>O</td>
<td>-</td>
<td>-0.2804</td>
<td>-</td>
<td>-</td>
<td>-0.3433</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>H</td>
<td>-</td>
<td>0.0063</td>
<td>-</td>
<td>-</td>
<td>0.0600</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>C</td>
<td>-</td>
<td>0.1248</td>
<td>-</td>
<td>-</td>
<td>0.0810</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>H</td>
<td>-</td>
<td>0.0379</td>
<td>-</td>
<td>-</td>
<td>0.0600</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>H</td>
<td>-</td>
<td>0.0083</td>
<td>-</td>
<td>-</td>
<td>0.0644</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>C</td>
<td>-</td>
<td>0.0550</td>
<td>-</td>
<td>-</td>
<td>0.0953</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>O</td>
<td>-0.3044</td>
<td>-0.3068</td>
<td>-0.3121</td>
<td>-0.3071</td>
<td>-0.3104</td>
<td>-0.3888</td>
</tr>
<tr>
<td>47</td>
<td>H</td>
<td>0.1772</td>
<td>0.1646</td>
<td>0.1819</td>
<td>0.1807</td>
<td>0.1806</td>
<td>0.2106</td>
</tr>
<tr>
<td>48</td>
<td>C</td>
<td>0.1634</td>
<td>-</td>
<td>-</td>
<td>0.2077</td>
<td>0.2118</td>
<td>0.0462</td>
</tr>
<tr>
<td>49</td>
<td>H</td>
<td>0.0002</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0521</td>
</tr>
<tr>
<td>50</td>
<td>H</td>
<td>-0.0016</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0521</td>
</tr>
<tr>
<td>51</td>
<td>N</td>
<td>-0.4299</td>
<td>-</td>
<td>-0.4418</td>
<td>-0.4434</td>
<td>-0.4382</td>
<td>-0.3671</td>
</tr>
<tr>
<td>52</td>
<td>C</td>
<td>0.1109</td>
<td>-</td>
<td>-</td>
<td>0.1099</td>
<td>0.1043</td>
<td>0.0368</td>
</tr>
<tr>
<td>53</td>
<td>C</td>
<td>-0.0711</td>
<td>-</td>
<td>-</td>
<td>-0.0796</td>
<td>-0.0771</td>
<td>-0.0387</td>
</tr>
<tr>
<td>54</td>
<td>H</td>
<td>0.0623</td>
<td>-</td>
<td>-</td>
<td>0.0602</td>
<td>0.0607</td>
<td>0.0644</td>
</tr>
<tr>
<td>55</td>
<td>C</td>
<td>-0.0433</td>
<td>-</td>
<td>-</td>
<td>-0.0408</td>
<td>-0.0436</td>
<td>-0.0602</td>
</tr>
<tr>
<td>56</td>
<td>H</td>
<td>0.0572</td>
<td>-</td>
<td>-</td>
<td>0.0576</td>
<td>0.0578</td>
<td>0.0623</td>
</tr>
<tr>
<td>57</td>
<td>C</td>
<td>-0.0716</td>
<td>-</td>
<td>-</td>
<td>-0.0718</td>
<td>-0.0698</td>
<td>-0.0621</td>
</tr>
<tr>
<td>58</td>
<td>H</td>
<td>0.0559</td>
<td>-</td>
<td>-</td>
<td>0.0571</td>
<td>0.0574</td>
<td>0.0623</td>
</tr>
<tr>
<td>59</td>
<td>C</td>
<td>-0.0452</td>
<td>-</td>
<td>-</td>
<td>-0.0413</td>
<td>-0.0450</td>
<td>-0.0602</td>
</tr>
<tr>
<td>60</td>
<td>H</td>
<td>0.0555</td>
<td>-</td>
<td>-</td>
<td>0.0568</td>
<td>0.0567</td>
<td>0.0623</td>
</tr>
<tr>
<td>61</td>
<td>C</td>
<td>-0.0837</td>
<td>-</td>
<td>-</td>
<td>-0.0858</td>
<td>-0.0844</td>
<td>-0.0387</td>
</tr>
<tr>
<td>62</td>
<td>H</td>
<td>0.0564</td>
<td>-</td>
<td>-</td>
<td>0.0566</td>
<td>0.0583</td>
<td>0.0644</td>
</tr>
</tbody>
</table>
### Appendix 1 Charge Calculations

