UNSATURATED BIS-ARYLIMIDES
CONTAINING FOUR PHENYLENE RINGS;
SYNTHESIS AND ADDITION
POLYMERISATION TO CROSSLINKED
RESINS.

A THESIS
SUBMITTED TO THE UNIVERSITY OF SURREY IN PARTIAL
FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY IN THE FACULTY OF SCIENCE

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MARCH 1988
Abstract

The synthesis of some imides including bis-maleimides, bis-citraconimides, and bis-nadimides containing four phenylene rings, some of which are novel, is reported. These compounds were purified using preparative high performance liquid chromatography giving compounds of a high purity not commonly observed for monomers of this type. Chapter 2 describes the results of the synthesis and purification of the compounds. The unsaturated imides were heated under nitrogen to obtain polymers. Characterisation of both the monomers and polymers by a variety of techniques is described. The major impurity in the crude bis-citraconimides was isolated and characterised. It was found to be a structural isomer of the desired compounds, the citraconimide-itaconimide mixed imide.

Chapter 3 describes the study of the bis-imides, both impure and pure samples, using differential scanning calorimetry. The purity of the compounds was shown to affect temperatures at which both liquification and polymerisation of these monomers occurred. Within the series of pure bis-maleimides and citraconimides studied it is noted that those bearing m-substituted rings liquified at much lower temperatures, and samples of these were apparently much less crystalline. Polymerisation rate was the same for m- and p-isomers, citraconimides were less reactive than maleimides. In very highly pure bis-maleimides a second exothermic reaction was observed.
The DSC data obtained was analysed to obtain Arrhenius parameters useful in predicting the relative rates of thermal polymerisation of some pure and impure samples of the compounds. The overall order of reaction was found to vary during the course of the reaction.

Chapter 4 describes the thermogravimetric analysis of polymer samples, and the bis-nadimide monomers. The results give some indication of thermal and thermo-oxidative stability of the polymers.

Experimental details are given in Chapter 5.
Acknowledgements

I would like to express sincere thanks to my supervisors Professor J.B. Rose, Professor W.W. Wright, and Doctor J.M. Barton for much encouragement, firm and invaluable guidance, and for the opportunity to undertake this project.

Thanks are also due to the Materials and Structures Department, Royal Aircraft Establishment, Farnborough for the use of equipment and financial support.

Thanks to students and staff of the University of Surrey Chemistry Department and Materials and Structures RAE for constructive comments.
To Sara,

to my Mother,

and to the Memory of my Father
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Summary of Symbols and Abbreviations

$T = \text{temperature.}$
$T_g = \text{glass transition temperature.}$
$T_m = \text{melting or liquifaction point or range.}$
$t = \text{time.}$
$\alpha = \text{fractional conversion.}$
$R = \text{gas constant.}$
$x = \text{order of reaction.}$
$\ln = \text{natural logarithm of...}$
$E_a = \text{Arrhenius activation energy.}$
$\frac{dq}{dt} = \text{rate of heat flow.}$
$\frac{d\alpha}{dt} = \text{rate of change of conversion} = \text{rate of reaction.}$
$\Delta H = \text{total area between DSC curve and baseline representing enthalpy of reaction.}$
$a = \text{area representing heat already released at a time t during polymerisation in a DSC run.}$
$k = \text{rate constant.}$
$A = \text{whole pre-exponential factor.}$
$M_n = \text{number average molecular weight.}$
$DP = \text{mean degree of polymerisation.}$
$n = \text{no of molecules of cyclopentadiene lost/bis-nadimide molecule.}$
$\text{IR} = \text{infrared.}$
$\text{NMR} = \text{nuclear magnetic resonance (spectroscopy).}$
TGA = thermogravimetric analysis/analyser.

HPLC = high performance liquid chromatography.

THF = tetrahydrofuran.

ppm = parts per million.

UV = ultra-violet.

DMF = N,N-dimethylformamide.

DMSO = dimethyleulphoxide.
Chapter 1

Introduction
1.1 INTRODUCTION

As early as the 19th century, work was being carried out on naturally occurring polymers with patenting of vulcanisation by Hancock and later the discovery of Ebonite by Goodyear, which heralded the development of thermosetting polymers. However, it was not until the 1930s that the macromolecular nature of the materials now known as polymers was generally accepted. This acceptance was largely the result of the pioneering work of Staudinger. Since then, polymer science has grown inexorably to the point where our understanding may now permit polymer synthesis catered to produce particular desired properties in the resulting material. Synthetic polymers have achieved high importance in daily life.

1.1.1 Classification of Polymers According to Use

It is the macromolecular nature of polymeric materials that gives them their exceptional mechanical properties as compared with most other chemicals. The molecular structure of a polymer gives rise to the character of its morphology which in turn gives rise to main features of its bulk physical properties. Various polymers may be described as amorphous, semi-crystalline, or crystalline. Crystallinity depends upon a number of factors including chain polarity and intermolecular attraction, and the regularity of the chain structure and stereochemistry.
Polymers may be characterised by two temperatures; melting point Tm, and the glass transition temperature Tg. For highly crystalline polymers the former is perhaps a more important transition, whereas for highly amorphous polymers it is the latter. The glass transition temperature defines a temperature above which drastic changes in physical properties such as elasticity, hardness, specific volume, and heat capacity occur. The glass transition process is a complex one, and involves a rapid increase in molecular motion in sections of chain. This is exhibited as a softening of the material. The temperature at which this occurs, Tg, depends on a large number of factors including molecular weight and chain flexibility. Chain flexibility in turn depends on bond order in the main chain, and size, polarity, and inherent flexibility of side groups or chains. Melting temperatures predominantly depend upon molecular chain flexibility, polarity, symmetry, and molecular weight. Since these factors are similar to those influencing glass transition temperature, some correlation between Tg and Tm is observed.

Crosslinking the polymer chains results in insolubility because the polymer is no longer composed of large discreet molecules but chains joined at intervals by the crosslinks. The material is also incapable of melting without some preceding decomposition for the same reason. However, the material may still be capable of softening, i.e. undergoing a glass transition process, because sections of the chain are still capable of undergoing motion.
However, the higher the crosslink density the higher the glass transition temperature, and it is possible to produce materials in which $T_g$ exceeds decomposition temperature and is thus never observed.

Figure 1.1 depicts a crude classification of technological use of various types of polymer, with state. Polymers with glass transition temperatures below ambient temperature are represented above the line, those with $T_g$ at greater than ambient below the line.

Soft and Flexible

Rubbers*  Plastics

$T_g$

Glassy  Rigid Plastics  Artificial  Thermoset
Plastics  Fibres*  Plastics

Amorphous  Semi-crystalline  Crystalline  Crosslinked

------------------- INCREASING CHAIN ASSOCIATION -------------------

Figure 1.1

*Amorphous polymers above $T_g$ normally require a light degree of crosslinking to prevent creep before a satisfactory elastomer is produced.

*Artificial fibres often have orientated crystallinity.

Most polymers examined in this work are thermoset resins.
1.1.2 Classification of Polymers According to Synthesis

Two main types of reaction exist for reacting monomer with itself or comonomer - step-growth polymerisation and addition polymerisation. The former is normally a condensation polymerisation but is better referred to as step-growth since some reactions of this type do not result in the elimination of small molecules (or ionic salts); eg polyurethane formation by reaction of diisocyanate and diol. It naturally follows in this type of reaction that if even one of the monomers is trifunctional then the resulting polymer may be a thermoset material.

Addition polymerisation is a very different reaction kinetically. Chains grow from monomer and initiator fragments and the reactions involve the opening of double (or triple) bonds, eg polymerisation of ethylene to polyethylene. The polymerisation of maleimides (VII) and citraconimides (VIII) are of this type².

\[ \text{VII} \]
\[ \text{VIII} \]
\[ \text{IX} \]
Initiation may be of three types; free radical, cationic, or anionic. Maleimides have been polymerised by both free radical and anionic means. Free radical polymerisations may be initiated by addition of a free radical initiator. In certain cases, heat or photochemical irradiation may generate free radicals from the monomer itself and no additional initiator is required. Many monomers are known to polymerise thermally including maleimides, citraconimides, and nadimides (IX), but few monomers have been demonstrated to spontaneously polymerise thermally in the absence of oxygen. Purely thermal mechanisms are known for styrene and methyl methacrylate.

The free radical homopolymerisation of maleic anhydride as a 1,2-disubstituted monomer is extremely difficult as expected, although Lang et al. have reported benzoyl peroxide-initiated polymerisation in the melt at 70°C. It is not clear why maleimides and related imides should polymerise so much more easily. Joshi has determined that the chain transfer constants with monomer and initiator are very high for the homopolymerisation in solution of maleic anhydride, and that these reactions are prevalent enough to account for the reluctance of the anhydride to polymerise.

The value for the heat of polymerisation, \( \Delta H_p \), for maleimide in solvents such as dimethylformamide and acetonitrile has been measured at approximately \((88 \pm 2)\) KJ/mole, and \((67 \pm 2)\) KJ/mole in chlorobenzene by Joshi. This compares with \((74 \pm 1)\) KJ/mole for acrylic acid in...
benzene, $(74\pm1)\ \text{KJ/mole}$ for 2-vinylpyridine in benzene, and $(74\pm2)\ \text{KJ/mole}$ for acenaphthylene in benzene. The high enthalpy indicates the polymerisability of the monomer which may be in part due to the change in imide ring strain on opening of the double bond.

1.1.3 Thermally Stable Polymers

Polymer thermal stability represents an enormous field and may only be briefly touched upon here. There are a large number of applications of heat resistant polymers, many being within the aerospace industry.

One of the main problems in discussing thermally stability is one of definition, there being different types of thermal stability. If high temperature retention of mechanical properties is desired, then it is important that $T_m$ and $T_g$ be greater than operational temperatures. Decomposition temperature is a loose term, stability depending upon the time of exposure to the high temperatures. Enduring continuous or repeated exposure to high temperatures is a different requirement than withstanding short term exposure of a material to a very high temperature. Decomposition temperature depends upon the environment of the material — many organic materials may bear higher temperatures under nitrogen than in air, thermo-oxidative stability being lower than simple thermal stability. Many materials such as epoxy resins may absorb moisture in a normal environment containing water vapour — the water acts as a plasticiser lowering $T_g$ and the
material softens at the elevated temperature no longer retaining rigidity. Other materials may hydrolyse, embrittle, or swell in the presence of chemical vapours. Higher Tg and solvent resistance are obtained by the use of thermoset resins.

At present epoxy resins represent the largest share of thermosetting polymers used to make structural composites for the aerospace industry. They are easily processed in that they require only relatively moderate temperatures and pressures - between 120 and 180°C, and 70 to 100 PSI. However, their upper temperature range for structural usage is approximately 180°C, and this is reduced in moist environment to approximately 150°C.

Whilst thermosets provide some advantages in terms of solvent resistance, aromatic and conjugated systems are generally more thermo-oxidatively stable than their aliphatic counterparts. Although poly-p-phenylene is highly intractible, the introduction of thermally stable flexibilising linkages such as sulphone, ether, and carbonyl groups into aromatic chains has lead to a series of successful and highly stable thermoplastics; ie the poly(arylene ether sulphones) and polyaryletherketones.

A typical order of increasing thermal stability of some common plastics under nitrogen as estimated by start of thermal decomposition in thermogravimetric analysis, might be poly(vinyl chloride) < poly(methylmethacrylate) < linear polyethylene < polytetrafluoroethylene < poly(arylene ether ketones) < polyimides.
Currently polyimides are favoured as the most likely candidates to meet high temperature polymer requirements relatively economically. One of the major problems within the field is that systems examined showing high thermal stability also present processing problems due to intractibility, and a number of approaches have been adopted to combat this problem.

1.2 IMIDES - STRUCTURE AND SYNTHESIS

Imides generally contain the group R-CO-NR"-CO-R' although most commonly R and R' are joined to form a cyclic five or six membered imide ring system. Much of the chemistry of the imide linkage is similar to that of the amide. A common method of synthesis, illustrated here for maleimide, is by spontaneous reaction of cyclic anhydride and amine to give an amide acid or amic acid:

\[
\text{Maleic anhydride} + \text{NH}_2-R \rightarrow \text{Maleiamic acid}
\]

Although the amic acids may be thermally cyclodehydrated\textsuperscript{20} to the corresponding imide and the method has been used to prepare bis-citraconimides\textsuperscript{21}, this method is inadvisable due to the possibility of subsequent
polymerisation via the imide double bond (eg ref. 21). The thermal method also involves a side reaction forming the trans-isomer - for maleimic acids conversion is to the fumaric amide-acid. The trans amic acid will not cyclise to the imide. The most commonly employed methods of cyclodehydration are modifications of Searle's method which employs acetic anhydride as cyclodehydration agent in the presence of anhydrous sodium or potassium acetate catalyst:

Normally the amic acid is not isolated but carried straight through to the imide.

The presence of the acetate ion is said to help prevent contamination of the product with isoimide by catalysing isomerisation of this compound to the imide. Following formation of the mixed anhydride of the amic acid and acetic anhydride, unwanted formation of the isoimide may occur in the following manner:
Acetate ion then catalyses isomerisation of isoimide to imide, a process said to proceed as follows:

Kretov studied the isomerisation of N-aryl maleimides, and concluded that the products formed from cyclodehydration of maleimides by acetic anhydride and sodium acetate are strongly dependent on reaction conditions. At 20°C isomaleimide is formed; at 70 to 100°C for 30 minutes maleimide; and at reflux for 90 to 120 minutes maleic anhydride, acetic acid, and the N-acetyl derivative of the precursor amine. Normally less vigorous conditions than those required without added solvent are used with dipolar aprotic solvents such as dimethylformamide (DMF). Such solvents are ideal in synthesising molecules such as I to VI since reactants, and intermediate amic acids are soluble. Acetone has also been used.
1.3 APPLICATION TO POLYMER FORMATION

1.3.1 Condensation-Type Polyimides

The anhydride-amine reaction may be utilised to form polyamic acids if tetracarboxylic dianhydrides and diamines are reacted together. Two of the commonest anhydrides that have been used are 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) on which LARC-TPI (thermoplastic polyimide) is based and pyromellitic dianhydride (PMDA). Usually the polymers are only processable at the polyamic acid stage. The next stage is the thermal or chemical cyclodehydration of the polyamic acid prepolymer to the intractible polyimide.

\[
\begin{align*}
\text{n NH}_2\text{C}_2\text{NH}_2 + \text{n OOOO} &
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{NH} \cdots \text{OH} &
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{NH} \cdots \text{OH} &
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} &
\end{align*}
\]

A Condensation Polyimide Synthesis
This type of system is highly heat resistant but suffers disadvantages. The polyamic acid prepolymer is susceptible to hydrolysis and heating to effect thermal cyclodehydration and solvent removal from the prepolymer can produce severe void formation.

1.3.2 Addition-Crosslinked Condensation Imide Oligomers

These, like the condensation polyimides, involve a linear condensation propagation, but amic acid oligomers are produced because of the addition of a monoanhydride such as nadic anhydride, or equivalent terminating species. Flexible procedures have been developed to synthesise a wide variety of nadic terminated oligomers of this type, where the polyamic acid prepolymer can be cyclodehydrated both thermally or chemically to give a soluble nadic terminated imide oligomer.
As with simple condensation polyimides, processing is normally carried out at the amic acid stage.

When Ar is 4,4'-diphenylene methane and R is >C=O then the above formula represents the commercially available P13N resin system\textsuperscript{32}. The equivalent system to P13N based on pyromellitic dianhydride is known as P10P. This resin is even more thermally stable than those of the P13N type, but solutions of the amide-acid prepolymer have a very limited shelf life, probably due to susceptibility to hydrolysis\textsuperscript{33}. This problem was alleviated by alternative strategies involving use of solutions of the monomeric reactants at the processing stage\textsuperscript{33,34,35,36}, giving rise to the PMR (Polymerisation of Monomer Reactants) approach to polyimide synthesis. These solutions are subsequently heated to drive off solvent, then further to form polyimide oligomer, then at higher temperatures under applied pressure to effect crosslinking. The large pressures required at the cure stage for these resins present problems in fabrication. They are required in order to prevent volatilisation of cyclopentadiene produced by retro Diels-Alder decomposition of the nadimide end groups. This might produce voids in the cured material. The mechanism of nadimide propagation is discussed further below in section 1.6. This type of polyimide is expected to be slightly less thermally stable than the purely condensation-type polyimides due to the additional saturated -C-H produced during crosslinking by addition polymerisation of imide.
1.4 BIS-MALEIMIDES, CITRACONIMIDES AND RELATED COMPOUNDS

1.4.1 Synthesised Bis-Imides

A great number of bis-maleimides have now been synthesised, and systems based on bis-4-maleimidophenyl methane are commercially available. Melting points are quite variable depending on structure, but generally the aromatic compounds are high melting. Most aromatic bis-maleimides that have been synthesised are relatively simple in structure, containing one or two arylene rings. Now well known, are maleimides with the following bridging groups between imide rings; p-diphenylene ether\(^27\), m- and p-diphenylene sulphone\(^27\), and p-diphenyl methane\(^27\). Although literature on citraconimides is less common than that concerning bis-maleimides, both the corresponding bis-citraconimides and itaconimides of the above aryl chains have been synthesised\(^3\). Some complex phosphorus containing imides including bis- and tris-maleimides and citraconimides, and dichloromaleimides have been synthesised in connection with thermal stability and fire resistance\(^4\). Siloxane containing bis-maleimides, bis-nadimides, and condensation-type polyimides have also been made\(^2\). Four ring maleimide systems of the type presented in this work have now been synthesised, and both \(I^4\) and \(II^4\) are known.

Synthesis has been mainly directed at producing technologically useful materials, and - with some exceptions - little effort has been directed at producing
pure materials. This is probably because impure materials generally have lower melting points or ranges — this is an advantage for reasons outlined below in section 1.4.2 — and the cost of obtaining pure materials on a large scale. The additional effort required to obtain pure monomers would be substantial especially with systems based on more complex monomers such as those reported in this thesis. Such difficulties are outlined in Chapter 2 for bis-imides I to IV. For these reasons it is of great practical importance to determine the behaviour of impure systems synthesised without rigorous purification.

1.4.2 Problems with Synthesised Systems

A great deal of success in the synthesis of thermally stable bis-imide systems has been obtained. However, the main problem associated with the materials that have been made is one of processability. Often, the minimum temperature at which the materials will polymerise is limited by melting point. In such materials the onset of polymerisation to insoluble material is simultaneous with the onset of melting. Alternatively, there is very little separation between melting point and temperatures at which polymerisation will occur. In these systems processing is very difficult, because melts are unstable and cannot flow to a sufficient extent before curing.

Impregnation of fibres using solutions of such high melting bis-imides involves difficulties due to the low solubility of such materials in a number of common
solvents. Typical solvents that can be used are high boiling, eg dimethylformamide, dimethylacetamide, dimethylsulphoxide, and N-methylpyrrolidone. Several of these solvents are toxic. Also the removal of high boiling solvents from bis-imides is very difficult. At least one bis-maleimide has been synthesised from amic acid by thermal cyclodehydration, because acetic acid (the byproduct of cyclodehydration using acetic anhydride) was difficult to remove from the product.22 The possibility of voids in the polymer becomes of concern with the use of solvents which are difficult to remove, or with gaseous byproducts during the polymerisation. The bis-maleimides and related imides have the advantage that they do not release such volatiles during curing.

The melting points of bis-imides are thus of importance. The melting points of bis-maleimides with greater distances between the chain ends are expected to be relatively lower, due to the general increase in chain flexibility with length. This is indeed observed for aliphatic bis-maleimides and aliphatic bis-citraconimides.

Several approaches have been adopted in commercial systems to enable processing of bis-maleimides. The resins known as H353 and Kerimid 353 are based on a low melting eutectic mixture of the bis-maleimides of methylene dianiline, toluene diamine, and trimethylhexamethylenediamine. The formulation melts between 70 and 125°C allowing it to be used as a melt for impregnating fabrics. An alternative strategy was adopted
for M751\textsuperscript{46,47} which contains a mono and bis-maleimide, and may be cured so as to have a glass transition temperature of approximately 240°C but with good retention of strength up to this temperature. Unfortunately M751 requires N-methyl pyrrolidone as solvent for processing. H795 is an oligomeric bis-maleimide synthesised by Michael addition of diamine to bis-maleimide\textsuperscript{46,49}. This type of reaction is discussed in greater detail below in section 1.5. The material has a relatively low melting range and is quite soluble in common low and moderate boiling solvents such as toluene, methyl ethyl ketone, and dichloromethane. Diluents may be incorporated to ease processing problems. Epoxy resins and vinyl compounds have been employed\textsuperscript{49}, and the thermal behaviour of bis-maleimide/amine/vinyl ester blends has been examined\textsuperscript{50}.

The thermoset polymers of these materials are expected to be slightly less thermally stable than those of the purely condensation-type, since there are additional sites of saturated C-H formed by the addition polymerisation of imide end groups.

Another major disadvantage of simple poly(bis-maleimide)s is their brittleness. Due to the high crosslink density of materials containing only short aromatic links between imide end groups, this type of material is of high modulus and low strength, with very low elongation at break\textsuperscript{37}. This problem is alleviated by increasing the distance between chain ends and thus the crosslinks in the final polymer. Convenient methods exist for the chain extension of bis-maleimides, and these are
Bis-maleimides, bis-citraconimides, bis-itaconimides, and dichloromaleimides have all been thermally polymerised by virtue of the double bond, despite the fact that they are 1,2-disubstituted monomers with the exception of itaconimide (X) which is 1,1-disubstituted.

Maleimides have been polymerised in a number of ways. Tawney et al.\textsuperscript{51} and Jousett\textsuperscript{52} have polymerised maleimide at 60°C in benzene using benzoyl peroxide and azobisisobutyronitrile as initiators. Polymers with molecular weights in the region of 1,000,000 were obtained, and the glass transition temperature was said to be greater than 400°C.
Cubbon\textsuperscript{3} polymerised a series of N-substituted maleimides in solution by both free radical and anionic means. The softening points were in the range 110 to 330°C. He carried out an X-ray crystallographic study of the stereochemistry of the linear polymers formed, and concluded that the products were probably predominantly threo di-isotactic, but with some threo di-syndiotactic sections of chain disrupting the crystallinity somewhat. These configurations are formed by trans opening of the double bond, there being large steric hindrance in the formation of polymers containing the cis configuration. However, the products of solution polymerisation of maleimides may be very different to those of the thermal polymerisation in bulk.