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>C</td>
<td>0.1702</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0353</td>
</tr>
<tr>
<td>64</td>
<td>H</td>
<td>-0.0183</td>
<td>-</td>
<td>-</td>
<td>-0.0053</td>
<td>0.0511</td>
</tr>
<tr>
<td>65</td>
<td>H</td>
<td>0.0277</td>
<td>-</td>
<td>-</td>
<td>0.0578</td>
<td>0.0511</td>
</tr>
<tr>
<td>66</td>
<td>C</td>
<td>0.1714</td>
<td>-</td>
<td>0.1753</td>
<td>-</td>
<td>0.1835</td>
</tr>
<tr>
<td>67</td>
<td>H</td>
<td>-0.0182</td>
<td>-</td>
<td>0.0100</td>
<td>-</td>
<td>0.0508</td>
</tr>
<tr>
<td>68</td>
<td>H</td>
<td>0.0275</td>
<td>-</td>
<td>-0.0053</td>
<td>-</td>
<td>0.0508</td>
</tr>
<tr>
<td>69</td>
<td>N</td>
<td>-0.4281</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.3832</td>
</tr>
<tr>
<td>70</td>
<td>C</td>
<td>0.1084</td>
<td>-</td>
<td>0.1019</td>
<td>-</td>
<td>0.0341</td>
</tr>
<tr>
<td>71</td>
<td>C</td>
<td>-0.0808</td>
<td>-</td>
<td>-0.0802</td>
<td>-</td>
<td>-0.0390</td>
</tr>
<tr>
<td>72</td>
<td>H</td>
<td>0.0565</td>
<td>-</td>
<td>0.0595</td>
<td>-</td>
<td>0.0644</td>
</tr>
<tr>
<td>73</td>
<td>C</td>
<td>-0.0469</td>
<td>-</td>
<td>-0.0458</td>
<td>-</td>
<td>-0.0602</td>
</tr>
<tr>
<td>74</td>
<td>H</td>
<td>0.0557</td>
<td>-</td>
<td>0.0571</td>
<td>-</td>
<td>0.0623</td>
</tr>
<tr>
<td>75</td>
<td>C</td>
<td>-0.0699</td>
<td>-</td>
<td>-0.0691</td>
<td>-</td>
<td>-0.0621</td>
</tr>
<tr>
<td>76</td>
<td>H</td>
<td>0.0558</td>
<td>-</td>
<td>0.0569</td>
<td>-</td>
<td>0.0623</td>
</tr>
<tr>
<td>77</td>
<td>C</td>
<td>-0.0448</td>
<td>-</td>
<td>-0.0461</td>
<td>-</td>
<td>-0.0602</td>
</tr>
<tr>
<td>78</td>
<td>H</td>
<td>0.0573</td>
<td>-</td>
<td>0.0577</td>
<td>-</td>
<td>0.0623</td>
</tr>
<tr>
<td>79</td>
<td>C</td>
<td>-0.0691</td>
<td>-</td>
<td>-0.0752</td>
<td>-</td>
<td>-0.0390</td>
</tr>
<tr>
<td>80</td>
<td>H</td>
<td>0.0629</td>
<td>-</td>
<td>0.0608</td>
<td>-</td>
<td>0.0644</td>
</tr>
<tr>
<td>81</td>
<td>H</td>
<td>0.1800</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1607</td>
</tr>
</tbody>
</table>

**Table A1.1.** Charge results from MNDO and Gasteiger calculations. The atom number and atom types correspond to numbers and atoms in figure A1.1.

### A1.3 Discussion

The results show good correlation between the MOPAC charge values, while the Gasteiger values for the aromatic portion of the molecule are in the same order of magnitude as the MNDO values. There are slight discrepancies in the highlighted atom values between the semi-empirical and empirical methods, with the Gasteiger
being consistently lower for nitrogen atoms but higher for the oxygen and hydrogen atoms charge values.

Since the Gastieger method was easy to calculate and in general correlated with MOPAC calculations no attempt was made to refine the Gastieger values in light of this. It was concluded that the MNDO values were specific to the molecules energy-minimum conformation, therefore the Gastieger method would be more appropriate, as a more general method. This empirical method is dependent on the position of the atom in relation to other neighbouring atoms, rather than on the chains conformation.
Crystal Structures
Appendix 2 Crystal Structures
Appendix 2 Crystal Structures
Appendix 2 Crystal Structures
Appendix 2 Crystal Structures
ERRATUM

Note 1 (Page 4)
replace "steady state" with "local energy minima"

Note 2 (Page 5)
"softening" rather than " melting"

Note 3 (Page 8)
remove "...and $T_m$"

Note 4 (Page 34)
replace "are undetectable amounts..." with "are no detectable..."

Note 5 (Page 43)
"Mark Houwink constant"

Note 6 (Page 45)
replace "The sampling became more viscous..." with "The samples became more viscous..."

Note 7 (Page 70)
"The expansion coefficient below $T_g$ is weakly dependent on ....."

Note 8 (Page 76)
replace sentence beginning "To correctly....." by "The level of detail required in a model depends on the properties of interest. It is not necessary to include electronic details to satisfactorily sample the configuration space of a macro molecule."

Note 9 (Page 88)
replace "....pair of dihedral angle of...." with "....pair of dihedral angles of...."

Note 10 (Page 90)
rewrite sentence "A cutoff is used to limit the computed short-range interactions to those from the closest neighbours."

Note 11 (Page 101)
ref. 11. Burkert U., Molecular Mechanics :ACS Publication 1982

Note 12 (Page 115)
"...likely conformation of bonds within an amorphous polymer."

Note 13 (Page 171)
replace "....a low volume/P.E. ...." with "....a low volume/potential energy...."

Note 14 (Page 197)
replace "For all the torsional...." with "For most of the torsional...."

Note 15 (Page 198)
replace "The volume fraction...." with "The volume fraction...."