The polymerisation of maleic anhydride and N-substituted maleimides using triphenylphosphine has been studied using \textsuperscript{31}P NMR\textsuperscript{33}. The mechanism involves formation of the ylid of maleimide.

The monomer does not undergo cationic polymerisation. Polymerisations initiated by anionic basic catalysts such as sodium n-butoxide or potassium t-butoxide results in a polymer containing residues of both the vinyl polymerisation type and the proton transfer type\textsuperscript{34} of the following composition:

![Diagram of polymer structures](image)
The free radical initiated solution polymerisation of N-n-butylmaleimide in dimethylformamide has been shown to obey the following rate expression:

$$-\frac{d[M]}{dt} = k [M][I]^{1/2}$$

where \([M]\) is monomer concentration, and \([I]\) is initiator concentration. This expression is the normal expression expected for a simple free radical initiated solution polymerisation of this type.

The most important method of polymerisation of this type of imide is the bulk thermal method, due to its applicability to the formation of thermoset resins from the bis-imides for composite applications. However, very little fundamental work on the thermal polymerisation of maleimides has been carried out. The most common method of study involves the use of DSC. This enables the temperatures at which melt, polymerisation, and other processes occur to be observed. It is also possible to obtain enthalpic and overall kinetic data on such processes. The technique lends itself very well to the study of such bis-imide systems. In the study of this type of polymerising system there is the problem of obtaining measurements on an amorphous melt at relatively high temperatures. Also the system is moving quickly towards an insoluble state. This type of work is discussed more fully in Chapter 3.

The polymerisation kinetics of aliphatic maleimides have also been studied by infrared spectroscopy by Hummel et al. They found that there was an almost linear correlation between overall Arrhenius activation energy
and the number of methylene groups between the imide rings in a series of linear aliphatic bis-maleimides. Their values obtained by infrared spectroscopy compare to those of Stenzenberger obtained by DSC in the following way:
For 1,12-bismaleimidododecane, 76.9KJ/mole (DSC) to 94.2KJ/mole (IR); for 1,6-bismaleimidohexane 126.2KJ/mole (DSC) to 140.2 KJ/mole (IR).

A simple standard kinetic scheme is shown below for a thermally initiated polymerisation.

\[ [M] = \text{concentration of double bonds.} \]
\[ [P.] = \text{concentration of propagating chain (including initiator radicals.)} \]
\[ P \text{ represents terminated chain of propagation.} \]

Initiation. \[ M + M \rightarrow P. + P. \] \[ k_i \]

Propagation. \[ P. + M \rightarrow P. \] \[ k_p \]

Termination. \[ P. + P. \rightarrow P \] \[ k_{tc} \]
\[ P. + P. \rightarrow P + P \] \[ k_{td} \]

\[ R_p = -d[M]/dt \]
\[ -d[M]/dt = k_i[M]^2 + k_p[P.][M] \]

Using the steady state hypothesis to remove the intermediate \([P.]\):

**Steady state expression.**
\[ d[P.]/dt = k_i[M]^2 - k_{tc}[P.]^2 - k_{td}[P.]^2 \]
Using the hypothesis we can say \( \frac{d[P]}{dt} = 0 \).

\[
\begin{align*}
\text{ki}[M]^2 &= \text{ktc}[P]^2 + \text{ktc}[M]^2 \\
\text{ki}[M]^2 &= [P]^2 (\text{ktc} + \text{ktc}) \\
[P]^2 &= \text{ki}[M]^2 / \text{ktc} + \text{ktc}
\end{align*}
\]

\[
(P.) = (\text{ki}[M]^2 / \text{ktc} + \text{ktc})^n
\]

\[
\begin{align*}
\therefore \frac{-d[M]}{dt} &= \text{ki}[M]^2 + \text{kp}[M][\text{ki}[M]^2 / \text{ktc} + \text{ktc})^n \\
\frac{-d[M]}{dt} &= \text{ki}[M]^2 + \text{kp}[M]^2 (\text{ki} / \text{ktc} + \text{ktc})^n
\end{align*}
\]

\[
\begin{align*}
\frac{-d[M]}{dt} &= [M]^2 (\text{ki} + \text{kp} (\text{ki} / \text{ktc} + \text{ktc})^n)
\end{align*}
\]

Thus \( \frac{-d[M]}{dt} = \text{ki}[M]^2 \)

where \( k \) is a pseudo second order rate constant, but may not vary with temperature in a simple manner due to the component rate constants of the elementary reactions having different activation energies.

It is assumed that the rate of propagation (ie kp) is independent of the propagated chain length already formed; eg initiator radicals are treated as propagating chain radicals, and all are considered the same in terms of propagation rate. This is a common assumption in this type of kinetic scheme. The steady state hypothesis is invoked.

Any such simple kinetic scheme for thermal polymerisation predicts overall second order kinetics. Contrary to this, the general kinetic treatment in the literature on bis-maleimide polymerisation has been treated as first order, as is discussed in Chapter 3.
1.4.4 Relative Reactivities of Imides

The thermal isomerisation of itaconic anhydride to citraconic anhydride takes place readily. The reason that this reaction occurs easily is that the removal of a hydrogen atom from the saturated methylene group of the itaconic anhydride produces a resonance-stabilised allylic-type free radical. The simple addition of the hydrogen atom onto the remaining methylene group rather than the methinyl group (which would reform the itaconic group) gives citraconic anhydride:

The formation of such a stable radical might occur during the thermally initiated polymerisation of citraconimide. If this occurs, it is expected to slow the polymerisation. In addition to this, the polymerisation of citraconimide is also subject to steric hindrance due to
the methyl group. For these reasons, the polymerisation of citraconimide is expected to occur less readily than that of maleimide. Pyriadi and Mutar have reported the complete failure of the attempted polymerisation of N-phenyl and N-cyclopropyl citraconimides by free radical initiated solution polymerisation. Their suggested explanation was that given above. The failure of the bromination of these compounds with N-bromosuccinimide was also attributed to the exceptional stability of the allylic-type radical intermediate XI.

However, several workers have observed that citraconimides have polymerised at relatively lower temperatures than the corresponding maleimides. The corresponding dichloromaleimides have been observed to polymerise at higher temperatures than the corresponding maleimides (references 40 and 41). The observation has been made that with the electron releasing methyl group, polymerisation becomes easier; with the electron withdrawing chlorine atoms in dichloromaleimides the polymerisation becomes more difficult. It would appear that some clarification of the situation regarding the relative reactivities of various types of imide would be an advantage in view of apparently conflicting results. It is possible that some other factors may have an influence on polymerisation reactivity in addition to those already mentioned. The influence of purity has not been examined. It is not inconceivable that certain impurities might act as retarders or accelerators during the thermal polymerisation of these monomers. It has been mentioned
that a large amount of practically important work has been carried out on crude samples of bis-imides. Some investigation of the effect of purity would be advantageous in view of this fact. This is especially important if the relationship between the chemical structure and reactivity of the imides is to be made clear.

1.5 Chain-Extended Bis-Imines

As has been seen in the discussion in section 1.4.2, the extension of the chain length between imide end groups represents an approach to produce less brittle materials. The most common method of chain extension, is by Michael addition of amine group to the maleimide double bond.

The double bond of the maleimide group is relatively electron deficient, due to the two adjacent carbonyl groups. These may be regarded as both inductively and mesomerically electron withdrawing. For this reason the maleimide double bond is susceptible to attack by nucleophiles, a reaction which has been studied in some detail\textsuperscript{61,62}. The double bond is susceptible to a number of other bimolecular reactions such as Diels-Alder cycloaddition\textsuperscript{63,64} and dipolar cycloaddition\textsuperscript{65,66,67,68}, and the nucleophilic attack of aryl azides on the double bond has been described\textsuperscript{69}. 
1.5.1 Polyaspartimides

Crivello first applied the amine-maleimide reaction to the synthesis of high molecular weight linear polyaspartimides. The net reaction is as follows:

\[
\text{NH2-Ar-NH2} \quad + \quad \text{NH2-Ar-NH2} \quad \rightarrow \quad \text{NH-Ar-NH}
\]

The reaction was carried out using equimolar quantities of bis-maleimide and diamine in cresol, with small amounts of acetic acid as catalyst. Crivello found that the reaction was catalysed by weak protonic acids, but not bases or strong acids. A kinetic study using \( N \)-phenylmaleimide and aniline as a model system was carried out, and the reaction obeyed second order kinetics. A variety of polyaspartimides were synthesised in addition to a number of simple adducts of various amines and diamines and \( N \)-phenylmaleimide. The microanalyses were of
a very high standard indicating products of high purity. The polymers synthesised were amorphous, high softening, pale yellow solids soluble in a limited number of solvents including phenolic solvents, DMF, and amide solvents from which flexible films could be cast. The high softening points are expected in this type of structure in view of the high degree of rigidity present in the chain by virtue of the aspartimide and p-phenylene units.

In line with that expected of these structures, thermal stability was lower than of the poly(bis-maleimides). The addition of amine to maleimide produces both additional saturated >CH₂ and secondary amine linkages into the chain, neither of which are conducive to high thermal stability. Decomposition temperatures were in the region of 350°C as indicated by thermogravimetric analysis, in both nitrogen and air (reference 70). The most likely explanation of this is that the decomposition is predominantly thermal rather than oxidative, and Crivello suggested that this was retro Michael addition.

Varma et al. have used the Michael addition reaction to produce a series of amine-maleimide adducts that are maleimide terminated97,71,72. The syntheses were carried out in acetone with a 1:0.3 or 1:0.4 excess of the bis-maleimide. The crosslinking of such chain-extended materials may then occur via thermal addition polymerisation of the maleimide end groups on the linear chains. This may be effected isothermally in the region of 220°C. The temperatures of maximum rate of reaction as measured by scanning DSC were quite variable, between 130
and 270°C. In certain cases two exotherms were visible on the thermograms. Some of the oligomers were the Michael addition products of phosphorus containing bis-maleimides and diamines, synthesised in connection with their fire resistant properties. The incorporation of m-phenylene rather than p-phenylene linkages was aimed at producing structures with enhanced elongation at break.

Varma et al. also investigated the crosslinking of bis-maleimides in the presence of di- and tri-amines; both addition polymerisation of maleimide end groups and Michael reaction occurring simultaneously by thermal means. The commercial Keramid 601 resin is of this type, being available as a blend of 4,4'-bismaleimidophenylmethane (2.5 moles) with 4,4'-diaminodiphenylmethane (one mole) premelted together. The polymerisation and crosslinking of this complex system also involves both Michael reaction of amine and bis-maleimide and thermal addition polymerisation of maleimide end groups. The crosslinking of the system has been studied using Fourier Transform infrared spectroscopy by Di Giulio et al., who determined a linear relationship between residual double bond content in the resin, and cure temperature. The glass transition temperatures of the crosslinked products were approximately the same as the temperatures at which the thermal polymerisations were carried out.

Kumar, Fohlen and Parker reacted two moles of amine to every mole of bis-maleimide in N,N-dimethylacetamide using acetic acid as catalyst in order to synthesise amine
terminated trimers. The materials thus produced were stable to approximately 370°C. Polymerisation could not occur by Michael addition or thermal addition polymerisation of maleimide double bonds. However, the materials could be cured between 230 and 250°C. Characterisation was carried out by Fourier Transform infrared spectroscopy, and ¹H and ¹³C nuclear magnetic resonance spectroscopy, which indicated that in this case the crosslinking occurred via an amidation reaction between the amine end groups and aspartimide links. The following reaction and consequent structure was proposed:
It seems possible that this type of reaction might also occur in the thermal crosslinking of maleimide-amine mixtures which is carried out at similar temperatures, but this is not generally considered along with the Michael addition and thermal addition polymerisation reactions that are known to occur.

The polyaspartimides are less thermally stable than the bis-maleimides\textsuperscript{70, 73}. However, high char yields are produced by pyrolysis of some phosphorus containing polyaspartimides\textsuperscript{97}. The resins are less brittle than those cured in the absence of di- and triamines\textsuperscript{73} and some systems may be processed at low temperatures\textsuperscript{72}.

1.5.2 Chain-Extended Dichloromaleimides

As has already been mentioned, dichloromaleimides have been synthesised, and are said to thermally polymerise at relatively higher temperatures than maleimides due to the electron withdrawing effect of the chlorine atoms on the double bond\textsuperscript{40-41}. Varma et al.\textsuperscript{76} have reported an unusual chain extension of dichloromaleimides with diamines. The amine group reacts with the dichloromaleimide by nucleophilic substitution at the highly electron deficient double bond. Apparently only one chlorine atom per dichloromaleimide end group is displaced, giving a linear polymer. According to the method of Relles et al.\textsuperscript{77} the diamine was reacted with a bis-dichloromaleimide in a 1:1 molar ratio in DMF with two moles equivalent of triethylamine as acid acceptor. The
linear polymerisation occurred without applied heat over a two hour period.

Unlike Michael addition chain extensions, the polymerisation does not remove the double bond of the imide. These polymers were crosslinked by heating in air at 300°C over 30 minutes.

The poly(maleimide-amine)s were stable up to 300°C in air or nitrogen but decomposed at temperatures much above this.

The above work followed the discovery of the phenoxide-dichloromaleimide reaction by Relles and Schluenz, where the nucleophilic substitution with bisphenoxide as the nucleophile attacking bis-dichloromaleimide led to poly(maleimide-ether)s. A homopolymer from N-(m-hydroxyphenyl)dichloromaleimide was
also produced. Reaction of bis-phenoxide with mono-
(dichloromaleimides) to displace two chloride ions from
each dichloromaleimide gave only low molecular weight
polymers.

1.5.3 Polyimidothioethers

Crivello has reported the synthesis of a whole
series of linear polymers formed by reaction of both
hydrogen sulphide and a variety of aliphatic dithiols with
aromatic bis-maleimides. The reaction is the sulphur
analogue of the chain extension of bis-maleimides by
ammonia or diamines in Michael addition reactions to give
polyaspartimides.

\[
\begin{align*}
&\text{HS}-R-SH \\
\downarrow H_2S
\end{align*}
\]

The reaction occurs spontaneously in DMF but is
accompanied by the formation of insoluble gels. Crivello reported that the addition of small quantities of acetic acid to the reaction mixture prevented the formation of crosslinked material, which was presumably formed by anionic polymerisation of maleimide double bond initiated by hydrosulphide or mercaptide in the polar medium. A better method used, was to carry out the polymerisations with hindered tertiary amine base as catalyst in cresol, the latter acting as both solvent and proton donor. The polymers were high softening high melting materials which begin decomposition at 325°C with loss of hydrogen sulphide from the polymer. The thioether linkage can readily be oxidised to sulphone by peracetic acid giving polyimidosulphones which may decompose at their melting points. White and Scaia have reported number average molecular weights of between 20000 and 80000 for fully aromatic thermoplastics of this type.

Fully aliphatic polymers have also been reported. Unlike the aromatic systems, these are amorphous, and elastomeric with relatively low glass transition temperatures in the region of 6.5 to 13°C.

The polyimidothioethers reported are thermoplastics of relatively low thermal stability, due to the thioether linkage, and not suitable for applications where high temperature retention of mechanical properties is required.
A great deal of work has been done relating to the nadimide end group, including the nadimide terminated oligomers described above in section 1.3.2. The addition of the nadimide end group in place of maleimide, represents one approach that may be adopted to increase the temperature required to polymerise the system, thus enabling a melt stable system to be formulated.

The mechanism of addition polymerisation is more complex than that of the maleimides, and not all aspects are entirely understood yet. Evidence for at least four different reactions has been obtained:

1. **ENDO-EXO ISOMERISATION**
   - Some volatilises

2. **Maleimide, Nadimide, XII, (Cyclopentadiene)**
   - Random Polymer
It is known that the endo-exo isomerisation of the nadimide end group occurs thermally as low as 200°C\textsuperscript{54,55,66}, although it is not certain if this has a significant effect on the polymerisation rate.

The first step in thermal polymerisation is believed to be the retro Diels-Alder decomposition of the nadimide end group\textsuperscript{57}, which is an adduct of maleimide and cyclopentadiene. Polymerisation has not been detected in the absence of this reaction. Lauver\textsuperscript{68} has carried out a kinetic study of the crosslinking of the bis-nadimide of bis-(4-aminophenyl)methane as model compound. The kinetics were obtained by examination of DSC exothermic peak data. The data fitted a first order model well, and yielded an Arrhenius activation energy of (184±8) KJ/mole and \( \ln A = 31 \). This data was in the region expected from previous Arrhenius kinetic parameters for Diels-Alder reversion reactions discussed by Wasserman\textsuperscript{69}. These \( E_a \) values were approximately between 100 and 240 KJ/mole, and the \( \ln A \) values, 25 and 32. The overall first order kinetic behaviour suggested that the nadimide decomposition is the rate limiting step. However, this analysis has to be based on the assumption that there is no invisible underlying endotherm or exotherm such as might be caused by either the retro Diels-Alder decomposition or endo-exo isomerisation.

Cyclopentadiene volatilising from the system altogether from the reverse Diels-Alder decomposition reaction has been detected\textsuperscript{67,90,91}. However, the extent of cyclopentadiene volatilisation has not been recorded.
Wong et al. have detected the double Diels-Alder adduct XII in pyrolysis products of N-phenylnadimide and as a residue in insoluble crosslinked nadimide end capped oligomers by solution and solid state $^1$H and $^{13}$C NMR. There are eight stereochemical possibilities for this structure; the two predominantly found were endo-exo-exo and exo-endo-exo:
These are the products of cyclopentadiene addition by the two possible modes to the exo-isomer of nadimide. This exo-isomer is said to be the more stable thermodynamically\textsuperscript{94}, and thus the isomer predominantly formed in the initial isomerisation equilibrium at lower temperatures.

The various species formed then polymerise together to form polymer that is probably random in ordering of the various monomer fragments in the chain as indicated by the broad $^1$H and $^{13}$C NMR resonances in the polymer spectrum obtained by Wong et al. \cite{(reference 84)}. No residual double bond content was detected in the polymer spectrum, suggesting that the polymerisation of cyclopentadiene into the system as a discreet monomer did not occur as was previously believed.

The polymerisation follows the retro Diels-Alder reaction which is probably the rate determining step in the polymerisation. This suggests that the generation of maleimide is necessary to initiate the thermal polymerisation. Since maleimide is known to thermally polymerise without added initiator, this is quite possible. The fact that maleimide has an electron deficient double bond and the other species relatively electron rich double bonds, may facilitate the polymerisation following rate determining maleimide generation by the retro Diels-Alder reaction. This explanation is supported by the observation that addition of maleimide to nadimide lowers polymerisation exotherm temperature as observed by DSC\textsuperscript{92}. The temperature lowering
is dependent upon the quantity of added maleimide.

1.7 TECHNIQUES USED TO EXAMINE POLYMERS

The techniques described in this section are only those that were used for examination of the polymers described in this work. Although the methods are often used in the synthetic polymer field, they may also be used for a variety of other types of material.

1.7.1 Analytical Techniques and Polymerising System

There are special problems in the investigation of melt-crosslinking systems including bis-imides. The systems not only undergo chemical changes during heating; eg, monomer to polymer containing monomer and initiator fragments; but also physical changes; eg, viscosity, density, solubility, heat capacity, and in particular changes of state. During a successful thermal cure the system changes from a solid to a melt when heated; and the melt, which may be mobile, becomes more viscous setting into a softened insoluble infusible solid which eventually hardens remaining insoluble and infusible. The material is amorphous throughout the course of the reaction, and relatively high temperatures - specifically dependent on the system being examined - are required to effect a complete cure. The nadimide based systems also release volatiles97. Such systems do not lend themselves to examination by chemical techniques commonly used to
examine reaction kinetics, which often rely on solubility and seldom have provision in the instrumentation for the high temperatures required, e.g., UV spectroscopy, NMR, chemical analysis, etc.

One solution to this problem is to break down the final polymer structure into soluble fragments which may then be examined by a variety of techniques. For example; such a method has been utilised to examine structural changes in an oxidised crosslinked polyimide film of the condensation type, by breakdown using hydrazine hydrate\textsuperscript{53}.

Infrared spectroscopy, and particularly Fourier Transform infrared spectroscopy (FTIR) represents another approach to the problem. The technique does not require samples in solution, and heated sample cells are available for modern instruments which may attain temperatures of up to 250°C or greater. Alternatively pre-cured samples may be examined. Both bis-maleimides\textsuperscript{37} and curing maleimide-amine adduct systems (polyaspartimides)\textsuperscript{74} have been successfully studied by IR spectroscopy, and kinetic parameters obtained for cure (ref. 57).

Another approach is to use Differential Scanning Calorimetry (DSC).

1.7.2 Basic Principles of DSC

This technique provides a convenient and relatively quick method for the examination of significantly endothermic or exothermic reactions, changes in heat capacity etc, with changes in temperature. The method
requires only relatively small quantities of material. It provides quantitative information on processes occurring at elevated temperatures, including overall reaction kinetics.

Differential scanning calorimetry is a technique which subjects a sample and reference to a controlled temperature-time programme. Two modes of DSC are commonly used, differing in measurement method and instrument design - power compensation and heat flux DSC.

Power compensation DSC instruments use separate sample and reference pan holders. Each holder is of low thermal mass, and has an individual heater and temperature sensor. Power is supplied to the heater of each holder, and the temperature thus raised or held as desired. The power supplied to the individual heaters is varied in such a way as to minimise the temperature difference between sample and reference pans as indicated by the temperature sensors. The power difference required to maintain this equality in temperature, is a measure of heat flow, dq/dt, into the sample relative to the reference material. The instrument is calibrated for output signal-heat flow proportionality using a standard, eg NFL indium, for which the heat of fusion, $\Delta H_\text{f}$, is accurately known. The heat flow will indicate the occurrence of a heat capacity change, endothermic, or exothermic reaction.

In heat flux DSC, the sample and reference pans are placed in the same cell. The path between the sample and reference stations is of relatively low thermal resistance and sample and reference are subjected to the effects of
the same heater. The sample-reference temperature
difference is related to heat flow. Both methods may yield
similar results.

Typically in temperature scanning experiments, the
temperature is raised (ramped) at a steady rate, eg 10°C/minute, from ambient to some preset desired
temperature, and the heat flow recorded as a function of
temperature and time during this period. This type of run
will be referred to as *scanning DSC*. The sample is weighed
into a disposable flat open-topped cylindrical aluminium
pan, the reference being such an empty pan. Normally runs
are carried out under nitrogen. Alternatively, some
instruments having high performance temperature control,
may be used to attain a desired temperature at a very fast
rate (eg 200°C/minute), followed by an isothermal period
during which heat flow data are recorded as a function of
time. This type of experiment will be referred to as
*isothermal DSC*.

Both scanning and isothermal DSC have been used to
obtain kinetic data in this work.

**The Scanning DSC Thermogram**

The DSC trace, or thermogram, is a plot of heat flow
versus temperature or time. In the absence of exothermic
or endothermic reaction in sample or reference, the heat
flow is proportional to the sample-reference heat capacity
difference in a constant ramp-rate scanning DSC
experiment. Changes in heat capacity are normally
associated with glass transition processes, and these may often thus be detected in this way. Crystalline melting points are also detectable as endothermic reactions which are visible on the DSC trace as described below.

The heat flow signal during a temperature scan is a linear function of the heat capacity of the sample and its variation with temperature. In the absence of physical transitions and chemical reactions it may be taken to represent a baseline. This is usually linear over moderate temperature intervals. Derivations from this baseline are due to endo- or exothermic reactions or transitions. These take the form of a peak above or below the baseline. Sign convention determines which direction is endothermic, which exothermic. The height above the baseline at any time projected onto the y axis is taken as the heat flow \(dq/dt\) which is due to the process occurring in the sample. Since the x axis is either time or temperature as a known function of time, the area of the peak thus represents \(\Delta H\) for the reaction:

\[
\Delta H = \int_{t_1}^{t_2} (dq/dt) \, dt
\]

1.7.3 Thermogravimetric Analysis (TGA)

A thermogravimetric analyser is essentially composed of a sensitive balance. The sample is placed in an inert holder, eg a platinum boat, in a stream of nitrogen, air, or some other chosen medium. The sample may be subjected to a temperature-time programme by means of a surrounding
furnace, and weight recorded as a function of temperature and time.

The method is useful in assessing temperature and rate of thermal decomposition under inert and aerobic conditions. Samples of a whole variety of materials may be examined, and temperatures approaching 1000°C may be attained. Extent of thermal polymerisation or crosslinking of condensation polymers may be assessed where volatiles are lost during the condensation.

The method has the advantage that measurements may be made in a variety of atmospheres and that no particular sample shape is required - powders may be used. Only relatively small (milligramme) quantities of material are required. Most instruments are now computer controlled, and in some cases measurements may be utilised to obtain kinetic data on decomposition, condensation, and other reactions by computer analysis.

However, for comparable measurements similar quantities and sample forms are preferable, as measurements (both weight loss and rate of weight loss) may depend on sample size and shape.

1.7.4 Vapour Pressure Osmometry

This technique is a solution method, and may be used to measure relative molecular masses in the range of 50 to 20000. For polymers the molecular weight measured is the number average, Mn.

The apparatus contains a thermostatted chamber
saturated with solvent vapour. This chamber contains two matched differential thermistors which are capable of measuring temperature differences extremely accurately. A drop of solvent is applied to one of the thermistors by syringe, a drop of the polymer solution to the other. The polymer solution has a lower vapour pressure than the pure solvent and thus some solvent condenses on the polymer solution causing the temperature of the thermistor to rise. The difference in temperature of the two thermistors is measured when equilibrium is attained, and is proportional to the difference in vapour pressure of solvent and solution. Evaporation of solvent from the solvent drop is negligible due to the large excess of solvent vapour present in the thermostatted chamber. The two thermistors are connected into a Wheatstone bridge, and thus their temperature difference ΔT is measured as a difference in resistance Δr.

The following relation may be used to calculate the number average molecular weight of the polymer M_n:

\[ M_n = \langle \lambda / c / \Delta r \rangle_{c \to 0} \]

where \( \lambda \) is a calibration constant obtained by use of a known standard in the solvent, and \( c \) is the weight per unit volume concentration of the polymer solution. \( \Delta r \) is measured as a function of known concentrations \( \langle c \rangle \), and the molecular weight is obtained by extrapolating data to \( c=0 \).
1.8 SCOPE OF THE WORK

The chain extension of bis-unsaturated imides results in a variety of materials, with a variety of properties. They often have superior processability and mechanical properties compared with the non-extended short chain bis-imides. However, by all chain-extension methods described so far a reduction in thermo-oxidative stability is also encountered. Compatible with requirements of the aerospace and other industries where applications are demanding ever more thermally stable but processable materials, it was decided that a series of structurally related bis-imides of different imide types would be synthesised.

A large amount of the previous work on bis-maleimides and related compounds had been carried out on impure materials for sound practical reasons. However, the effect of purity in influencing polymerisation reactivity had not been investigated. This was desirable, especially in view of the difficulty involved in explaining some orders of reactivity. In order to compare the relative reactivities of the related structures without possible interference by impurities the imides described here, some of which were previously known, were synthesised in a highly pure state. This also enabled some study on the influence of purity to be carried out. The compounds I to VI were synthesised with these objectives in mind.

The examination of m-substitution was chosen with the objective of producing more soluble and lower melting monomer systems, properties that reduce certain difficult
aspects in processing of the materials. Examination of literature melting points of o-, m-, and p-substituted isomers of even the bis-maleimidobenzenes, indicates that the incorporation of m-linkages in arylimide chains generally, but not always, reduces the melting or softening points of bis-imides, polyaspartimides, polyimidothioethers, and poly(arylene ether sulphones) as compared with o- and p-isomers. Four ring aromatic systems were chosen as the increased chain length between imide rings (as compared with systems well known at the time) might produce more tractible and perhaps less brittle systems.

The synthesis and investigation of polymerisation and physical properties of the selected materials are described in the following chapters.
Chapter 2

Synthesis
2.1 INTRODUCTION

This chapter describes the syntheses of model compounds and monomers I to VI, and their purification and attempted purification by various means including preparative scale HPLC. Thermal polymerisation tests of monomer samples was carried out. Samples were characterised by nuclear magnetic resonance (NMR), infrared (IR), and mass spectroscopy, and purity was tested by hot stage microscope melting point test, microanalysis, and analytical HPLC. Vapour pressure osmometry was used to determine number average molecular weights of soluble polymer samples.

The following reactions were carried out:
Mechanisms and general synthetic methods for the above reactions are discussed in greater detail in Chapter 1.

Of the above compounds, N-phenylmaleimide, N-phenylnadimide and N-phenylcitraconimide are well known. The bis-maleimides I and II have been previously synthesised, although neither were characterised by microanalysis and no melting point was recorded for I. The two citraconimides III and IV have not been reported. The nadimide V is known although not reported in Chemical Abstracts; the 3,4-isomer VI has not been reported.

The synthesis carried out was aimed at producing pure and well characterised compounds. A number of synthetic methods were adopted in order to determine which gave the purest N-phenylimide model compound. That synthetic method was then used to synthesise the bis-imides of that type. The methods were to be procedures that could be applied to the synthesis of the desired bis-imides, which have different solvent properties than the simple N-phenylimide model compounds.

A number of procedures were adopted in order to attempt to purify the samples synthesised. These included solvent washing, reprecipitation, recrystallisation, preparative high performance liquid chromatography (HPLC), and column methods.

The structures were examined by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. Purity was tested by melting point, microanalysis (elemental analysis), and analytical HPLC.
2.2 RESULTS AND DISCUSSION

2.2.1 N-Phenylmaleimide

A variety of synthetic procedures were used to synthesise this model compound as a development of the best synthetic procedure for the more complex bis-maleimides I and II. The maleimide acid is produced spontaneously on careful mixing of cooled solutions of the appropriate amine and maleic anhydride. If the amic acid is isolated Searle's method \(^{23}\) may be used to cyclodehydrate to the imide. It involves heating the amic acid at 90°C for one hour in acetic anhydride acting as a dehydrating agent in the presence of sodium acetate isomerisation catalyst. This method, which had been used to synthesise N-phenylmaleimide previously \(^{37}\), was found to be satisfactory. However, it could not be utilised for the formation of the bis-maleimides I and II since the intermediate bis-amic acids were not sufficiently soluble in acetic anhydride alone. Also, two recrystallisations were necessary in order to achieve the literature melting point for the N-phenylmaleimide.

Less vigorous conditions were found to be required when dimethylformamide (DMF) was used as a solvent in addition to the acetic anhydride and sodium acetate of Searle's method. The amic acid could be produced by controlled mixing of cooled solutions of aniline and maleic anhydride in DMF. The acetic anhydride and sodium acetate were then added, and heating at temperatures of
70°C over one hour produced a product with the correct melting point after recrystallisation, but with a greenish cast to the more usual canary yellow colour. The same procedure carried out at 55°C over the one hour dehydration period gave the product in reasonable yield (76%) with the correct melting point of 90 to 91°C (ref. 97) before recrystallisation. This was particularly advantageous, since pure products before recrystallisation are desired in this type of system, because more complex bis-maleimides synthesised using this method might not be easy to recrystallise. The results given in table 2.1 are those for this procedure, and this method was used for the synthesis of I and II. This method is that given in the experimental in Chapter 5.

A method based on that of Searle reported for the synthesis of I⁴ using N,N-dimethylacetamide (DMAC) as solvent at room temperature produced the N-phenylmaleimide acid intermediate in a pure state instead of the cyclodehydrated imide.

A method previously used to synthesise maleimides⁹⁸,⁹⁹ was used for the cyclodehydration of the amic acid in DMF using p-toluenesulphonic acid catalyst. Toluene was used to remove water by azeotropic distillation out of the reaction vessel into a trap. The correct product was obtained, but a long reflux time was necessary and only a low (29%) yield obtained.
TABLE 2.1 SUCCESSFUL N-PHENYLMALEIMIDE SYNTHESIS

YIELD - 76%
MP - (90-91)°C. Literature97 - (90-91)°C.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
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<td>4.07</td>
<td>8.09</td>
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<tr>
<td>Found</td>
<td>69.10</td>
<td>3.99</td>
<td>8.12</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.26</td>
<td>-0.08</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Analysts quoted region of uncertainty in any element is ±0.3.

'H NMR - Figure 2.1
Solvent - CDCl₃

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>7.6-7.2</td>
<td>Complex</td>
<td>5</td>
</tr>
<tr>
<td>Maleimide</td>
<td>6.84</td>
<td>Singlet</td>
<td>2</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the upper trace in figure 2.2 with possible band assignments.

The above results indicate the successful synthesis of the model compound in a pure state. To test the polymerisation of the compound a sample was heated under nitrogen (approximately 260°C, 150 minutes.) The polymer was investigated by 'H NMR and infrared spectroscopy, microanalysis, and vapour pressure osmometry to determine number average molecular weight Mn.

TABLE 2.2 POLY(N-PHENYLMALEIMIDE)

SOLUBILITY TEST: Polymer was a glassy material soluble in DMF, DMSO, acetone, and chloroform. In all of these solvents, a very small proportion of the material was insoluble.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>69.36</td>
<td>4.07</td>
<td>8.09</td>
</tr>
<tr>
<td>Found</td>
<td>68.56</td>
<td>4.14</td>
<td>8.08</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.80</td>
<td>0.07</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

VAPOUR PRESSURE OSMOMETRY: Solvent - DMF
Mn = 2510±100

.: DP = 14±1
Figure 2.1: $^1$H NMR run in CDCl$_3$

Figure 2.2: FTIR Spectra
1H NMR - Figure 2.3
Solvent - CDCl₃

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.3-6.3*</td>
<td>Complex</td>
<td>≈5/repeat unit</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>6.84</td>
<td>Singlet</td>
<td>≈1/6/repeat unit*</td>
</tr>
<tr>
<td>Saturated</td>
<td>-</td>
<td>-</td>
<td>≈2/repeat unit*</td>
</tr>
</tbody>
</table>

*Ill defined region of resonance.
*This is an average of <2/polymer molecule. Although this resonance is sharply defined, the relative integral is inaccurate because the peak is not resolved from the aromatic region. The value of the relative integral per monomer fragment (ie versus aromatic) was calculated, and multiplied by the mean degree of polymerisation as obtained from vapour pressure osmometry and recorded below. This gave an average value of two of this proton type per polymer molecule. Because underlying aromatic peak contributes to this integral, it is thus known that the average value is less than two per polymer molecule.
*This is the total integration between 5ppm and 1ppm.

INFRARED SPECTRUM: A comparison of monomer and polymer spectra is shown in figure 2.2. Differences between the two are indicated by arrows.

The microanalysis indicated that some thermal decomposition might have occurred during the thermal polymerisation, since that of the monomer was within the analysts region of uncertainty (±0.3%).

The vapour pressure osmometry result indicated that the material referred to as the polymer, was in fact only a low average molecular weight oligomer. Presumably a side reaction caused some crosslinking to take place resulting in some insoluble material. A sample of the polymer was boiled in acetone, the insoluble material filtered off, the acetone removed and polymer sample dried, and the soluble material used to make up the solutions in DMF for vapour pressure osmometry. A similar result (2070±300) g/mole was obtained if this precaution was not carried out.
Figure 2.3: $^1$H NMR run in CDCl$_3$

Figure 2.4: FTIR Spectra, Monomer and Polymer, N-Phenylmaleimide
The majority of the infrared spectrum of the polymer was similar to that of the monomer, but several changes are to be noted—these are indicated by the arrows on the spectra in figure 2.2. The reduction in bands at 3106 and 3093cm⁻¹ due to =C-H stretch is evident. The appearance of an absorption about 2923cm⁻¹ was due to saturated -C-H stretch. These changes are expected on polymerisation along the double bond.

A band at 1311cm⁻¹ was also reduced.

A broad and very strong absorption about 1188cm⁻¹ appeared on polymerisation. This may have been due to C-N-C of the succinimide-type residue produced during the polymerisation. The C-N-C group of succinimide is known to produce an absorption at 1182cm⁻¹, whereas that of maleimide is at 1137cm⁻¹ (reference 74). The band at 1146cm⁻¹ in the monomer, probably due to the C-N-C of maleimide, was not evident in the spectrum of the polymer. Bands at 1031cm⁻¹ and 950cm⁻¹ had reduced in intensity.

There was a major difference in monomer and polymer spectra at 833cm⁻¹ where the sharp strongly absorbing band in the monomer had virtually disappeared after the polymerisation. This band may have been due to =C-H deformation, and this being the case a reduction would be expected. There is a residual absorption in the polymer at a similar but different position which may be due to residual double bond in the polymer. This weak band was at 828cm⁻¹ as compared with the very strong absorption at 833cm⁻¹ in the monomer. This is shown on an expanded scale in figure 2.4. If any unreacted monomer was present in the
polymer sample, then a shoulder on the weak band at 828 cm$^{-1}$ would be expected. Since none was observed, it is unlikely that this was the case. This is important, because there was a peak due to unsaturated $=\text{C-H}$ in the NMR spectrum of the polymer. This was thus possibly due to a feature of the polymer structure and not unreacted monomer contaminating the polymer.

In addition to the changes already mentioned on polymerisation bands at 735 and 658 cm$^{-1}$ appeared, and a weak band at 586 cm$^{-1}$ was reduced in intensity.

The $^1\text{H NMR}$ spectrum of the poly($N$-phenylmaleimide) sample is shown in figure 2.3. The broadening of the aromatic resonance and the appearance of broad resonances in regions of the spectrum assignable to aliphatic protons is indicative of polymer formation. The sharp peak at 6.84 ppm is at exactly the same chemical shift as that of the double bond in the monomer. However, since there is probably no monomer contaminating the polymer, these may be unsaturated $=\text{C-H}$ protons of a similar type to those found in the monomer but in the polymer structure. In such a system where polymerisation occurs thermally without added initiator residual double bonds are expected. One possible initiation mechanism might be as follows where transfer of a hydrogen atom from one molecule of monomer to another occurs giving two types of free radical, XIII and XIV, capable of initiating (and terminating) the polymerisation.
These fragments would then be found in the polymer chain, and since the polymer was only of low molecular weight, then they would be observable in the spectrum. The resonance at 6.84ppm might be due to the proton on the double bond in fragments of the type XIII at the polymer chain ends. If the proposed mechanism were operative alone in the initiation and termination, then an average of one fragment of type XIII and one fragment of type XIV would be expected per polymer molecule. The expected relative integral of the proton at 6.84ppm would then be one per polymer molecule. The determined integral of less than two is not inconsistent with this but does not confirm the proposed mechanism either. Neither is there evidence to suggest the presence of fragments of type XIV on the chain ends. The triplet centred at 1.23ppm and the doublet about 2.90ppm suggest that the polymerisation is not operative by the proposed mechanism alone. The broad peak approximately between 5ppm and 3ppm constitutes most of the relative integral of the saturated -C-H resonance, and is therefore probably due to the saturated -C-H in the succinimide-type residue XV in the propagated chain as shown below. The integral is approximately correct for this as compared with the aromatic protons.
2.2.2 N-Phenylnadimide

The procedure of Marcus et al.\textsuperscript{100} was used to synthesise a sample of N-phenylnadimide. This involved the mixing of warm benzene solutions of aniline and nadic anhydride, with the immediate precipitation of N-phenylnadimide without any special procedure for the cyclodehydration step which occurred spontaneously on the addition. The product was recrystallised from an acetic acid-water mixture. Although the method was excellent for the synthesis of the N-phenyl compound giving the correct melting point and a reasonable yield (72%), it could not be applied to the longer chain bis-imides due to the insolubility of the reactants in benzene.

The following procedure was found to be successful for the synthesis of N-phenylnadimide and the longer chain bis-nadimides described later. The successful method was one used with less success for the synthesis of maleimides described above for N-phenylmaleimide and adapted from references 98 and 99 involving p-toluenesulphonic acid catalysed cyclodehydration of the nadamic acid with azeotropic removal of water. The nadamic acid is formed by
mixing cooled solutions of nadic anhydride and aniline in DMF. The experimental for this procedure is given in Chapter 5 and the results below in table 2.3.

**TABLE 2.3 SYNTHESIS OF N-PHENYLNADIMIDE**

<table>
<thead>
<tr>
<th>Yield</th>
<th>77%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>(144-145) °C</td>
</tr>
</tbody>
</table>

**Microanalysis:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>75.30</td>
<td>5.48</td>
<td>5.85</td>
</tr>
<tr>
<td>Found</td>
<td>75.16</td>
<td>5.31</td>
<td>5.80</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.14</td>
<td>-0.17</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

**1H NMR - Figure 2.5**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>7.45-7.05</td>
<td>Complex</td>
<td>5</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>6.22</td>
<td>Fine triplet</td>
<td>2</td>
</tr>
<tr>
<td>Bridgehead</td>
<td>3.44*</td>
<td>Fine doublet</td>
<td>2</td>
</tr>
<tr>
<td>Ring Junction</td>
<td>3.37*</td>
<td>Fine doublet</td>
<td>2</td>
</tr>
<tr>
<td>-CH₂- bridge</td>
<td>1.58</td>
<td>Singlet</td>
<td>2</td>
</tr>
</tbody>
</table>

*Alternatively, these two assignments may be reversed.

**Infrared Spectrum:** This is the upper trace in figure 2.6 with possible band assignments.

The product was produced in reasonable yield and purity as indicated by the results. The NMR spectrum indicated formation of the desired product. The melting point was that of the endo-isomer, which is reported at 145°C as opposed to that for the exo-isomer of 198°C.

There were no obvious signs of the presence of the other isomer in the NMR spectrum.

A sample of the N-phenylnadimide was polymerised thermally by heating under a stream of nitrogen. No change was observed in the melt after 120 minutes at 200°C, or after a further 120 minutes at 275°C. However, after a third further heating period over 90 minutes at 300°C the
Figure 2.5: $^1$H NMR run in d$_6$ DMSO

Figure 2.6: FTIR Spectra
melt had thickened to a darkened highly viscous liquid.

This product was tested, and results given below in table 2.4.

**TABLE 2.4 POLY(N-PHENYLNADIMIDE) ANALYSIS**

SOLUBILITY TEST: The polymer was entirely soluble in DMF and DMSO.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated*</td>
<td>75.30</td>
<td>5.48</td>
<td>5.85</td>
</tr>
<tr>
<td>Found</td>
<td>74.31</td>
<td>5.37</td>
<td>5.87</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.99</td>
<td>-0.11</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Calculated value based on that of the monomer. However, real value depends on amount of cyclopentadiene lost from the system - see below.

VAPOUR PRESSURE OSMOMETRY: Solvent - DMF

Mn = 690±25    
DP = 2.9±0.1*

*This DP value has limited value since it is based on a repeat unit based on the monomer structure - see below.

'H NMR: Figure 2.7
Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>≈7.8-6.8</td>
<td>Unresolved</td>
<td>≈5</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>≈3.5-0.5</td>
<td>Unresolved</td>
<td>≈6</td>
</tr>
<tr>
<td>d6 DMSO water</td>
<td>3.37</td>
<td>Singlet</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>2.49</td>
<td>Unresolved</td>
<td></td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the lower trace in figure 2.6 shown compared with that of the monomer. Differences between the two are indicated by arrows.

MASS SPECTRUM: This is shown in figure 2.8

The polymerisation mechanism of nadimides was discussed in Chapter 1. Because cyclopentadiene is lost during polymerisation, the microanalysis of the polymer should not necessarily be equal to that of the monomer because of the change in elemental content of the system. During the thermal polymerisation of N-phenylmaleimide described above in section 2.2.1 some change in elemental
content was observed and presumed due to some decomposition at the elevated temperatures. These two factors are thus likely to cause the change in the elemental analysis. If it is assumed that the change in microanalysis is entirely caused by the loss of cyclopentadiene, then the loss may be calculated.

MASS OF CARBON IN ONE MOLE OF N-PHENYLNADIMIDE - 180g.
MASS OF CARBON IN ONE MOLE OF CYCLOPENTADIENE - 60g.
MOLECULAR WEIGHT OF N-PHENYLNADIMIDE = 239g/mole.
MOLECULAR WEIGHT OF CYCLOPENTADIENE = 66 g/mole.

Therefore the obtained percentage carbon is given by the following equation;

\[ \%C = \frac{(180-60n)}{(239-66n)} \times 100 \]

Eqn 2.1

where \( n \) is the average number of cyclopentadiene molecules lost from the solid material by volatilisation per N-phenylnadinamide molecule present at the start of the reaction. Using this equation and the microanalysis result \( n \) is calculated as 0.22. The calculation is of limited value because of the possibility of change caused by degradation of the material.

The number average molecular weight of the polymer sufficed to show that the material was a low molecular weight oligomer. This is in agreement with previous findings for thermally polymerised N-phenylnadinamide.**

The proton NMR spectrum in figure 2.7 shows resonances due to residual or exchanged protons in the \( d^6 \) DMSO solvent, and the associated water. The relative integrals of five aromatic protons to approximately six other types of proton is consistent with loss of
Figure 2.7: $^1$H NMR run in d$_6$ DMSO

Figure 2.8: Mass Spectrum
cyclopentadiene from the system, since the ratio would be five aromatic to eight of other types for a straight polymer of the nadimide propagated via the nadimide double bond. There is a very small remaining resonance at 6.22ppm - exactly the same chemical shift as that of the double bond in nadimide - and a very small new peak near to this at 6.35ppm. The latter might be due to the corresponding double bond in the double Diels-Alder adduct or perhaps the exo isomer. The peaks are too broad and unresolved to obtain any definite polymer structural information. The broadening is indicative of polymerisation.

The infrared spectrum of the polymer is shown in figure 2.6 as the lower trace. Changes observed on polymerisation included the loss or possibly change of position of a band at 2993cm⁻¹ on polymerisation possibly due to saturated C-H. Other reductions at 1290, 957, 843, 723, and 652cm⁻¹ are observed. The reduction in the band at 843cm⁻¹ might be due to loss of unsaturated =C-H, the band being due to =C-H deformation.

The mass spectrum of the polymer is shown in figure 2.8. The mass of maleimide added to that of cyclopentadiene is the same as that of nadimide, the Diels-Alder adduct of the two. The fragment of mass 305 corresponds to nadimide and cyclopentadiene (or maleimide and two cyclopentadiene units). The fragment of mass 371 corresponds to the mass of the nadimide and two cyclopentadiene units (or maleimide and three cyclopentadiene units). The detection of these fragments strongly indicates that part of the cyclopentadiene
produced by retro Diels-Alder decomposition of nadimide is incorporated into the solid polymer as opposed to the total quantity volatilising from the system. However, the spectrum gives no information on the structure formed by the incorporated cyclopentadiene, which may be as a discreet monomer residue (1,4-polymerised into the chain), or added to nadimide double bond to form the double Diels-Alder adduct as described in Chapter 1. The fragment at 66 corresponds to the mass of (mono)cyclopentadiene, that at 173 of N-phenylmaleimide, that at 239 of N-phenylnadimide, and that at 479 of dimer of N-phenylnadimide or corresponding combinations of the maleimide, cyclopentadiene, and nadimide.

2.2.3 N-Phenylcitraconimide

The procedure used successfully to obtain N-phenylnadimide from aniline and nadic anhydride described above was used for the synthesis.

TABLE 2.5 SYNTHESIS OF N-PHENYL CITRACONIMIDE

<table>
<thead>
<tr>
<th>YIELD</th>
<th>65%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>(95-96)°C</td>
</tr>
<tr>
<td>Literature</td>
<td>98°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MICROANALYSIS:</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>70.58</td>
<td>4.58</td>
<td>7.48</td>
</tr>
<tr>
<td>Found</td>
<td>70.37</td>
<td>4.72</td>
<td>7.59</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.21</td>
<td>0.14</td>
<td>0.11</td>
</tr>
</tbody>
</table>

'\text{H} NMR - Figure 2.9
Solvent - d₆ DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>7.7-7.2</td>
<td>Complex</td>
<td>5</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>6.79</td>
<td>Quadruplet</td>
<td>1</td>
</tr>
<tr>
<td>Methyl</td>
<td>2.07</td>
<td>Doublet</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 2.9: $^1$H NMR run in $d^6$ DMSO

Figure 2.10: FTIR Spectrum
The results indicate the correct compound was obtained as expected.

The thermal polymerisation of the compound was attempted. A sample was heated under a stream of nitrogen over 90 minutes at between 210 and 220°C. After this time nearly all the compound had been lost due to volatilisation, and there was no sign of increase in viscosity in the melt. A different sample heated at 300°C quickly volatilised causing nitrogen-tube blockage. Under the same conditions, N-phenylmaleimide (whilst showing signs of volatilisation) quickly became a highly viscous melt. Under the conditions used the melt evaporated more quickly than the monomer propagated. The compound thus either required more vigorous conditions to polymerise it than the corresponding maleimide or does not polymerise. However, since other citraconimides have been shown to polymerise\(^\text{8,21}\) it is probably the former case. The lower reactivity of the citraconimide compared with the maleimide is consistent with that expected of the structure as explained in Chapter 1.

\subsection*{2.2.4 Bis-4-Maleimidophenylmethane}

The crude 95\% commercially available product melting at (156-158)°C was purified by passing a solution in dichloromethane through a neutral alumina column followed
by recrystallisation from methyl ethyl ketone (MEK). The dull mustard-yellow powder starting product yielded a bright yellow crystalline material. The product was tested for purity by microanalysis, melting point and by analytical HPLC.

![HPLC Trace](image)

**Figure 2.11: HPLC Trace**

**TABLE 2.6 PURIFICATION OF BIS-4-MALEIMIDOPHENYLMETHANE**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Literature</th>
<th>160°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>YIELD</td>
<td>43%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP</td>
<td>(159-160)°C</td>
<td>160°C</td>
<td></td>
</tr>
</tbody>
</table>

**MICROANALYSIS:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>70.39</td>
<td>3.94</td>
<td>7.82</td>
</tr>
<tr>
<td>Found</td>
<td>70.21</td>
<td>3.92</td>
<td>7.88</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.18</td>
<td>-0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.11

PURITY = >100%
The removal of dark colour, rise in melting point, correct microanalysis and HPLC analysis are all indicative of the successful purification of the bis-maleimide. The other peak in the HPLC trace was confirmed as a solvent peak by varying the concentration of the solution - the most dilute produced the largest solvent peak, the most concentrated produced the smallest. The smaller peak was present in solvent alone.

2.2.5 Bis-4-((4-Maleimidophenoxy)phenyl Sulphone (I)

**Synthesis of Crude Material**

Two moles of maleic anhydride were reacted with one mole of the diamine precursor under similar conditions to those developed for the synthesis of N-phenylmaleimide as described in section 2.2.1. The results for the beige-coloured material as obtained by work up without any purification are given in table 2.7. The result clearly indicates an impure sample. The infrared and proton NMR spectra for this material were similar to those recorded later for the pure material.

Any attempt to recrystallise this material from acetone, chloroform, dichloromethane, p-dioxane and various solvent mixtures resulted in a beige tarry material. The material was insoluble in methanol and ethanol, benzene and toluene, but was readily soluble in DMF, DMAC, DMSO, and p-dioxane. It was soluble in hot acetone, dichloromethane and chloroform but only sparingly
so in the cold solvents.

**TABLE 2.7 CRUDE BIS-MALEIMIDE I**

<table>
<thead>
<tr>
<th>YIELD</th>
<th>93%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>no sharp transition was observed up to 330°C, but heating in a capillary produced a brown glassy material.</td>
</tr>
</tbody>
</table>

**MICROANALYSIS:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td>Found</td>
<td>63.99</td>
<td>3.34</td>
<td>4.72</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.87</td>
<td>-0.06</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

**Bis-Maleimide I - Intermediate Material**

A number of solvent washing procedures were tried, but only one method was successful in producing a material with the correct microanalysis within experimental error. This is recorded in Chapter 5 and was based on washing the material with cold acetone. Although the spectra of this intermediate material were similar to those recorded for the crude material the microanalysis was now correct within experimental error. This is recorded in table 2.8. This material was then tested by analytical HPLC which showed that **despite the correct microanalysis the material was only 96.5% pure** as measured by this technique. This indicates that the main impurities had similar elemental constitution as that of the bis-maleimide. For this reason the synthesis of samples with correct microanalysis results alone was not considered satisfactory, and samples of greater than 99% purity as measured by analytical HPLC were desired. **This material was that used in DSC analysis**
of impure material described in Chapter 3 and referred to as 96.5% pure material.

**TABLE 2.8 INTERMEDIATE BIS-MALEIMIDE SAMPLE**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculated</strong></td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td><strong>Found</strong></td>
<td>64.61</td>
<td>3.28</td>
<td>4.67</td>
</tr>
<tr>
<td><strong>Difference</strong></td>
<td>-0.25</td>
<td>-0.12</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

**MP** - no sharp transition was observed up to 330°C, but heating in a capillary produced a brown glassy material.

**HPLC** - Figure 2.12

**PURITY** - 96.5%

**Bis-Maleimide I - Pure Material**

The pure material was obtained by carrying out preparative scale HPLC on the material of intermediate purity as described above. The preparative scale HPLC method is described in Chapter 5. The final bright yellow crystalline solid (needles) was analysed and the results are presented in table 2.9.

The change from an unrecrystallisable dull mustard-yellow powder to sharply-melting bright yellow needle-shaped crystals suggested an increase in purity. The sample had the correct microanalysis (showing no inorganic contaminant within limits of technique), whilst the HPLC trace shows 99.9% one compound. The spectra were consistent with the desired structure (I).
TABLE 2.9 PURE BIS-MALEIMIDE I FROM PREPARATIVE HPLC

YIELD - 66% of the 96.5% pure sample passed through column.
MP - 220°C

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td>Found</td>
<td>64.59</td>
<td>3.25</td>
<td>4.67</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.27</td>
<td>-0.15</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.13
PURITY - 99.9%

'H NMR - Figure 2.14
Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.3-6.9</td>
<td>Complex</td>
<td>-</td>
</tr>
<tr>
<td>Maleimide</td>
<td>7.20</td>
<td>Singlet</td>
<td>-</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the upper trace in figure 2.15, possible assignments are given.

The 'H NMR spectrum showed an aromatic region, in which it is believed the maleimide =C-H protons also resonated at 7.20ppm. The resonance either side of 8ppm have the form of half of an A-B quartet of a p-disubstituted benzene ring and is probably due to the four protons closest to the sulphone group. This double peak integrates at approximately 4 protons to the remainder in the aromatic region of 16 consistent with this assignment.

The infrared spectrum is consistent with the desired structure.

A sample of the pure bis-maleimide I was heated in a stream of nitrogen at 230°C for 10 minutes, to test whether crosslinking had occurred. The resulting solid was tested for solubility and a microanalysis carried out. Results are given in table 2.10.
Figure 2.12: HPLC Trace, Intermediate Purity Material

Figure 2.13: HPLC Trace, Pure Material from Preparative HPLC
Figure 2.14: $^1$H NMR run in $d^6$ DMSO

Figure 2.15: FTIR Spectra

POLYMER
TABLE 2.10 THERMALLY CROSSLINKED BIS-MALEIMIDE I

SOLUBLITY TEST: Sample was insoluble in boiling DMF.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td>Found</td>
<td>64.70</td>
<td>3.23</td>
<td>4.53</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.16</td>
<td>-0.17</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the lower trace in figure 2.15. Differences between monomer and polymer spectra are indicated with arrows.

The milder conditions required to produce an insoluble material were reflected in the correct microanalysis, presumably because no decomposition occurred during the thermally induced crosslinking as it did for the N-phenyl compound. Almost no difference was observed between the infrared spectra of the crosslinked material and the monomer. A slight absorption at 2922 cm\(^{-1}\) appeared due to saturated -C-H.

2.2.6 Bis-4-(3-Aminophenoxy)phenyl Sulphone

The crude material was synthesised in a DMSO-toluene mixture by nucleophilic substitution of chloride by m-aminophenoxy ions under nitrogen. The substitution is activated by the electron-withdrawing sulphone group. The crude product was found to be unrecrystallisable - a brown tarry material precipitated on cooling hot saturated solutions in ethanol under nitrogen. A procedure for purifying the crude material was developed based on a known method for this compound\(^1\). The purification was performed in batches as follows. The crude diamine was
dissolved in dilute hydrochloric acid forming an aqueous solution of the dihydrochloride. The aqueous solution was boiled with activated charcoal whilst steam was passed through in order to distill out any impurities. After this operation the material was then recrystallisable under nitrogen. Part of the material settled out as tar, part as crystals which were easily separated off. The recrystallisation method was repeated on the tar until no further crystals were obtained.

At all stages where the method involved hot solutions the procedure was carried out under nitrogen. The entry of oxygen caused immediate darkening of the diamine solution resulting in an intractable tar. Special care was required during the nucleophilic substitution since aminophenoxide salts are highly oxygen sensitive. Excess phenol was used in order to help counteract this oxidation. Excess phenol to the amount of alkali added is required since it is possible to remove protons from the amine group of the aminophenoxide. This enables nucleophilic attack by the reactive nitrogen centre to occur resulting in the formation of a secondary amine linkage in the chain in place of the desired ether.

Results are given in table 2.11 and detailed experimental in Chapter 5.

The crystalline material was obtained as platelets. The results indicate the correct material was obtained in a reasonably pure state. The yield was poor principally due to the large amount obtained as tar from which no further crystals could be produced.
Figure 2.16: $^1$H NMR run in $d^6$ DMSO

Figure 2.17: FTIR Spectrum
TABLE 2.11 BIS-4-(3-AMINOPHENOXY)PHENYL SULPHONE

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
<th>MP</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42%</td>
<td>(134-135)°C</td>
<td>(132-134)°C</td>
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MICROANALYSIS:

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<th>%H</th>
<th>%N</th>
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<td>Calculated</td>
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<td>4.66</td>
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<td>Found</td>
<td>66.79</td>
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<td>6.62</td>
</tr>
<tr>
<td>Difference</td>
<td>0.14</td>
<td>-0.08</td>
<td>0.14</td>
</tr>
</tbody>
</table>

'\text{H} NMR - Figure 2.16

Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.3-6.0</td>
<td>Complex</td>
<td>16</td>
</tr>
<tr>
<td>Amine</td>
<td>5.3</td>
<td>Broad Singlet</td>
<td>4</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is shown in figure 2.17 with possible assignments.

2.2.7 Bis-4-(3-Maleimidophenoxy)phenyl Sulphone

This bis-maleimide was synthesised in the same manner as I but from the diamine described above. No method for recrystallisation could be found for the crude product which was not purified by a variety of reprecipitation or solvent washing procedures. The material was purified by preparative scale HPLC. Results are given in tables 2.12 and 2.13.

The product was impure before preparative HPLC as indicated by microanalysis. However, the results given in table 2.13 indicate that the method was successful in purifying the compound. The melting points of impure and pure materials were similar as were the infrared and '\text{H} NMR spectra.
TABLE 2.12 SYNTHESIS OF THE CRUDE BIS-MALEIMIDE II

<table>
<thead>
<tr>
<th>Yield</th>
<th>41%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>(90-100)°C</td>
</tr>
<tr>
<td>Literature</td>
<td>(90-100)°C</td>
</tr>
</tbody>
</table>

**MICROANALYSIS:**

<table>
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<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td>Found</td>
<td>64.09</td>
<td>3.31</td>
<td>4.51</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.77</td>
<td>-0.09</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.18
PURITY - 74.6%

---

TABLE 2.13 PURE BIS-MALEIMIDE II FROM PREPARATIVE HPLC

<table>
<thead>
<tr>
<th>Yield</th>
<th>53% of crude material purified</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>(93-100)°C</td>
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</tbody>
</table>

**MICROANALYSIS:**

<table>
<thead>
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<th>%C</th>
<th>%H</th>
<th>%N</th>
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</tr>
<tr>
<td>Difference</td>
<td>-0.18</td>
<td>0.01</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.19
PURITY - 99.8%

'H NMR - Figure 2.20
Solvent - d⁶ DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.2-6.9</td>
<td>Complex</td>
<td></td>
</tr>
<tr>
<td>Maleimide</td>
<td>7.18</td>
<td>Singlet</td>
<td></td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the upper trace in figure 2.21, where possible assignments are given.

The peak at 7.18ppm in the proton NMR spectrum has been assigned as due to maleimide protons. A similar tall peak was observed in the spectrum of I (the isomer of II) at 7.20ppm. Additionally peaks at 3.32ppm (water from DMSO) and 2.50ppm (residual or exchanged protons in incompletely deuterated DMSO) were observed.

A sample of the pure bis-maleimide was heated under a stream of nitrogen at approximately 230°C for ten minutes. The resulting material was tested for solubility and
Figure 2.18: HPLC Trace

Figure 2.19: HPLC Trace
Figure 2.20: $^1$H NMR run in $d^6$ DMSO

Figure 2.21: FTIR Spectra
microanalysis and infrared spectra run, the results of which are given in table 2.20

TABLE 2.20 THERMALLY CROSSLINKED BIS-MALEIMIDE II

SOLUBILITY: The material was insoluble in boiling DMF.

**MICROANALYSIS:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>64.86</td>
<td>3.40</td>
<td>4.73</td>
</tr>
<tr>
<td>Found</td>
<td>64.93</td>
<td>3.49</td>
<td>4.53</td>
</tr>
<tr>
<td>Difference</td>
<td>0.07</td>
<td>0.09</td>
<td>-0.20</td>
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</tbody>
</table>

**INFRARED SPECTRUM:** This is the lower trace in figure 2.21. Differences between monomer and polymer spectra are noted with arrows.

The material was crosslinked using only mild conditions, and consistent with this the microanalysis was correct within experimental error indicating that little decomposition had occurred. The infrared spectrum of the crosslinked material was very similar to that of the monomer. On polymerisation a very weak absorption at 2925 cm⁻¹ was noted consistent with the appearance of saturated -C-H on polymerisation.

2.2.8 Bis-4-((4-Citraconimidophenoxy)phenyl Sulphone (III)

This compound was synthesised in a similar manner to that of N-phenylcitraconimide by use of p-toluenesulphonic acid catalyst and azeotropic removal of water with toluene into a trap. The results for the crude bis-citraconimide are shown in table 2.21. These results show that purification of the citraconimide was required. No successful recrystallisation procedure was found for the
material. No reprecipitation or solvent washing procedure could be found that successfully purified the crude material. The purification using preparative HPLC was successful.

**TABLE 2.21 SYNTHESIS OF THE CRUDE BIS-CITRACONIMIDE III**

<table>
<thead>
<tr>
<th>YIELD</th>
<th>70%</th>
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<tbody>
<tr>
<td><strong>MP</strong></td>
<td>(151-155)°C</td>
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</table>

**MICROANALYSIS:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
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<tr>
<td>Found</td>
<td>64.75</td>
<td>4.01</td>
<td>4.70</td>
</tr>
<tr>
<td>Difference</td>
<td>-1.05</td>
<td>0.11</td>
<td>0.19</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.22

**PURITY** - 76.9%

Two main peaks were observed in the preparative HPLC trace - one very large peak followed by a smaller peak. Both of these compounds were collected and analysed. The results for the main peak which was the desired compound are given in table 2.22, those for the main side product in table 2.24 later.

**TABLE 2.22 PURE BIS-CITRACONIMIDE III**

<table>
<thead>
<tr>
<th>YIELD</th>
<th>56% of crude fed into column.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MP</strong></td>
<td>(190-193)°C</td>
</tr>
</tbody>
</table>

**MICROANALYSIS:**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
</tr>
<tr>
<td>Found</td>
<td>65.59</td>
<td>3.97</td>
<td>4.22</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.21</td>
<td>0.07</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

'H NMR - Figure 2.24

<table>
<thead>
<tr>
<th>Solvent - d6 DMSO</th>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aromatic</td>
<td>8.2-7.1</td>
<td>Complex*</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Unsaturated</td>
<td>6.81</td>
<td>Fine quadruplet</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Methyl</td>
<td>2.08</td>
<td>Doublet</td>
<td>6</td>
</tr>
</tbody>
</table>
Two A-B quartets are visible due to the protons of the two different types of p-disubstituted aromatic ring in the compound. The peaks at 8.01ppm, 7.92ppm, 7.22ppm and 7.13ppm form one A-B quartet due to the protons of the benzene rings between the sulphone and ether linkages. Those at 7.48ppm, 7.38ppm, 7.28ppm, and 7.19ppm are due to the protons of the benzene rings between the imide rings and ether linkages.

INFRARED SPECTRUM: This is the upper trace in figure 2.25

HPLC - Figure 2.23
PURITY - 99.8%

The infrared and NMR spectra and microanalysis were consistent with the desired product. The product was yellow-white as opposed to the brown colour of the crude material. The melting point was considerably higher than that of the crude material. The large amount of impurity in the synthesised material had successfully been removed as indicated by analytical HPLC on the final product. Despite 23.1% impurity in the crude material as estimated by analytical HPLC, the microanalysis of the crude material was incorrect by only 1.05% in 65.80% (ie 1.60%). This suggested that the major impurity was an isomer of the desired compound, ie had the same elemental constitution. This was the case as is shown below.

A sample of the pure bis-citraconimide III was heated under a stream of nitrogen at 335°C for 240 minutes and the yellow brown glass tested for DMF solubility, and an infrared spectrum and microanalysis carried out. The results obtained are listed in table 2.23 Samples heated at 270°C for 120 minutes and 300°C for 120 minutes were completely soluble indicating that crosslinking was not complete.
Figure 2.22: HPLC Trace

Figure 2.23: HPLC Trace
Figure 2.24: \(^1\)H NMR run in \(d^6\) DMSO

Figure 2.25: FTIR Spectra
TABLE 2.23 THERMALLY CROSSLINKED BIS-CITRACONIMIDE III

SOLUBILITY: The material was insoluble in a large excess of boiling DMF although a little pink colour strained into the solvent.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
</tr>
<tr>
<td>Found</td>
<td>64.36</td>
<td>3.81</td>
<td>4.33</td>
</tr>
<tr>
<td>Difference</td>
<td>-1.44</td>
<td>-0.09</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the lower trace in figure 2.25, differences between this and the upper trace (monomer spectrum) are indicated with arrows.

The material heated at the highest temperature was sufficiently crosslinked to be insoluble. Rigorous conditions were required to obtain it. This is consistent with that expected in view of the failure of N-phenylcitraconimide to polymerise thermally as described in section 2.2.3. The greater reluctance of citraconimides as compared with maleimides to thermally polymerise is expected as explained in Chapter 1. Results of DSC studies in Chapter 3 show clearly that this is the case.

The rigorous conditions used are reflected in the deterioration in the microanalysis, that of the pure monomer being correct within experimental error (±0.3%).

Comparison of the infrared spectrum with the monomer and polymer show reduction in a band at 3088cm⁻¹ due to saturated =C-H, and appearance of additional absorption at 2974, 2930, and 2874cm⁻¹ due to saturated -C-H. Bands at 1195 and 685cm⁻¹ also appeared on polymerisation. The band at 1195cm⁻¹ might be due to the C-N-C absorption in the saturated methyl-succinimide type residues in the polymer since the C-N-C infrared absorption band of succinimide is
2.2.9 Citraconimide-Itaconimide Mixed Bis-imide

The analysis results of the main impurity separated in the preparative HPLC purification of the bis-citraconimide III described above are given in table 2.24. It was identified as the mixed citraconimide-itaconimide isomer of the desired compound with the following structure:

![Chemical Structure Image]

**TABLE 2.24 MAIN IMPURITY (XVI) IN THE SYNTHESIS OF III**

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
</tr>
<tr>
<td>Found</td>
<td>65.34</td>
<td>4.22</td>
<td>4.22</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.46</td>
<td>0.32</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

**HPLC - Figure 2.26**

**PURITY - 99.1%**

'H NMR - Figure 2.27, please see above for H atom labels.

Solvent - CDCl₃

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.2-8.8</td>
<td>Complex</td>
<td>16</td>
</tr>
<tr>
<td>Hv + Ha</td>
<td>6.50</td>
<td>Triplet+shoulder</td>
<td>2</td>
</tr>
<tr>
<td>Hb</td>
<td>5.77</td>
<td>Triplet</td>
<td>1</td>
</tr>
<tr>
<td>Hc</td>
<td>3.52</td>
<td>Triplet</td>
<td>2</td>
</tr>
<tr>
<td>Hm</td>
<td>2.18</td>
<td>Doublet</td>
<td>3</td>
</tr>
</tbody>
</table>

**INFRARED SPECTRUM: This is shown in figure 2.28. The spectrum is compared with that of III in the C-H stretch region of the spectrum in figure 2.29.**
Figure 2.26: Main Impurity from III, HPLC Trace

Figure 2.27: $^1$H NMR of Main Impurity from Crude III
Figure 2.28: FTIR Spectrum of Isomeric Impurity from Crude III

Figure 2.29: FTIR Spectrum, =C-H Region, III and Isomer
The yield of 24% is consistent with the HPLC estimate of this compound constituting 23% of the total material. This compound (XVI, MP-202 to 210°C) and III (MP-190 to 193°C) probably formed a eutectic mixture to give the crude compound melting point of 155°C along with any other impurities.

The microanalysis and NMR are consistent with the proposed structure, although both indicate slight impurity. Slight bumps in the NMR baseline are observed between 1.5 and 2ppm. The microanalysis is slightly outside experimental error (±0.3%) in both carbon and hydrogen. However, the analytical HPLC indicates a reasonably pure compound.

The infrared spectrum was consistent with the proposed structure. It was very similar to that of III as expected, but the main differences between the two were observed in the C-H region as expected, this is shown in figure 2.29.

To confirm the structure of the main impurity $^{13}$C NMR was also run on both the bis-citraconimide III and the citraconimide-itaconimide isomeric impurity XVI. It should be possible to pick out the pattern of lines of the spectrum of III in that of XVI since the latter contains the chain structure of III on one side of the sulphone group only. In fact this is the case as may be seen comparing the $^{13}$C NMR spectra in figures 2.30 (III) and 2.31 (XVI). The apparent doubling of aromatic carbon lines is due to the similarity of the environments of aromatic carbon atoms either side of the sulphone group in...
Figure 2.30: $^{13}$C NMR Spectrum run in CDCl$_3$

Figure 2.31: $^{13}$C NMR Spectrum run in CDCl$_3$
the citraconimide-itaconimide.

Hartford et al. in attempting to synthesise the bis-itaconimides of p-diaminodiphenyl sulphone by refluxing in acetic anhydride in the presence of sodium acetate produced mixtures of the bis-citraconimide and the itaconimide-citraconimide mixed bis-imide. Similarly Galanti and Scola have observed the production of bis-citraconamic acids when trying to synthesise bis-itaconamic acids. With the work presented here this suggests that there is an equilibrium between citraconimide and itaconimide in these syntheses, and that the equilibrium lies in favour of citraconimide. The likely route of isomerisation is that suggested for citraconic anhydride in Chapter 1 and shown below for the imides:
2.2.10 Bis-Citraconimide IV

The m-isomer of the citraconimide described above was synthesised in a similar manner. A method of obtaining product with correct microanalysis was determined, but the HPLC trace showed high levels of impurity despite this - this impurity was probably the citraconimide-itaconimide isomer of IV. The product was then purified by preparative HPLC. Results of analysis of the crude material are given in table 2.25 below.

**TABLE 2.25 SYNTHESIS OF CRUDE BIS-CITRACONIMIDE IV**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>YIELD</td>
<td>11%</td>
<td></td>
</tr>
<tr>
<td>MP</td>
<td>(104-108)°C</td>
<td></td>
</tr>
<tr>
<td>MICROANALYSIS:</td>
<td>%C</td>
<td>%H</td>
</tr>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
</tr>
<tr>
<td>Found</td>
<td>65.51</td>
<td>3.72</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.29</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.32
PURITY - 81.0%

The low yield was due to the work up procedure which involved precipitation in large amounts of solvent. This was used because it initially removed any impurities which altered the microanalysis.

The results for the purified material are shown below in table 2.26. The significance of the particularly low melting point is discussed in Chapter 3 where polymerisation temperatures are determined.
Figure 2.32: HPLC Trace

Figure 2.33: HPLC Trace
TABLE 2.26 PURE BIS-CITRACONIMIDE IV

YIELD - 43% of crude material loaded onto column.
MP - (79-85)°C

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
</tr>
<tr>
<td>Found</td>
<td>65.73</td>
<td>3.90</td>
<td>4.49</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.07</td>
<td>0</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.33
PURITY - 99.8%

'H NMR - Figure 2.34
Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.3-7.0</td>
<td>Complex</td>
<td>16</td>
</tr>
<tr>
<td>=C-H</td>
<td>6.80</td>
<td>Doublet</td>
<td>2</td>
</tr>
<tr>
<td>Methyl</td>
<td>2.07</td>
<td>Singlet</td>
<td>6</td>
</tr>
</tbody>
</table>

Resonance at 2.51ppm due to DMSO and 3.35ppm water associated with DMSO.

INFRARED SPECTRUM: This is the upper trace in figure 2.35.

The HPLC, microanalysis, NMR and IR spectra show that the desired compound was isolated in a pure state.

A sample of the monomer was heated at 350°C for 120 minutes under nitrogen to determine whether an insoluble material would be produced. The resulting brown glassy material was tested for solubility in boiling DMF, and an infrared spectrum and a microanalysis run. Results are given in table 2.27.

TABLE 2.27 THERMALLY CROSSLINKED BIS-CITRACONIMIDE IV

SOLUBILITY: Polymer was insoluble in boiling DMF.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>65.80</td>
<td>3.90</td>
<td>4.51</td>
</tr>
<tr>
<td>Found</td>
<td>65.05</td>
<td>3.82</td>
<td>4.09</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.75</td>
<td>-0.08</td>
<td>-0.42</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the lower trace in figure 2.35. Differences between monomer and polymer spectra are noted.
Figure 2.34: $^1$H NMR run in d$^6$ DMSO

Figure 2.35: FTIR Spectra
The material was insoluble indicating crosslinking had taken place. The microanalysis showed that decomposition had occurred because of the rigorous conditions required to polymerise the compound.

The infrared spectrum is shown in figure 2.35 below that of the monomer. Differences between the two are indicated by arrows. Differences noted are the reduction of a band at 847 cm\(^{-1}\) on polymerisation. This band might have been due to \(-\text{C}-\text{H}\) deformation. There is a reduction in the absorption of a band at 3094 cm\(^{-1}\) due to \(-\text{C}-\text{H}\) stretch, and the appearance of additional absorption at 2970, 2933, and 2875 cm\(^{-1}\). These changes in the spectrum are expected and are consistent with polymerisation of the citraconimide along the double bond.

2.2.11 Bis-4-(4-Nadimidophenoxy)phenyl Sulphone (V)

This was synthesised in a manner similar to that used for N-phenyl nadimide by reacting two moles of nadic anhydride - the endo isomer of Diels-Alder addition product of cyclopentadiene and maleic anhydride - with the diamine precursor. The cyclodehydration was catalysed by p-toluenesulphonic acid, the water was removed into a trap with toluene as a toluene-water azeotrope. No purification was performed on the product. Results for the material as obtained from the reaction after drying are given in table 2.28. The product was a coffee-coloured powder.
TABLE 2.28 SYNTHESIS OF BIS-NADIMIDE V

YIELD - 98%
MP - (210-214)°C Literature96 - (210-225)°C

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>69.60</td>
<td>4.45</td>
<td>3.86</td>
</tr>
<tr>
<td>Found</td>
<td>69.85</td>
<td>4.75</td>
<td>3.85</td>
</tr>
<tr>
<td>Difference</td>
<td>0.25</td>
<td>0.30</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.36
PURITY - 99.0%

'1H NMR - Figure 2.37
Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.1-6.9</td>
<td>A-B quartet</td>
<td>16</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>6.22</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>Bridgehead</td>
<td>3.48</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>Ring Junction</td>
<td>3.32</td>
<td>Singlet</td>
<td>-</td>
</tr>
<tr>
<td>Bridge</td>
<td>1.60</td>
<td>Singlet</td>
<td>4</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the upper trace in figure 2.38.

The results show that the compound was that desired and pure as synthesised.

The integral for ring junction protons is not certain because protons of water associated with the DMSO solvent resonate at this chemical shift.

A sample was tested for thermal polymerisation by heating under a stream of nitrogen at approximately 330°C over a 165 minute period. The sample was tested for solubility and by infrared spectroscopy and microanalysis. Results are given in table 2.29.

TABLE 2.29 THERMALLY CROSSLINKED BIS-NADIMIDE V

SOLUBILITY: The sample was insoluble in boiling DMF.

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated (monomer)</td>
<td>69.60</td>
<td>4.45</td>
<td>3.86</td>
</tr>
<tr>
<td>Found (polymer)</td>
<td>65.53</td>
<td>4.06</td>
<td>3.85</td>
</tr>
<tr>
<td>Difference</td>
<td>-4.07</td>
<td>-0.39</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
INFRARED SPECTRUM: This is the lower trace in figure 2.38, differences from the monomer spectrum (the upper trace in the figure) observed are indicated by arrows.

Figure 2.36: HPLC Trace
Figure 2.37: $^1$H NMR run in $d^6$ DMSO

Figure 2.38: FTIR Spectra
The insoluble polymer was a brown glass. The microanalysis was very different from that of the monomer due to retro Diels-Alder decomposition with subsequent loss of cyclopentadiene as explained in section 2.2.2 for N-phenynnadimide.

The main differences observed between monomer and polymer spectra were in the saturated C-H stretch region. The band at 2994cm⁻¹ in the monomer was reduced or removed in the polymer. The bands at 2941cm⁻¹ and 2870cm⁻¹ were apparently shifted to higher frequencies to 2954cm⁻¹ and 2890cm⁻¹ respectively. All of these bands were due to saturated C-H stretching. These were similar to the changes noted on thermal polymerisation of N-phenynnadimide. Changes are expected in this region not only due to the creation of saturated C-H from polymerisation along double bonds, but also due to the other complex mix of reactions that are believed to occur in this type of system as described in Chapter 1 including Diels-Alder addition of cyclopentadiene to the existing nadimide to give double Diels-Alder adduct, endo-exo isomerisation of nadimide, and possibly the incorporation of cyclopentadiene as a discreet monomer unit 1,4-polymerised into the network.

This bis-nadimide was insoluble in acetone, chloroform, methanol, ethanol, toluene, cyclohexane, diethyl ether, and only slightly soluble in DMF and DMSO.
2,2,12 Bis-4-((3-Nimidophenoxy)phenyl Sulphone (VI)

This was synthesised in the same manner as its all 4-
substituted isomer V described above. Results are given in
table 2.30.

![Chemical Structure]

6.77 min.
97.2%

4.69 min.
1.4%

5.27 min.
1.4%

Figure 2.39: HPLC Trace
YIELD - 42%

MP - (210-215)°C

MICROANALYSIS:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>69.60</td>
<td>4.45</td>
<td>3.86</td>
</tr>
<tr>
<td>Found</td>
<td>69.49</td>
<td>4.38</td>
<td>3.74</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.11</td>
<td>-0.07</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

HPLC - Figure 2.39

PURITY - 97.2%

'H NMR - Figure 2.40

Solvent - d6 DMSO

<table>
<thead>
<tr>
<th>Assignment</th>
<th>δ / ppm</th>
<th>Multiplicity</th>
<th>Relative Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>8.2-6.8</td>
<td>Complex</td>
<td>16</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>6.20</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>Bridgehead</td>
<td>3.45</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>Ring Junction</td>
<td>3.33</td>
<td>Singlet</td>
<td>-</td>
</tr>
<tr>
<td>Bridge</td>
<td>1.59</td>
<td>Singlet</td>
<td>4</td>
</tr>
</tbody>
</table>

INFRARED SPECTRUM: This is the upper trace in figure 2.41.

Yield was low due to the number of recrystallisations required to obtain material with correct microanalysis.

The melting point was found to be similar to that of the p-isomer. This is in contrast to the m-isomers of the maleimides and citraconimides which have much lower melting points than the corresponding all 4-substituted isomers.

The purity was not high as indicated by HPLC. However, it was considered that the purity was acceptable enough for this particular compound as no polymerisation kinetic parameters were derived for the nadimide materials. DSC and TGA were run on this material as described in Chapter 3.

Since the melting point of the material was the same as that of the p-isomer it is important to determine that
Figure 2.40: $^1$H NMR run in d$_6$ DMSO

Figure 2.41: FTIR Spectra
isomerisation had not taken place by an undetermined mechanism. The NMR (figure 2.40) shows that isomerisation had not occurred because the aromatic resonance substitution pattern is more complex than that shown in figure 2.37 for the p-isomer. The peaks at 8.01 ppm, 7.91 ppm, 7.19 ppm, and 7.10 ppm form part of the A-B quartet of the two p-disubstituted benzene rings. The integral of the peak due to ring-junction protons could not be determined as the protons of water associated with the DMSO solvent also resonate at this chemical shift.

The thermal polymerisation of a sample was attempted by heating at approximately 330°C over a 150 minute period then for a further 120 minutes at 350 to 360°C under a stream of nitrogen. The yellow-brown glassy product was tested for solubility, and an infrared spectrum and microanalysis run. Results are given below in table 2.31.

**TABLE 2.31 THERMALLY CROSSLINKED BIS-NADIMIDE VI**

<table>
<thead>
<tr>
<th>SOLUBILITY: The polymer was insoluble in boiling DMF. However, a slight yellow colour strained into the solvent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MICROANALYSIS:</td>
</tr>
<tr>
<td>Calculated (monomer)</td>
</tr>
<tr>
<td>Found (polymer)</td>
</tr>
<tr>
<td>Difference</td>
</tr>
</tbody>
</table>

**INFRARED SPECTRUM:** This is the lower trace in figure 2.41. Differences between monomer and polymer spectra are indicated by arrows.

A thermoset material was produced as indicated by the insolubility of the polymer. The microanalysis was changed owing to the loss of some cyclopentadiene from the system.
following retro Diels-Alder reaction.

The main changes in the infrared spectrum noted on polymerisation were the reduction in size of a band at 2989 cm\(^{-1}\). A change at approximately this frequency was noted for the other nadimides.

2.3 SUMMARY

Crude samples of the bis-maleimides and bis-citraconimides could not be completely purified by recrystallisation, reprecipitation or solvent washing. Preparative HPLC and column methods were found to be excellent procedures for this.

With the exception of the bis-nadimide VI all bis-imides were obtained in greater than 99% purity as estimated by analytical HPLC (280 nM UV detector). In two cases samples with correct microanalysis still contained unacceptable levels of impurity as indicated by analytical HPLC.

The major impurity in the synthesis of the bis-citraconimides was found to be the corresponding citraconimide-itaconimide mixed imide isomer.

All samples of bis-imide formed insoluble glassy materials on heating with infrared spectra consistent with loss of unsaturated =C-H and generation of saturated -C-H.

The melting points of monomers are discussed more fully in Chapter 3 (DSC) where temperatures required to polymerise the materials were determined more precisely.
Chapter 3

Differential Scanning Calorimetry Studies
3.1 INTRODUCTION

3.1.1 Studies Carried Out

Temperature scanning DSC at different heating rates was used to examine melt, softening, and cure behaviour of the synthesised bis-imide monomers. In some cases further simple experiments were carried out to assist in the assignment of DSC peaks to physical processes. Polymers formed in the DSC scans were rescanned to determine whether glass transition processes could be detected in the resins.

Some experiments were carried out to examine the effect of pressure on the DSC behaviour of synthesised bis-nadimides.

Cure peaks were analysed to obtain kinetic parameters for the polymerisation of various samples of bis-imides varying in structure and purity where this was possible.

Isothermal DSC programmes at different temperatures were carried out to determine kinetic parameters for the polymerisation of some samples.

The purpose of the work was to attempt to relate monomer structure with parameters such as polymerisation temperature and kinetics, sharpness and temperature of melting range, and softening behaviour. It was also desired that some information be obtained on the influence of purity on the behaviour of the materials.

Any such successful correlation would aid the tailoring of synthesis to give monomers with
polymerisation and flow characteristics optimised for processing and fabrication.

The DSC data obtained in this work has been obtained by two methods, isothermal DSC and scanning DSC which are described later. Data have been obtained for compounds not previously reported.

3.1.2 Derivation of Kinetic Parameters from Scanning DSC

The following is a derivation of equations used in this work in order to obtain kinetic parameters for the polymerisation of the materials. Figure 3.1 is an example of a DSC trace illustrating the type of exothermic peak obtained for such a process.

As a convenient measure of concentration, \( \alpha \), the fractional conversion is used. Similarly, \( \frac{d\alpha}{dt} \) is used as a measure of rate of reaction.

DSC equations:

\[
\alpha = \frac{a}{\Delta H} \quad \text{Eqn 3.1}
\]

\[
\frac{d\alpha}{dt} = \frac{(dq/dt) \cdot (1/\Delta H)}{\Delta H} \quad \text{Eqn 3.2}
\]

\( a \) is the area representing the heat released by time \( t \) as shaded in figure 3.1. Both equations 3.1 and 3.2 are assumptions which may not be justified if the contribution of simultaneous elementary reactions to the overall enthalpy release varies widely throughout the reaction (i.e. with \( \alpha \)).
For this type of system:

\[ M \rightarrow P \]

\[ 1-\alpha \quad \alpha \]

\[ M = \text{maleimide or citraconimide end group.} \]

\[ P = \text{imide residue in polymer.} \]

The overall rate expression assumed is:

\[ \frac{d\alpha}{dt} = k(1-\alpha)^x \tag{Eqn 3.3} \]

where \( x \) is the overall order of reaction.

\( k \) is an apparent overall rate constant dimensionally correct only for first order reactions because \( \alpha \) is used as a measure of concentration.

\[ \therefore \ln(\frac{d\alpha}{dt}) = \ln k + x\ln(1-\alpha) \tag{Eqn 3.4} \]

and \[ \ln k = \ln(\frac{d\alpha}{dt}) - x\ln(1-\alpha) \tag{Eqn 3.5} \]

But temperature varies throughout the run:

Arrhenius equation \[ \ln k = \ln A - \frac{E_a}{RT} \tag{Eqn 3.6} \]

Equating 3.5 and 3.6:

\[ \ln(\frac{d\alpha}{dt}) - x\ln(1-\alpha) = \ln A - \frac{E_a}{RT} \tag{Eqn 3.7} \]

\( \frac{d\alpha}{dt} \) and \( \alpha \) are obtained from the DSC equations, the temperature \( T \) is known. \( \ln(\frac{d\alpha}{dt}) - x\ln(1-\alpha) \) is plotted against \( 1000/T \) giving a slope of \(-E_a/R\), and intercept \( \ln A \).

The overall reaction order is unknown and must either be obtained by multi-linear regression or some other method such as isothermal DSC. The multi-linear regression method finds a value of \( x \) at which the best straight line
Figure 3.1: A Scanning DSC Thermogram

Figure 3.2: Experiment and Baseline Isothermal Runs, dq/dt is Displaced
is obtained with the data. This assumes that the plot should be a straight line, ie that overall reaction order is invariant over the region of conversion examined. This need not necessarily be the case, as the rate equation is an overall equation for several elementary reactions occurring during a period of marked viscosity change in the polymerisation environment.

The investigation that has been presented in this work involved DSC scans at a variety of heating rates for each compound. For each heating rate experiment, $E_a$ and $\ln A$ were derived from equation 3.7, and the values averaged to produce final results for the polymerisation kinetics of the compound in question.

### 3.1.3 Derivation of Kinetic Parameters from Isothermal DSC

Isothermal DSC runs were carried out at five temperatures per material. In this work, an isothermal DSC run consisted of the following procedure.

The sample was allowed to stabilise at 60°C in the cell chamber. When the heat flow signal had stabilised, data recording was begun and the sample held at 60°C for a further minute. The temperature was then ramped at 200°C/minute to $T$, the desired isothermal temperature. Data collection was continued until further change in heat flow was no longer discerned, and for an additional time after this. Data collection was then stopped. This procedure will be referred to as the experiment or experimental run.
The temperature was raised by 20°C for five minutes to ensure complete cure of the material. The cell was then cooled to 60°C. At this point, as during runs, it was essential not to alter nitrogen pressure or flow rate, or to interfere with sample or reference pans in any way.

The above temperature-time programme was repeated as in the experimental run on the now polymeric sample, regarded as inert. This latter run will be referred to as the rescan or baseline run. This procedure was necessary due to the large changes in heat flow, instrumental in nature, occurring during the fast ramp to T. These were due to the instrument attempting to compensate for temperature differences between the two holders. A fast ramp was necessary in order to prevent significant reaction occurring before temperature was attained. It was necessary to distinguish changes in heat flow due to reaction and physical processes in the sample, from those of instrumental origin. This was achieved by the subtraction of the rescan data from those of the experiment. The rescan thermogram was normally displaced on the dq/dt axis with respect to that of the experimental - an example of this is depicted in figure 3.2. The initial 60°C isotherm provided a steady heat flow over a one minute period. The difference in heat flow over this period, \( \Delta(dq/dt) \), was used to match the experiment and baseline run data, by addition of \( \Delta(dq/dt) \) to all baseline data heat flow values for that run. This produced matching data like that shown in figure 3.3.
Figure 3.3: Matched Baseline and Experiment Isothermal DSC

Figure 3.4: Subtracted Isothermal DSC Data Corrected for \( t = 0 \)
The intersection of the two curves after the start of the isothermal period was taken to be zero reaction time. The reaction heat flow was then taken as the difference between the two curves. Data corrected in this way are illustrated in figure 3.4 which is essentially a rate of reaction vs time plot assuming equation 3.2 to be correct. This plot is the isothermal equivalent of the exothermic peak depicted in figure 3.1; and \( \Delta H, dq/dt, \) and \( \alpha \) may be determined in the same way from the data. Thus \( \alpha \) and \( dq/dt \) values may be obtained according to equations 3.1 and 3.2.

To test the fit of the data to equation 3.4, \( \ln(d\alpha/dt) \) is plotted against \( \ln(1-\alpha) \) yielding a slope whose value is the overall order of reaction \( (x) \), and a \( dq/dt \) axis intercept of \( \ln k \). Since runs were carried out at five different temperatures per sample, \( \ln k \) could be plotted against \( 1/T \) according to the Arrhenius equation to yield the apparent overall Arrhenius activation energy and pre-exponential factor.

Instrument control, data collection and analysis were carried out by computer – software and instrumental details are given in Chapter 5. Similar methods have been used previously to obtain isothermal DSC data\(^{106}\), and other methods of isothermal DSC on imide systems involving sample insertion into a pre-heated cell have also been reported\(^{37}\).
3.2 RESULTS AND DISCUSSION - GENERAL DSC FEATURES

3.2.1 Detailed DSC Behaviour of Pure Monomers

Bis-Maleimide I

Figure 3.5 depicts the DSC trace of the pure material. There was a sharp endothermic peak corresponding to crystalline melt. During and immediately following this, was an extremely rapid exotherm which overlapped the preceding endotherm. The two peaks were thus not resolved, and \( \Delta H \) for neither process could be measured. No exotherm was observed below the melting point of the bis-maleimide so that in the solid material on the time scale of the experiment the exothermic process did not occur. At point A as marked on figure 3.5, the brittle material was found to be insoluble in boiling DMF so that the preceding exotherm was assigned as being due to the addition polymerisation of maleimide double bonds. This DSC curve shape indicating that addition polymerisation of maleimide does not occur before the melting of the solid is not unique. It was, for example, obtained by Ninan, Krishnan, and Mathew\(^{27}\) for a sample of bis-4-maleimidophenyl sulphone, and also for bis-itaconimides\(^{33}\).

The trace also depicts a second exotherm of unknown origin. Due to the insolubility of the materials at both A and B the techniques available to examine the materials were limited. Infrared spectra of materials corresponding to those at points A and B as marked on figure 3.5 were
run and are shown in figure 3.6. The spectrum of material A was typical of the thermoset resin of the crude compound. (The latter was made from the material obtained from the reaction vessel by heating at 230°C under nitrogen over a two hour period, and yielded a glassy polymer insoluble in boiling DMF.) The spectrum of A was very similar to that of the monomer; a slight reduction in the unsaturated =C-H stretch region at 3082cm⁻¹ was visible, and the appearance of an absorption due to saturated -C-H stretching at 2925cm⁻¹ was observed. Only slight differences between monomer and polymer infrared spectra were expected, because of the relatively small change in the overall structure on removal of the double bonds. The regions of the spectrum between 3100 and 3000cm⁻¹ containing unsaturated =C-H absorption are dominated by absorption attributed to aromatic Ar-H because of the large proportion of aromatic structure in the molecule. Although the reduction in one band in the region at 3082cm⁻¹ compared with the remaining two at 3095cm⁻¹ and 3068cm⁻¹ is apparent the bands are not distinguished by positive assignment to aromatic or unsaturated =C-H, and they overlap.

The main feature of the spectrum after the second exotherm, was a further increase in the saturated -C-H absorption at 2925cm⁻¹. In material B the additional -C-H absorption between 3000 and 2800cm⁻¹ might have been due to reaction involving the phenylene rings in the resin and need not be due to removal of double bonds alone. An additional band was present at 1199cm⁻¹ being in
Figure 3.5: Scanning DSC, 10C/min.

Figure 3.6: FTIR Trace, Materials A and B from Bis-Maleimide I
the C-O single bond stretching region. However, this may be C-N-C stretch in the saturated imide ring residues, as the succinimide C-N-C absorption is found at 1180 cm\(^{-1}\) (ref. 74). Bands at 853 cm\(^{-1}\) and 746 cm\(^{-1}\) in the spectrum of material A had reduced in intensity in that of B. This may be due to further reduction in double bond content. Whilst overlapping two peak exotherms have been obtained for the thermal polymerisation of bis-maleimide/amine adducts\(^{37}\), and also for bis-imides with imide rings of two different types\(^{41}\), such widely spaced separate exothermic processes are not reported for bis-imides containing only one type of imide ring, probably for purity reasons discussed below in section 3.2.3. There was no weight loss during the unknown reaction as is shown in Chapter 4. The information obtained is insufficient for a conclusive explanation of the process occurring between A and B in the DSC scans of this compound but a possible explanation is given below.

**Bis-Maleimide II**

In figure 3.7 is depicted the DSC trace of the 3-substituted bis-maleimide II at different heating rates. The temperatures of peak minima and maxima increase slightly with increasing heating rate as expected. The same two exotherm situation as was observed during the DSC of the 4-substituted isomer I, is exhibited. However, due to the low melting point of the compound - (93-100)°C - and the imperceptibility of an interfering melt endotherm, the whole polymerisation exotherm (first exotherm before
A) is visible on the trace. The size of the exotherm corresponds to those of the single exotherm obtained on polymerisation of the crude samples of both I and II - discussed in section 3.2.3. The magnitude of the two exotherms summed is larger than any polymerisation exotherm assigned for any of the compounds examined in this work. At A the solid was found to be insoluble in boiling DMF. For these reasons the first exotherm was again assigned to the addition polymerisation of the maleimide end group - not necessarily to completion - by opening of the double bond. However, a polymerisation exotherm peak maximum at 148°C is at a low temperature compared with many reported previously. Values of between 170°C and 285°C have been reported. In many cases the melting point of the material is the overriding factor governing the polymerisation temperature range. A table of some literature melting points and polymerisation temperatures is given in Appendix 1.

The reactivity of the double bonds are said to vary according to the structure and molecular weight between the two terminating maleimido groups and the polar environment of the olefinic double bonds. Whilst this is undoubtedly so, impurities in the monomer systems may also play a large role in reactivity of maleimides and related compounds, and it is believed that the reported lower maleimide reactivity may be attributed to monomer impurity as discussed in section 3.2.3.

The infrared spectra of materials A and B from II are shown in figure 3.9. The main features of the spectrum of
Figure 3.7: Scanning DSC Traces of II

Figure 3.8: FTIR of Materials A and B obtained from II
the material B were the increased saturated -C-H absorption at 2926cm⁻¹ and the appearance of a band at 1188cm⁻¹. Differences at similar wavenumbers were observed in the spectra of materials A and B of the bis-maleimide I system. There was also the reduction of bands at 883cm⁻¹ and 1033cm⁻¹ which might have been due to loss of double bond =C-H, and the further increase in a band at 3645cm⁻¹ possibly due to pick up of water whilst heating under nitrogen.

The second exotherm was (30±1) KJ/mole for II as compared with between 14 and 17 KJ/mole for I. The apparent difference in extent of the second reaction for the two isomers might be due to the difference in the aryl sulphone ether chain present in the thermoset resin. This suggestion is consistent with the appearance of the saturated -C-H being due to loss of aromatic =C-H in the aryl sulphone ether chain. It may also be due to a difference in the extent of the vinyl polymerisation governing the number of unpolymerised maleimide groups left at point A. These residual double bonds may be involved in the second reaction. The second exotherm for highly pure bis-4-maleimidophenyl methane is shown in figure 3.16. It is 2.3 KJ/mole. The ability of the unknown process to occur might be associated with the availability of the aryl chain in the thermoset network for interchain interaction of some type. This would presumably involve the saturated imide ring residues in the propagated chain or, more likely, residual maleimide double bonds, since such reactions are not reported for poly(aryl ether
sulphones).

It seems unlikely that the first exothermic process (assigned to polymerisation) would stop and restart at a higher temperature. It is not likely that the softening temperature of the material is capable of overtaking the scan temperature by a large amount, due to diffusion control in densely crosslinked networks\(^{11,13}\). A clear gap between the exotherms is thus inconsistent with further polymerisation of the same type occurring during the higher temperature process.

The following is a suggested scheme for the reaction giving rise to the second exotherm and the infrared results. It is an intramolecular electrophilic attack by one of the maleimide double bond carbon atoms on the phenylene ring at the position ortho to the maleimide group. This is illustrated for both the p-isomer (I) and the m-isomer (II):
The generation of saturated \(-\text{CH}_2-\) in this reaction to give material B would increase infrared saturated C-H stretch absorption (around 2926 cm\(^{-1}\)) by a larger amount than on polymerisation of monomer to polymer (material A) because saturated \(-\text{CH}_2-\) absorbs strongly whereas saturated >CH- is very weakly absorbing\(^{120}\). The appearance of infrared bands at 1199 cm\(^{-1}\) on going from material A to material B (that of I) and at 1188 cm\(^{-1}\) (material B of II) is consistent with the generation of C-N-C absorption. This gives a band at 1182 cm\(^{-1}\) in succinimide, whereas that of maleimide is at 1137 cm\(^{-1}\) (ref. 74). As seen in the above diagram, in the m-isomer (II) the position attacked is ortho to the ether linkage and thus activated for electrophilic substitution. In the p-isomer (I) this position is meta to the ether group and thus not activated by it, hence the second reaction might occur less readily. This might explain the lower magnitude of the second exotherm in I (14 to 17 KJ/mole) as compared with that of II (30±1 KJ/mole).

There was no weight loss during the second exotherm as shown in the TGA trace discussed in Chapter 4.

The endotherm at 83\(^\circ\)C (10\(^\circ\)C/minute heating rate) was possibly due to a glass transition in the monomer. The trace shape is typical of a glass transition of a thermally aged sample. This was tested by taking the material past the endotherm temperature without melting, and then immediately quenching the material in order to retain the thermally induced free volume. The same material was then rescanned, and a step transition was
exhibited as shown in figure 3.9. This is the expected behaviour of the sample after inducing further free volume. The material initially behaves as a thermally aged sample - the sample contains reduced free volume. The endothermic effect is a kinetic one. The heat capacity of the material changes as it softens, and the material reaches a point in time when the increasing molecular motion requires further free volume in order to accommodate it. This volume has not yet been produced.

When there is sufficient energy, increase in free volume occurs, and there is a sudden absorption of energy (the endotherm) on onset of further molecular motion occurring with the increase in the free volume. If the sample is then quenched, this free volume is "frozen" into the system - the material suddenly hardens without time for the system to relax and shrinkage in the free volume to occur. On rescan, the sudden absorption of energy is not expected - the free volume is still available and a step transition is seen due to the change in heat capacity on softening. The scan-endotherm, rescan-step transition pattern is thus characteristic in DSC traces, depicting glass transition processes\(^{108,109}\). The rescan shows some sign of the original endotherm, perhaps due to a certain amount of relaxation in the sample despite the rapid cooling.

If the above exotherm was due to a glass transition process then the relatively low melting range of this monomer (93-100°C) is not evident on the trace at all. This is probably due to lack of crystallinity in the
Figure 3.9: Scan-Rescan DSC Behaviour of Monomer

Figure 3.10: Scanning DSC Traces of Bis-Citraconimide III
sample. Low crystallinity gives rise to low enthalpy of melting and broadened melting range - the latter is evident in the melting range measured (hot stage microscope) despite high sample purity. This is quite different from the well defined crystalline melting of the all 4-substituted isomer I evident by DSC and hot stage microscope observations. The onset of monomer step transition was at 64°C and the midpoint at 73°C. An alternative explanation of the behaviour is that the endotherm is due to the melting of the material and quenching destroys crystallinity in the sample leaving the step transition due to glass transition only. This would mean the melting and glass transition being very close together in temperature, which would explain the lack of crystallinity in the material. However, the endotherm position does not correspond to the measured liquifaction temperature of the material, which was determined by use of a hot stage microscope.

**Bis-Citraconimide III**

Figure 3.10 shows scanning DSC traces on the same scale of the all 4-substituted bis-citraconimide III at a variety of heating rates. The compound shows a double endothermic peak where the material first melts, then possibly crystallises from the melt in a different form from the original, and then remelts.

There is then a substantial gap in temperature between the melt and the following exothermic
polymerisation peak. The peak maximum was at 362°C (10°C/minute). This is a very high temperature compared with those obtained for the maleimides. This was expected for two reasons. The steric effect of the methyl group in the propagated chain is expected to reduce the stability of the polymer, and slow the propagation. Under the polymerisation conditions, radicals formed by the removal of a hydrogen atom from the methyl group may be formed. There is evidence that these allylic-type radicals are very stable as described in Chapter 1. The free radical initiated solution polymerisations of N-phenyl- and N-cyclopropylcitraconimides are believed to have failed for these reasons.

Literature values for citraconimide cure peak maxima lie between 230 and 250°C \(^{5,40,41}\) as compared with the value obtained here of 362°C. In certain cases contrary to the above explanation and the results obtained here, literature peak maxima are lower than those for the corresponding maleimides \(^{5,40}\). The reasons for these anomalies are similar to the explanations for the lower cure temperature of the bis-maleimides I and II as compared with literature values and lie with considerations of purity as detailed in section 3.2.3 below.

The melting point of this bis-citraconimide (III) was lower than that of the corresponding maleimide (I). However, the polymerisation temperature was much higher for the reasons detailed above.

The size of the cure exotherm was \((86\pm3)\) KJ/mole.
This was larger than the cure exotherm for II of (63±2) KJ/mole. This was not expected. The citraconimide is essentially a 1,1,2-trisubstituted vinyl monomer, and as such additional thermodynamic instability in the polymer structure is expected because of the presence of the methyl group, which should lead to additional steric interactions within the polymer. The explanation for the higher heat of polymerisation, $\Delta H_f$, is not certain. It may be due to the higher temperatures at which the polymerisation is carried out. It is also possible that the single exothermic peak observed in the DSC trace represents both of the exothermic processes that have been observed for the bis-maleimides I and II, but simultaneously occurring because of the higher polymerisation temperature of the citraconimide. If this were the case then the $\Delta H_f$ of the citraconimide could be lower than that of the maleimides as expected. The effect of substitution is not relevant in this context, since exotherms for III and IV are of the same magnitude.

**Bis-Citraconimide IV**

The scanning DSC traces of the 3,4-substituted bis-citraconimide IV at a variety of heating rates, are shown in figure 3.11. The material again requires very high temperatures to effect cure, as for the p-isomer (III), and the discussion concerning III above is also applicable to IV. The cure peak maximum occurred at a temperature of 351°C (10°C/minute) compared with a peak at 362°C.
Figure 3.11: Scanning DSC Traces of Bis-Citraconimide IV

Figure 3.12: Scan-Rescan DSC Behaviour of Monomer IV
(10°C/minute) for the 4-substituted isomer III. Whilst there is approximately 10°C difference between the two isomers, they are close in behaviour, and both differ considerably in reactivity in cure from literature samples as described above for III.

Similar softening and melt behaviour to that exhibited by the corresponding 4,3-substituted maleimide (II) was observed in the DSC of IV. Figure 3.12 illustrates the scan-quench-rescan behaviour of the monomer, showing an endothermic peak at 72°C (10°C/minute) in the monomer comparing with an endothermic peak in the DSC trace of II, at 83°C (10°C/minute). The scan-quench-rescan procedure and the subsequent type of result were as explained above for monomer II. The onset of the step transition was at 62°C and the midpoint at 66°C.
Figure 3.13: 10°C/min. DSC Scans of Pure Monomers, Same Scales

Table 3.1 Some Characteristic DSC Parameters

<table>
<thead>
<tr>
<th>Compound/monomer</th>
<th>Monomer Tg*/°C</th>
<th>Monomer Mp*/°C</th>
<th>T_g/°C</th>
<th>A_H*/kJ.mol⁻¹</th>
<th>A_H/kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-maleimide I</td>
<td>-</td>
<td>220</td>
<td>-</td>
<td>-</td>
<td>15.5±1.5</td>
</tr>
<tr>
<td>Bis-maleimide II</td>
<td>73</td>
<td>93-100</td>
<td>148</td>
<td>63±2</td>
<td>30±1</td>
</tr>
<tr>
<td>Bis-citraconimide III</td>
<td>-</td>
<td>190-193</td>
<td>362</td>
<td>86±3</td>
<td>-</td>
</tr>
<tr>
<td>Bis-citraconimide IV</td>
<td>66</td>
<td>79-85</td>
<td>351</td>
<td>86±2</td>
<td>-</td>
</tr>
</tbody>
</table>

ΔH. Values are averages of figures obtained at different heating rates.

ΔH₂ magnitude of second exotherm.

# Midpoint of step transition used as an estimate of Tg.

* Measurement by hot stage microscope - liquifaction of m-isomers not seen on the DSC traces.

† 10°C/minute.
3.2.2 Summary of DSC Behaviour of Pure Monomers

A comparison of the 10°C/minute scanning DSC traces and melting points of the structures shown in figure 3.13, gives the following structure-property relations for the four arylene ring systems examined:

**Maleimides:**
1. They undergo two exothermic processes on heating.
2. Relatively low temperatures are required for the thermal cure.

**Citraconimides:**
1. Only one exothermic process is discernable by DSC.
2. Relatively very high temperatures are required to effect cure thermally.
3. Melting points are slightly lower than those of the corresponding bis-maleimides.
4. The change of substitution of the imide group appears to have little, if any effect on the cure reactivity.

**All 4-substituted isomers:**
1. Crystalline when pure.
2. Sharp melting point at relatively high temperatures.
   **4,3-substituted isomers:**
1. Samples tend to behave amorphously in comparison with the 4,4-substituted isomers.
2. They exhibit a monomer glass transition process prior to melting.
3. Relatively broad liquifaction range. Much lower temperatures are needed to produce melts, than
required for the all 4-substituted structures.

A monomer glass transition has been observed for the four aryl ring bis-4-(4-maleimidophenoxy)phenyl methane. The large reduction in melting point on incorporation of m-phenylene links is supported by the literature values for a variety of different types of aromatic compound and polymer. The pattern is observed in the simplest of all aromatic bis-maleimides with melting points of (346-350)°C for bis-p-maleimidobenzene, (243-244)°C for bis-o-maleimidobenzene, and 202°C for bis-m-maleimidobenzene. The polyimidothioether of the m-phenylene isomer of these three compounds melts at lower temperatures than the p- or o-chain polymers. Comparable bis-maleimides chain extended with m-diaminobenzene melt at lower temperatures than those extended by p-diaminobenzene. The melting point of bis-p-maleimidobenzophenyl sulphone is (246-250)°C whereas that of bis-m-maleimidobenzyl sulphone is (203-205)°C. The same effect is observed with the glass transition temperatures of isomeric poly(arylene ether sulphones) where the order is p- > o- > m- in Tg. Other traits in melting point have been observed, e.g. the longer the chain in aliphatic bis-citraconimides and bis-maleimides the lower the melting point of the monomer.

The aim of the synthesis of the citraconimides was to obtain a gap in temperature between melt and cure. With
such a gap, these materials are able to form a stable melt. This removes the necessity of having to solution process the materials during the formulation of laminates or "prepregs" - fibres or woven matting pre-impregnated with the resin. The resin is necessarily in the form of a liquid which is often a solution. Many solvents necessary to dissolve polyimides are toxic and high boiling. They can be very difficult to remove from the resin, and residual solvent in the monomer can give rise to bubbles during the following cure. When such bubbles are locked into the final solid cured resin, they form voids which may seriously weaken the product. However, for the same reasons that this material has the advantage of a stable melt, very high cure temperatures are required. This is a serious disadvantage, both in the cost of formulation of finished products, and in the quality of the final product. Temperatures required for full cure are approaching decomposition temperatures. This is evident in weight loss during isothermal cure as described in the kinetics section of this chapter.

3.2.3 Effect of Purity on Thermal Cure

Bis-Maleimide I

Figure 3.14 depicts the traces of a series of 10°C/minute DSC scans of the material at different purities. The lowest plot (96.5%) is that of the material as synthesised and acetone washed, without any HPLC
Figure 3.14: The Effect of Purity on Thermal Behaviour of I
purification. The uppermost plot (99.9%) is the DSC plot of the same material after purification by preparative HPLC. The intermediate plots are those of simple mixtures of the two powders mentioned above. The purities quoted are based on those measured by analytical HPLC for the two components.

Because the mixtures were of the dry powders, the behaviour of the two different constituents was quite separate until after melting. Thus the ratio of them may be seen from the ratio of the sizes of the two individual endothermic melting peaks.

Following melt, the material behaved homogeneously. The presence of even the smallest quantity of impurity in the monomer had a marked effect on the cure. The sample estimated at 99.6% purity behaved in a manner similar to that of the crude material at 96.5%, and only when the material approached absolute purity was the two exotherm behaviour - which was previously described as characteristic of the two bis-maleimides - observed. Clearly this is a likely explanation of the lower reactivity in cure and one-exotherm behaviour of maleimides observed in the literature, where often elemental analyses of the materials show significant discrepancy with calculated values. Both the crude (96.5%) and pure (99.9%) materials had the correct elemental analyses. The measurements on less pure materials made in the literature and here are important, because they show how the materials as synthesised behave. The pure sample of I is of little practical importance due
to its extremely rapid cure on melting. Suitable behaviour in a crude material is advantageous, because it renders unnecessary the expensive and often very difficult purification of these materials, and often a cruder material will have a lower melting point in addition to the higher cure temperature - both advantageous in product formulation.

One of the impurities thus acted as a powerful retarder in the cure reaction. The situation regarding the presence of the second exotherm is clarified below, where the effect of purity on the cure of II is examined, and the nature of the retarder further discussed.

*Bis-(4-Maleimidophenyl)methane*

Figure 3.15 depicts the DSC trace of 95% pure commercially available material as compared with that of material purified by passing a solution through an alumina column, and shown to be near 100% purity by analytical HPLC. The plots demonstrate that the increased reactivity in highly pure samples is not restricted to four arylene ring bis-maleimide systems, but is probably characteristic of all highly pure maleimide systems. The result also demonstrates that nothing inherent in the preparative HPLC method has caused the subsequent and previously unreported behaviour.

In figure 3.16 a portion of the curve for the pure material has been scaled up to illustrate more clearly the very small second exotherm.
Figure 3.15: The Effect of Purity on Thermal Behaviour of Bis-(4-Maleimidophenyl) Methane

Figure 3.16: Possible Second Exotherm in DSC Trace of Pure Bis-(4-Maleimidophenyl) Methane
ΔH° has been measured at 95.3kJ/mole. This compares with values of between 61 and 68kJ/mole obtained for bis-maleimides I and II given in table 3.2 below.

**Bis-Maleimide II**

Figure 3.17 illustrates the effect of purity on this maleimide in a similar manner to that described for I. HPLC purified material (99.8% by HPLC) and crude material as obtained from the reaction vessel (74.6%) were mixed intimately by dissolving together in acetone and allowing the solvent to evaporate off. The experiment was designed to illustrate the decreased reactivity and one exotherm cure behaviour of less pure samples. The p-system (II) did not appear to be quite so sensitive to impurity as did the all 4-substituted system (I) and the sample estimated as 99.2% pure still exhibited behaviour of a pure material, but this may have been because the method of mixing of the pure and crude components differed to that used in the study of I. However, the 96.6% sample behaved in a manner much the same as that of the corresponding p-maleimide isomer of the same purity. The first exotherm of the pure material II corresponded approximately in magnitude to the only exotherm area of the impure material II and also to that of the impure material I as shown in table 3.2. However, since enthalpy values vary with temperature and these exotherms occurred at a variety of different temperatures, this correspondance does not conclusively prove that they are due to the same reactions.
Table 3.2

\[ \Delta H_f \text{ IMPURE I} = (61\pm2)\text{KJ/mole} \]
\[ \Delta H_f \text{ IMPURE II} = (68\pm1)\text{KJ/mole} \]

FIRST EXOTHERM  PURE II - (63\pm2)KJ/mole
SECOND EXOTHERM  PURE II - (30\pm1)KJ/mole

Although quoted regions of uncertainty are themselves only estimates, it appears that the exothermic peaks shown by the materials before HPLC purification correspond to the first exotherms in the pure materials. The first and second exotherms summed are too large to correspond to the impure material exotherms. It is suggested these peaks are due to cure of the materials by addition polymerisation of the maleimide double bonds, and that in the impure materials a free radical retarder was present which slowed the polymerisation rate thus raising the temperatures required to cure the materials. This retarder may have inhibited the reaction giving rise to the second exotherm altogether, and so this second reaction may thus have been a process which required higher than decomposition temperatures to occur within the impure materials.

Further evidence for this was obtained on addition of 2% (by weight) of hydroquinone - a known inhibitor - to the pure material. Only one exotherm was apparent, and this is illustrated in figure 3.18. The peak maximum was back up to temperatures characteristic of the impure materials and was roughly comparable to the material of 87% purity. The experiment demonstrated that common
Figure 3.17: The Effect of Purity on Thermal Behaviour of II

10°C/MIN

Figure 3.18: Scanning DSC Trace of II Doped with 2% Inhibitor
inhibitors can cause the polymerisation exotherm of the pure material to move to a higher temperature range more comparable with those of the impure materials, suggesting that the impurities are retarders of some type. However, the size of the exotherm was 83KJ/mole corresponding more closely to both first and second exotherms summed, indicating that both processes occurred. This was not observed in the impure samples of the materials, where the size of the exotherm observed corresponded to that of the first exotherm of the pure materials only.

When the powder is placed in the DSC pan, it seems highly likely that some air is trapped between the particles of the material, and that some of this air is retained perhaps dissolved in the melt despite the nitrogen flow. This is also confirmed in this experiment, because it is known that hydroquinone will only act as inhibitor in the presence of oxygen\textsuperscript{113}. This is important in the context of the cure mechanism, which is discussed later in the kinetics section of this chapter.

Bis-Citraconimide III

DSC thermograms obtained at 10°C/minute heating rate for the 4-substituted citraconimide III are shown in figures 3.19 and 3.20 for the pure and unpurified samples respectively. The material of figure 3.20 was estimated at 76.9% purity by HPLC, and the microanalysis was low in carbon by 1.1% in 65.8%. The two traces show completely different temperatures of cure, and the cure peak maximum
Figure 3.19: Scanning DSC Trace of Bis-Citraconimide III

Figure 3.20: Scanning DSC Trace of Crude Bis-Citraconimide III
of the impure material at 242°C corresponds with literature values of between 230 and 250°C. The impurity in this citraconimide apparently has an accelerating effect on the cure. This is in contrast to the maleimides where the effect of impurities is retardation of cure. It is thus possible to understand the slightly greater reactivity of citraconimides compared with their corresponding maleimides which is reported in the literature for impure materials contrary to expectations based on mechanism.

Additionally, the size of the exotherm which was 
\( (39 \pm 1) \text{ KJ/mole} \) did not correspond to that of the pure material which was 
\( (86 \pm 3) \text{ KJ/mole} \).

The impurities also have a detrimental effect on any structure-physical property relationship investigation. The cure peak in figure 3.20 which is expanded in scale compared with that in figure 3.19, is smaller than that for the pure material and at a different temperature. The melting behaviour was totally different, the impurities rendering the material much more amorphous. Had the materials not been purified, the true effect of substitution on melt-softening behaviour would not have been observed, although the behaviour of the impure materials could be of great practical importance. The impure material shown had a melting point of 155°C compared with \( (190-193)°C \) for the pure.
Figure 3.21: Scanning DSC of Pure Bis-Citraconimide IV

Figure 3.22: Scanning DSC of Crude Bis-Citraconimide IV
Figures 3.21 and 3.22 above illustrate the DSC traces of pure and impure IV respectively. The cure and melt-softening behaviour of the two materials was similar as shown. This was not the same case as that of its p-isomer III where thermal behaviour of impure and pure was very different. It has been shown that the cure behaviour of the two pure bis-citraconimide isomers is very similar as expected with comparable ΔHf values and exotherm temperatures. Comparison of figures 3.20 and 3.22 shows the two impure isomers having very different polymerisation temperatures due to their impurities. The size of the exotherm was (45±5) KJ/mole and corresponded to that of the impure sample of III of (39±1)KJ/mole, but not that of the pure material IV which was (86KJ/mole).

Summary

It must be concluded that whilst the work examining materials as synthesised is of great importance, it is necessary to obtain the materials in a pure state - in some cases extremely pure state - in order to carry out a more fundamental investigation of structure property relations. The examination of pure materials here enabled conclusions to be drawn on the effect of substitution on melt-softening behaviour, and showed that substitution had little effect on cure reactivity in the pure citraconimides. The removal of an unknown impurity in both
maleimides uncovered the presence of a second exothermic reaction, and showed that the bis-maleimides are much more reactive than previously thought, the impurity apparently having an inhibiting effect on the thermal polymerisation.
3.3 RESULTS AND DISCUSSION - POLYMERISATION KINETICS

This section puts some of the relative cure reactivities seen in part 3.2 on a more quantitative level. Part 3.3.1 discusses individual isothermal DSC kinetic run results; 3.3.2, scanning DSC kinetic data obtained from cure exotherm peaks shown in section 3.2; and 3.3.3 is a summary and discussion of the kinetic data.

Because of the very high reactivities of the two pure bis-maleimides, results were not obtained by isothermal DSC. However, in order to obtain a comparison of their cure kinetics, the crude sample of I (no preparative HPLC purification, ≈96% pure) was used in isothermal runs. A sample of the pure m-substituted bis-maleimide II (≈100%) was purposely doped with crude II (≈75% pure, as synthesised - no purification) in order to obtain material of comparable purity to the crude sample of I, ie ≈96%. Isothermal DSC was carried out on the pure citraconimides III and IV.

The scanning DSC traces of those samples described above were also analysed. Again, the pure bis-maleimide I was too reactive to analyse. There was inseparable melt endotherm-polymerisation exotherm peak overlap. However, during the polymerisation of II there was no interference of the first exothermic peak from a melt endotherm. This peak was analysed as the polymerisation exotherm. Thus in addition to the four samples examined by isothermal DSC, pure II was also analysed by the scan method.
The isothermal experiments provide an order of reaction based on the models used, and these are presented first. The analyses of scanning DSC cure exotherm peaks gave results entirely dependent upon $x$, the order of reaction chosen for the Arrhenius-type plots of $\ln(\frac{da}{dt}) - x.\ln(1-a)$ vs. $1000/T$. The plots and subsequent results were obtained for two types of value of $x$.

Isothermal analyses were carried out between 20 and 90% conversion. Within the first 20% conversion the data obtained showed that the reaction rate was still increasing. In order that the scan data be comparable with isothermal results, the analyses were carried out over the same (20-90)% conversion range.

3.3.1 Isothermal DSC, Individual Runs

Figure 3.23 is the fractional conversion versus time plot obtained for a 96% sample of the bis-maleimide I at 280°C. Figure 3.24 is the corresponding plot of heat flow versus fractional conversion plot. Both plots are typical of the type of plot obtained for all samples. It is a simple consequence of equation 3.3 that the latter plot should be linear for a first order reaction. The curve obtained is not consistent with a first order reaction over the entire range of conversion. The plot does, however, serve to show that in the absence of any attempt to determine the reaction order, sections of the curve might be interpreted as linear - for example over the first 20 to 30% conversion - and a first order rate
Figure 3.23: A Typical Conversion versus Time Plot, Isothermal DSC

Figure 3.24: A Typical Heat Flow versus Conversion Plot, Isothermal DSC
constant derived.

However, in this work the data were plotted in such a way as to determine order of reaction. The slope of the \( \ln(\frac{da}{dt}) \) vs. \( \ln(1-\alpha) \) plot from \( \alpha=0.2 \) to 0.9 was taken as the average reaction order over this conversion range according to the model used (as described in section 3.1.6). This type of plot was of the same form for all samples run by isothermal DSC and for all runs. One typical plot from the 20 produced is shown in figure 3.25. The plot shows a clear variation in reaction order over the range of interest - the straight line is that of the best fit by least squares. A variety of methods for DSC data analysis have been used for bis-maleimide polymerisation kinetic studies assuming a first order reaction, where parameters are derived from appropriate plots based on this assumption.

Figure 3.25: An Isothermal DSC Kinetic Plot
Each of the tables 3.3 to 3.6 gives results of individual runs for a sample. \( x \) is the average slope of the \( \ln(dx/dt) \) vs. \( \ln(1-\alpha) \) plot for the run in question, \( \ln k \) the intercept. \( \Delta H_f \) is the integral of the appropriate heat flow vs. time plot (eg figure 3.4). \( \Delta H \) and \( x \) values obtained at different isothermal temperatures were averaged to give average values for the temperature range examined. This provided figures for comparison between samples. The \( \ln k \) and \( T \) values provided five point Arrhenius plots.

Table 3.3, Bis-Maleimide I 96%, Isothermal DSC Runs

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( x )</th>
<th>( \ln k )</th>
<th>( \Delta H_f/\text{KJ-mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>1.405</td>
<td>-4.546</td>
<td>57</td>
</tr>
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<td>275</td>
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<td>-4.040</td>
<td>73</td>
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<td>290</td>
<td>1.788</td>
<td>-3.875</td>
<td>77</td>
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</table>

Table 3.4, Bis-Maleimide II 96%, Isothermal DSC Runs

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( x )</th>
<th>( \ln k )</th>
<th>( \Delta H_f/\text{KJ-mol}^{-1} )</th>
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<tbody>
<tr>
<td>300</td>
<td>1.277</td>
<td>-4.366</td>
<td>67</td>
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<td>305</td>
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<td>-4.220</td>
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<tr>
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<td>1.333</td>
<td>-4.037</td>
<td>69</td>
</tr>
<tr>
<td>315</td>
<td>1.521</td>
<td>-3.595</td>
<td>68</td>
</tr>
<tr>
<td>320</td>
<td>1.452</td>
<td>-3.726</td>
<td>72</td>
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</table>
Table 3.5, Bis-Citraconimide III Pure, Isothermal DSC Runs

<table>
<thead>
<tr>
<th>T/°C</th>
<th>x</th>
<th>lnk</th>
<th>ΔHf/KJ·mol⁻¹</th>
<th>%WT LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>1.257</td>
<td>-4.867</td>
<td>102</td>
<td>2.73</td>
</tr>
<tr>
<td>380</td>
<td>1.224</td>
<td>-4.579</td>
<td>93</td>
<td>2.43</td>
</tr>
<tr>
<td>385</td>
<td>1.219</td>
<td>-4.391</td>
<td>91</td>
<td>2.30</td>
</tr>
<tr>
<td>390</td>
<td>1.332</td>
<td>-4.167</td>
<td>88</td>
<td>3.05</td>
</tr>
<tr>
<td>395</td>
<td>1.491</td>
<td>-3.875</td>
<td>88</td>
<td>3.04</td>
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</tbody>
</table>

Table 3.6, Bis-Citraconimide IV Pure, Isothermal DSC Runs

<table>
<thead>
<tr>
<th>T/°C</th>
<th>x</th>
<th>lnk</th>
<th>ΔHf/KJ·mol⁻¹</th>
<th>%WT LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>1.273</td>
<td>-4.522</td>
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<td>380</td>
<td>1.354</td>
<td>-4.433</td>
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<td>2.14</td>
</tr>
<tr>
<td>385</td>
<td>1.290</td>
<td>-4.140</td>
<td>97</td>
<td>2.14</td>
</tr>
<tr>
<td>390</td>
<td>1.293</td>
<td>-3.773</td>
<td>84</td>
<td>2.77</td>
</tr>
<tr>
<td>395</td>
<td>1.397</td>
<td>-3.724</td>
<td>94</td>
<td>3.52</td>
</tr>
</tbody>
</table>

These results gave rise to the Arrhenius plots shown in figures 3.26 to 3.29 inclusive.

With all compounds a rather large variation in ΔHf between runs was observed. This is difficult to explain—the values for the two citraconimides appeared to generally decrease with increasing temperature, but no such correlation was observed for the bis-maleimides III (96%) or IV (96%). If the reactants and products differ in heat capacity then ΔH may vary according to the Kirchoff Equation. However, a random variation is likely to be due to experimental error.
Figure 3.26: Isothermal DSC Arrhenius Plot, 20-90% Conversion

Figure 3.27: Isothermal DSC Arrhenius Plot, 20-90% Conversion
Figure 3.28: Isothermal DSC Arrhenius Plot, 20-90% Conversion

Figure 3.29: Isothermal DSC Arrhenius Plot, 20-90% Conversion
Variations in the x values with temperature were also observed, which appeared to show a general increase with increase in temperature. This may perhaps have been due to gradual variation in mechanism with temperature.

Variation in x and \(\Delta H\) between runs may also be have been due to variations in extent of vinyl polymerisation.

Additional random variations in x and \(\Delta H\) might have been due to some irreproducibility in sample behaviour in the DSC cell. If changes in sample shape or surface area of contact with the cell or pan occurred between experiment and baseline runs, then this would give rise to some irreproducibility in the relevant subtracted data. Since each run gave rise to a characteristic baseline run, comparisons could not be made to confirm this explanation.

The Arrhenius plots obtained (figures 3.26 to 3.39 inclusive) were good for the two all 4-substituted compounds, more scatter was observed in those for the 4,3-isomers. The straight line is that for the best fit from least squares analysis.

Isothermal DSC temperatures were in the ranges shown because at temperatures much higher than those used, high reaction rates gave rise to a significant amount of conversion before isothermal period temperature and instrument control were attained. At lower temperatures either \(\Delta H\) values obtained were drastically reduced or no reaction could be discerned.

The temperatures necessary in order to obtain data for the two pure citraconimides caused some decomposition. This is evident in the weight loss figures accompanying
the kinetic results above. These were obtained by weighing DSC pan containing the sample before and after the runs. The weight losses generally increased with increasing temperature as expected, but although the \( \Delta H \) values appeared to generally decrease with temperature, the \( \alpha \) values were not subject to any such straightforward variation. This suggests only limited effect on the kinetic results from the small amount of decomposition. No simple method of eliminating this decomposition was available.

3.3.2 Scanning DSC, Individual Run Kinetic Results

Irrespective of sample or scan rate, the features of \( \ln(\frac{d\alpha}{dt})-x\ln(1-\alpha) \) vs. 1000/T plots were similar, and only one typical example of each reaction order type is presented.

Figure 3.30 depicts such plots for integral values of \( x \) from 1 to 3. The plots for \( x=2 \) and \( x=3 \) are curved. The plot for first order undulates about the best straight line, but is the closest fit. This latter plot illustrates how without any further information, a first order reaction is deduced from the scanning DSC curves. However, the isothermal DSC results suggested a continuously varying reaction order throughout the course of the reaction, with an average order of reaction between first and second. There is no reason for imposing an integral order of reaction as in these plots, since the value examined is an overall reaction order, not that for an
Figure 3.30: Scanning DSC Data Plotted for Integral Overall Reaction Orders

Figure 3.31: A Scanning DSC Kinetic Plot for Overall Reaction Order (x) Value of 1.5
elementary (molecular) reaction. If $x$ was fixed at an
order of reaction of 1.5, or fixed at an order
specifically obtained for that sample from isothermal DSC;
curves like that shown in figure 3.31 were produced with
the data. Curves were expected, because the reaction order
varies with $\alpha$. Results for Arrhenius activation energies
(from the slopes) and $\ln A$ (from the intercepts) were taken
from this type of plot where $x$ was either the average
value obtained by isothermal DSC for the sample in
question or 1.5. The value of 1.5 was chosen for reasons
explained below in section 3.3.3. The results for
individual runs are shown below in tables 3.7 to 3.11
inclusive.

Table 3.7 Bis-Maleimide I 96%, Scanning DSC Kinetic Results

<table>
<thead>
<tr>
<th>$(dT/dt)/^\circ \text{C-min}^{-1}$</th>
<th>$E_a/(KJ-mol^{-1})$</th>
<th>$\ln A$</th>
<th>$E_a/(KJ-mol^{-1})$</th>
<th>$\ln A$</th>
<th>$\Delta H/(KJ-mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>97</td>
<td>16.2</td>
<td>106</td>
<td>18.1</td>
<td>65</td>
</tr>
<tr>
<td>15</td>
<td>89</td>
<td>14.2</td>
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<td>15.5</td>
<td>103</td>
<td>17.4</td>
<td>58</td>
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</table>

* Value obtained from the corresponding isothermal experiment.
Table 3.8 Bis-Maleimide II 96%, Scanning DSC Kinetic Results

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</tr>
</thead>
<tbody>
<tr>
<td>(dT/dt)/°C/min⁻¹</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>ΔH_p/KJ-mol⁻¹</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>99</td>
<td>16.1</td>
<td>92</td>
<td>14.5</td>
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Table 3.9 Bis-Maleimide II Pure, Scanning DSC Kinetic Results

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</tr>
</thead>
<tbody>
<tr>
<td>(dT/dt)/°C/min⁻¹</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>ΔH_p/KJ-mol⁻¹</td>
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<td></td>
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Table 3.10 Bis-Citraconimide III Pure, Scanning DSC Kinetic Results

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</tr>
</thead>
<tbody>
<tr>
<td>(dT/dt)/°C/min⁻¹</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>Ea/KJ-mol⁻¹</td>
<td>lnA</td>
<td>ΔH_p/KJ-mol⁻¹</td>
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<td></td>
</tr>
<tr>
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<tr>
<td>5</td>
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<td>23.4</td>
<td>128</td>
<td>19.2</td>
<td>92</td>
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Table 3.11 Bis-Citraconimide IV Pure, Scanning DSC Kinetic Results

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$/*°C-min$^{-1}$</th>
<th>$E_a$/KJ-mol$^{-1}$</th>
<th>$\ln A$</th>
<th>$E_a$/KJ-mol$^{-1}$</th>
<th>$\ln A$</th>
<th>$\Delta H$/KJ-mol$^{-1}$</th>
</tr>
</thead>
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<tr>
<td>20</td>
<td>149</td>
<td>23.8</td>
<td>127</td>
<td>19.5</td>
<td>81</td>
</tr>
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<td>15</td>
<td>140</td>
<td>22.0</td>
<td>119</td>
<td>17.8</td>
<td>92</td>
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<td>85</td>
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<td>128</td>
<td>20.0</td>
<td>109</td>
<td>16.0</td>
<td>86</td>
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</table>

The results obtained for the bis-maleimide I (96%) do not include heating rates slower than 10°C/minute because these runs produced DSC traces with visible melt endotherm-polymerisation exotherm overlap. In fact the trend in the figures for $\Delta H$ suggest that slight overlap is still evident - the faster the heating rate, the greater the separation appears to be, thus the less the overlap, and the greater the area of visible polymerisation exothermic peak. However, the errors in the areas recorded do not seem to give rise to any greater variations in the figures than those obtained for the other samples. As was the case for isothermal DSC, rather large variations in $\Delta H$ were observed. Baseline positioning has a critical effect on the $\Delta H$ values obtained because any inaccuracy is at the widest point of the peak. This is a major disadvantage in scanning DSC. The chosen baselines also affect the derived kinetic parameters and this is reflected in the same type of variation in the $E_a$ and $\ln A$ values between runs. Scanning at different heating rates provides a method of testing reproducibility of runs and
obtaining more accurate mean values for lnA and Ea. The reproducibility between heating rates (as estimated by standard error) provides an estimate of uncertainty in the final figures.
3.3.3 Discussion

TABLE 3.12 FINAL ARRHENIUS PARAMETERS

<table>
<thead>
<tr>
<th>COMPUND</th>
<th>I (96%)</th>
<th>II (96%)</th>
<th>III (PURE)</th>
<th>IV (PURE)</th>
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<tr>
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<td>1.61</td>
<td>1.38</td>
<td>1.30</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>(±0.07)</td>
<td>(±0.05)</td>
<td>(±0.05)</td>
<td>(±0.02)</td>
</tr>
<tr>
<td>Ea/ KJ-mol⁻¹</td>
<td>86</td>
<td>110</td>
<td>156</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>(±3)</td>
<td>(±20)</td>
<td>(±5)</td>
<td>(±15)</td>
</tr>
<tr>
<td>lnA</td>
<td>14.4</td>
<td>18</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>(±0.6)</td>
<td>(±4)</td>
<td>(±1)</td>
<td>(±3)</td>
</tr>
<tr>
<td>ΔH/ KJ-mol⁻¹</td>
<td>69</td>
<td>68</td>
<td>93</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>(±4)</td>
<td>(±1)</td>
<td>(±3)</td>
<td>(±4)</td>
</tr>
</tbody>
</table>

| x       | 1.5     | 1lnA | 15     | 16     | 36     | 25.1   | 22     |
|         |        |      | (±1)   | (±1)   | (±1)   | (±0.6) | (±1)   |

| Ea/ KJ-mol⁻¹ | 94     | 99     | 142    | 158     | 138    |
|             | (±3)   | (±4)   | (±5)   | (±4)    | (±5)   |

| x         | iso    | 1lnA | 17     | 14     | 33     | 21     | 18     |
|           |        |      | (±1)   | (±1)   | (±2)   | (±1)   | (±1)   |

| ΔH/ KJ-mol⁻¹ | 61     | 66     | 63     | 86      | 86     |
|             | (±2)   | (±3)   | (±2)   | (±3)    | (±2)   |

"iso" is the value of x obtained in isothermal kinetic analysis for that sample, and is recorded above in the isothermal section under x. The value used for the
pure sample of the bis-maleimide II (no isothermal results) was 1.4, that obtained for the 96% pure sample.

The $\Delta H$ and $x$ results for the isothermal DSC of the pure bis-maleimide II were inconsistent from run to run. It is believed that this is because at temperatures high enough for complete conversion to occur, the reaction occurred too rapidly for the technique — large amounts of conversion occurred before the instrument had reached a controlled state. In cases where the reaction did not go to completion, presumably a melt gel point was reached, and the kinetics that occurred before this point were different than would otherwise have been the case at comparable $\alpha$ values. This would explain the differences in the results of isothermal runs carried out at different temperatures.

Errors

The regions of uncertainty quoted in table 3.12 are estimates only. The isothermally determined orders of reaction and $\Delta H$ values are standard errors for averages of small numbers of figures, as are all the scanning DSC Arrhenius parameters presented. Those of the isothermal $E_a$ and $\ln A$ values are based on least squares analysis of the five point Arrhenius plots (figures 3.26 to 3.29) and are thus also estimates only.
Reaction Order

All samples showed a similar pattern in the ln(\(\text{d}x/\text{d}t\)) vs ln(1-\(\alpha\)) plots, eg figure 3.25. The slope varied smoothly during the course of the reaction indicating that the overall order of reaction varied between 20% and 90% conversion. The determined kinetic parameters for the cure reaction were thus average figures for 20% to 90% conversion.

As described in Chapter 1, any simple thermal mechanism predicts second order reaction kinetics. This expected order was not observed. The values of 1.3 and 1.6 for the order of reaction can not be used as a guide for elucidating the detailed mechanism of cure for several reasons. The true thermal polymerisation of a material under these conditions involves physical as well as chemical control over the kinetics. As the system approaches the melt gel-point diffusion/viscosity control becomes more and more important - possibly explaining the gradual change in reaction order observed as the reaction proceeds. One suggestion that might explain the observed order is that the reaction starts near second order (chemically controlled) and then drops towards unity as physical control becomes more and more important.

Another further problem is that it has not been determined whether small amounts of oxygen may have influenced the polymerisation. In the past difficulties have been encountered in the study of the thermal polymerisation of styrene due to the effect of oxygen on
the polymerisation kinetics. The situation has been reviewed by Ebdon1211.

A further problem in the relation of the results to any chemical mechanism lies within assumptions made. The observed kinetics of enthalpy change, i.e., those measured, may not correspond to the kinetics of monomer to polymer conversion. Elementary reactions not involving simple conversion may contribute to the overall enthalpy release during the course of the reaction.

In general, the polymerisations of bis-maleimides and polyaspartimides are treated as first order in the literature, although no explanation of the reaction order is evident, probably because of the difficulties involved as explained above. It has already been shown how the reaction may be treated as a first order process by DSC. However, the results here do not agree with this assumption. Literature FTIR studies have suggested first order reactions for alkyl bis-maleimides57.

Heat of Polymerisation (ΔHp)

The ΔHp values of the two citraconimides obtained by both isothermal and scanning DSC agreed within experimental error. They were unexpectedly larger than those obtained for the maleimides. Values for ΔHp for citraconimides appear to be quite rare in the literature. However, the values of between 96 and 86 KJ/mole obtained here compare with a value of 67 KJ/mole obtained for a phosphorus containing bis-citraconimide41.
The $\Delta H_f$ values of 61 to 69 KJ/mol for the bis-maleimides by the two methods compares with values of 95.3 KJ/mol for bis-(4-maleimidophenyl) methane$^{38}$, and 79 KJ/mol for bis-2,2-[4-(4-maleimidophenoxy)phenyl] propane$^{107}$. Values of between 29 and 80 KJ/mole have been found for some phosphorus containing bis-maleimides$^{41}$. Where literature values are available they are quite variable, probably mainly due to the difficulty of interpreting the DSC trace; eg, whether there is endotherm-exotherm overlap, positioning of baseline etc.

The isothermal $\Delta H$ values of the two bis-maleimide samples examined were the same within experimental error, as were all three examined by scanning DSC.

The $\Delta H$ results from the two methods, scanning and isothermal, were similar - either they agreed within the estimated experimental error or were only just outside the limits. This is important in indicating that no major errors occurred in the isothermal DSC by not taking the cure to as near completion as possible as in scanning DSC. In fact, the isothermal values for $\Delta H$ were slightly higher in every case than the corresponding scanning case. The correspondence also serves to show that no major errors were made in the positioning of baselines in the scanning DSC - these were relatively straightforward to predict as was seen in thermograms presented in section 3.2.
Scanning DSC - Comparison with Isothermal Results. Problem with Reaction Order

The critical dependence of the Ea and lnA values on the value for the order of reaction is one major disadvantage of the method, since the reaction order is not actually determined by scanning DSC. The problem is one of too many variables to be determined, and has been summarised by Flynn\(^1\)\(^-\)\(^7\) in the following statement:

"Attention should be given to carrying out isothermal experiments since it is impossible to separate unequivocally the temperature dependent and concentration dependent parts of a rate expression by experiments in which temperature and concentration are changing simultaneously". The computer program could be used to derive by multiple linear regression the value of x for which the best straight line plot was produced for every run. The problem with this approach is that if, as was indicated by the isothermal results for x, the reaction order varies with conversion, the plots of $\ln(\frac{d\alpha}{dt})-x\ln(1-\alpha)$ vs 1000/T should not be linear. This means that the multi-linear regression would be working on a false assumption.

In table 3.12, are results of the plots done for values of x of 1.5 and the x=order derived from the corresponding isothermal run ("iso"). It is significant that if the scanning DSC data are plotted for x=1.5, all eight Arrhenius parameters derived from it compare most closely with those obtained by isothermal DSC. All the lnA
values agree within experimental error, and two of the Ea figures. The other two values of Ea are almost within experimental error of one another, and the quoted errors are only estimates at best for the reasons given above. This value of 1.5 is similar to the average order of reaction determined for all these imides by isothermal DSC of 1.4. This is significant, possibly suggesting that results for x for individual compounds are subject to larger errors than those estimated, and that the true average order from 20 to 90% conversion using this model is close to 1.5.

However, results from scanning DSC are gathered over much larger temperature ranges, and it is possible that mechanisms may change over these regions.

The Arrhenius results from plots done with x at the isothermal value bear some resemblance to those obtained by isothermal DSC, because none of these values is very much different from 1.5. However, the results do not agree within experimental error.

Comparison of Compound Reactivities

An important use of the DSC kinetic data is as a guide to compare the various compounds' rates of polymerisation as a function of temperature. Despite the dependence of individual results for Ea and lnA for the compounds on the value of x chosen for the scanning data, a comparison of the reaction rates based on the derived Ea and lnA values gives the same general result whatever the
chosen value of x. The same type of plot of lnk (calculated) vs 1000/T is obtained for isothermal data as for scanning data. Figures 3.32, 3.33, and 3.34 are diagrams of lnk vs. 1000/T based on the final Arrhenius parameters in table 3.12. They show more clearly a comparison of the temperature dependent reactivities of the samples examined. The diagrams represent very large extrapolations either side of regions of measurement - these are marked on the lines in the figures - to temperatures at which it is impossible for cure reactions to occur, eg above decomposition temperatures or below melting points.

The Arrhenius parameters for the two citraconimides are the same within estimated experimental error for isothermal results - almost for scan results. The same is observed for the two bis-maleimides once samples of similar purity are compared. This shows that little effect on the cure rates was detected by changing the substitution of the compounds.

The diagrams show clearly the very high reactivity of pure bis-maleimide II compared with the impure sample. The Arrhenius parameter values are to some extent artifacts of the DSC technique, but are useful in predicting variations in reaction rate with temperature.

Arrhenius activation energies of between 76 and 140 KJ/mole have been reported for aliphatic and aromatic bis-maleimides as determined by Fourier transform IR spectroscopy and DSC27,38,43,57. For bis-1,6-maleimidohexane a value of 140.2KJ/mole by IR compares
Figure 3.32: Calculated Arrhenius Plots from Isothermal DSC
Arrhenius Parameters
Figure 3.33: Arrhenius Plots from Scanning DSC Arrhenius Parameters, Calculated for x=1.5
Figure 3.34: Calculated Arrhenius Plots from Scanning DSC Arrhenius Parameters. Calculated according to Average Overall Reaction Orders from the Corresponding Isothermal DSC Results
with 126.2KJ/mole by scanning DSC. Similarly (by comparison of figures in references 43[DSC] and 57[IR]) 94.2KJ/mole by IR for bis-1,12-maleimidododecane compares with 76.9KJ/mole by scanning DSC. Despite problems with the methods some correspondence is observed.

It is known that the activation energy for thermal cure of bis-maleimide systems is dependent on chain length in aliphatic bis-maleimides\textsuperscript{43,57} - the longer the intermediate chain, the lower the activation energy.

Values for lnA parameters for this type of system are rare in the literature. The values obtained here were in the region of 15 for the 96% bis-maleimides, and between 20 and 25 for the pure bis-citraconimides. Values of approximately between 12 and 23 have been obtained for some simple bis-maleimides\textsuperscript{27}.

Conclusions

The rate constants (figures 3.32 to 3.34) obtained give practical information on rate of heat release and reaction with time and temperature. The figures give a quantitative comparison of the relative reactivities of the bis-imide systems, and how these change with temperature and structure.

However, the relation of the kinetic parameters to the fundamental chemistry and mechanism of the cure is extremely difficult given the assumptions that must be made, and the influence of other factors such as oxygen, purity, and physical control on the cure, and because data
obtained relate to overall reaction kinetics without any additional information concerning elementary reactions. Some of these factors would also apply to investigation by FTIR.

The rates of reaction of m-substituted isomers was the same within estimated experimental error as the corresponding all p-isomers of comparable purity.

Citraconimides were less reactive than their maleimide counterparts. Impure maleimides were much less reactive than pure maleimides.

Contrary to assumptions usually made in these types of bis-imide system, order of reaction was found to vary continuously throughout the course of the reaction. This was in accordance with a system constantly increasing in viscosity, but not in agreement with some previous literature reports.
3.4 DETAILED DSC BEHAVIOUR OF BIS-NADIMIDES

3.4.1 Bis-Nadimide V

Figure 3.35 depicts the DSC trace of the 4-substituted bis-nadimide V. This material was >99% pure as measured by analytical HPLC (280nM UV detector). The DSC trace is more complex than those obtained for bis-citraconimidites and bis-maleimides. The processes that may occur on pyrolysis of nadimides are not fully understood at the present time. The proposed mechanisms are more fully discussed in Chapter 1. However, four reactions occurring during pyrolysis are now well documented: The endo-exo isomerism of the nadimide ring system at temperatures lower than those required for cure; the retro Diels-Alder reaction of nadimide to cyclopentadiene and maleimide groups; the Diels-Alder addition of cyclopentadiene thus produced to existing nadimide end groups to produce a tetracyclic-system; and the polymerisation of part of the cyclopentadiene, nadimide, maleimide, and double Diels-Alder adducts together to form a complex polymer.\(^{32,64,65,66,67,96}\)

A crystalline melt endotherm on the trace was seen at 214°C, corresponding with a visual melting point measurement of (210-214)°C (by hot stage microscope), and a literature value of (210-225)°C.\(^{96}\) Following this is a broad endothermic peak attributed to the retro Diels-Alder reaction. Two components contribute to the endotherm; the actual endothermic decomposition of the nadimide end
group, and the endothermic volatilisation of some of the cyclopentadiene. During this broad endothermic region at 10°C/minute heating rate there was weight loss due to the cyclopentadiene lost from the system altogether. This is shown in Chapter 4 in the TGA trace of this material at a comparable heating rate, and has been observed previously.

The endothermic retro Diels-Alder reaction, which generates maleimide, thus allows for the initiation of the polymerisation. It is quite clear in figure 3.35 that the broad endotherm is followed by an exothermic peak, and this is attributed to the subsequent polymerisation. No attempt was made to integrate peak areas as there is no peak completely separated from any other. It would appear that the retro Diels-Alder reaction began before the melt from the baseline positions before and after the melt endotherm, but this is not certain. The retro Diels-Alder endotherm tails into the polymerisation exotherm.

The temperatures required to cure these materials are in the same order as those for the corresponding pure bis-citraconimides - albeit for different reasons. The nadimide groups, as Diels-Alder end capped maleimides, provide a method of increasing the temperatures required to effect cure, providing melt-stable systems. This temperature requirement of cure has been successfully utilised to delay cure for solvent removal and thermal imidisation of polyamic acid pre-polymers in PMR type polyimide systems. Such pre-polymers are more easily processed due to their higher solubility, and lower
Figure 3.35: Scanning DSC of Bis-Nadimide V Monomer

Figure 3.36: Scanning DSC Bis-Nadimide VI Monomer
188

melting points.

The sharp dip in the exothermic peak was almost certainly due to sample motion during the cure. The shape of the DSC trace is consistent with those observed previously for endo-nadimides$^{94,96,112}$.

3.4.2 Bis-Nadimide VI

The DSC trace of the 4,3-substituted bis-nadimide VI, shown in figure 3.36, is similar to that of V. The melting is a little broader which may be a consequence of the lower purity of this material - 97.2% by analytical HPLC. Within the bis-imides I to IV, the effect of m-substitution was to lower the melting point of the material considerably. However, this was not observed for the change in structure from V to VI. Presumably this is due to the melting behaviour of the two bis-nadimides being dominated by the two large endo-cis bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic imide end groups per molecule. The melt is followed by the retro Diels-Alder endothermic peak, the minimum of which is at 297°C, 10°C lower than that of V. This is then followed by the polymerisation exotherm, whose maximum is at a similar temperature to that of V. Sample motion is again observed during the exothermic process.
3.4.3 Pressure Cell DSC

Figures 3.37 and 3.38 illustrate the effect of pressure on the DSC behaviour of the two nadimides. The traces at different pressures are on the same scales as shown. Caution is required in the interpretation of the thermograms, because of highly uncertain baseline position, which appears to alter considerably during the retro Diels-Alder and cure processes. Although the DSC baselines for bis-imides I to IV were relatively stable during cure, this change for the nadimides is not unexpected. Unlike the simpler imides, the nadimides change weight and elemental constitution because of the loss of cyclopentadiene from the system. The retro Diels-Alder reaction also gives rise to possible subsequent reactions involving the cyclopentadiene, and thus their cure would involve much larger changes in structure than is predicted for the non end-capped imides.

Whilst it appears that the retro Diels-Alder endothermic peak is successively reduced with increase in pressure, it is unclear whether this is due to a shift in the position of the endotherm, or its removal. A likely explanation for the behaviour, is that the endotherm preceding the polymerisation is reduced in magnitude. The loss of cyclopentadiene from the system by volatilisation is almost certainly reduced due to the increased pressure. However, this does not necessarily imply loss or reduction in the extent of retro Diels-Alder reaction. Whilst cyclopentadiene is lost by volatilisation at one
Figure 3.37: The Effect of Pressure on DSC Trace of V

Figure 3.38: The Effect of Pressure on DSC Trace of VI
atmosphere, it is also taken up by polymerisation into the structure and by Diels-Alder addition to undissociated nadimide groups. Certainly, one or both of these latter two processes is operative as shown by the mass spectrum of poly(N-phenylnadimide) given in Chapter 2. It is believed that the cure reaction is rate limited by the retro Diels-Alder reaction. Exotherm due to polymerisation is still evident at the higher pressures in the traces shown here. It is therefore reasonable to assume that the retro Diels-Alder reaction still occurs, but that the reduced endothermic peak is concealed, perhaps by the larger polymerisation exotherm or uncertainty in baseline position.

3.5 POLYMER RESCANS

The materials taken to temperatures of between 400 and 430°C in the DSC were quenched and rescanned in an attempt to detect step transitions indicative of glass transition processes. The bis-maleimides were also scanned to temperatures that produced materials designated as A in section 3.2.1, where cure had taken place but not the reaction giving rise to the second exotherm.

The rescans of the bis-nadimides are shown in figures 3.39 and 3.40. The all 4-substituted trace shows no discontinuity, whereas that of the 4,3-substituted isomer shows a gradual ill defined step in slope approximately between 240 and 280°C. This may or may not be a glass transition process.
Figure 3.39: Rescan DSC of Polymer of Bis-Nadimide V

Figure 3.40: Rescan DSC of Polymer of Bis-Nadimide VI
Figure 3.41: Scanning DSC of Material A from Bis-Maleimide I

Figure 3.42: Scanning DSC of Material B from Bis-Maleimide I
The material produced by taking the maleimide through the first (lower temperature) exothermic process but not the second (higher temperature) exothermic process has been designated material A, whereas that taken through both processes by taking to higher temperatures was designated material B. Figure 3.41 shows the rescan of material A from bis-maleimide I after a preliminary scan to only 250°C maximum, and the second exotherm is evident on the trace. This exotherm is within the usual temperature range for the process on a 10°C/minute thermogram. This shows that the unknown reaction will occur in the material A if heated to a high enough temperature, even after cooling. No step transition in the curve is obvious. Figure 3.42 depicts the scan of material B of the same bis-imide, and no features are evident save background noise and the start of an exotherm at decomposition temperatures.

Figure 3.43 shows the scan of the material A of the bis-maleimide II. As was evident for I, the material exhibits the second reaction when heated, and at the temperatures normally observed for the process. There is a step in the slope approximately between 100 and 150°C which may or may not be a softening in the A material. This temperature range is similar to that of the original cure. Figure 3.44 is the scan of material B, and is featureless except for the upturn in the curve at decomposition temperatures.
Figure 3.43: Scanning DSC of Material A from Bis-Maleimide II

Figure 3.44: Scanning DSC of Material B from Bis-Maleimide II
Figure 3.45: Rescan DSC of Polymer of Bis-Citraconimide III

Figure 3.46: Rescan DSC of Polymer of Bis-Citraconimide IV
Table 3.13

Observed Transition Temperatures for Poly(Bis-Citraconimide)s

POLY(BIS-CITRACONIMIDE III), FIGURE 3.45

<table>
<thead>
<tr>
<th>STEP TRANSITION ONSET</th>
<th>225°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>STEP TRANSITION MIDPOINT</td>
<td>238°C</td>
</tr>
</tbody>
</table>

POLY(BIS-CITRACONIMIDE IV), FIGURE 3.46

<table>
<thead>
<tr>
<th>STEP TRANSITION ONSET</th>
<th>213°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>STEP TRANSITION MIDPOINT</td>
<td>224°C</td>
</tr>
</tbody>
</table>

Figures 3.45 and 3.46 show rescans of the two citraconimides III and IV respectively. Both show quite clear step transitions for the polymers at similar temperatures. These were reproducible on second rescan, and are displayed above in table 3.13.

The m-substituted bis-citraconimide IV is the only material examined for which both monomer and polymer glass transition processes were evident. Nielsen has developed an empirical relationship between Tg and number average molecular weight between crosslinks Mc:

\[ T_g - T_{g0} \approx \frac{39000}{M_c} \]

Tg is the glass transition temperature of the thermoset, whereas Tg0 is the glass transition temperature of the uncrosslinked polymer having the same chemical composition as the crosslinked system. The Tg of the monomer IV may be used as a measure of Tg0. If the midpoints of the step
transitions are used as estimates of $T_g$ for IV - the scans were at the same heating rates - then $T_g$ is 224°C and $T_g_0$ is at 66°C. Thus a value of $M_c$ of approximately 250 is calculated. In a fully cured homopolymer system of this type, $M_c$ is expected to be the molecular weight of the monomer divided by three according to methods of calculation found in the literature. Thus $M_c$ for a fully cured system calculated on this basis is approximately 210. The value of $M_c$ from the Nielsen equation is only an estimate, but the result suggests that there are longer units between the crosslinks than would be obtained in a fully cured system, and that there are probably some unreacted end groups in this particular sample. However, the difference between the two figures may merely be due to the empiricism of the Nielsen equation which was only based on the average behaviour of a number of experimentally observed systems.
Chapter 4

Thermogravimetric Analysis Studies
4.1 INTRODUCTION

The six bis-imides I, II, III, IV, V, and VI in their purest obtained states were polymerised in a differential scanning calorimeter under nitrogen. The temperature-time conditions used were specific to each polymer examined. In each case, the material was taken to a selected final temperature at 10°C/minute, and held at that temperature for a 15 minute period. The sample was then quenched, removed from the pan, and ground in mortar with pestle.

The samples were run on a thermogravimetric analyser at 2°C/minute heating rate under a nitrogen flow of 50cm³/minute and fresh samples rerun under an air flow of 50cm³/minute. Approximately five milligrammes of material were used for every run. Section 4.2 describes the thermal stabilities of the various polymers under nitrogen, section 4.3 under air.

The two bis-nadimide monomers V and VI were run under nitrogen at a heating rate of 10°C/minute. This heating rate was used to enable comparison between the 10°C/minute DSC scan results and those of the TGA. Because of the retro Diels-Alder reaction on heating these materials (as described in Chapter 1), and subsequent loss of weight due to cyclopentadiene loss, the thermogravimetric analysis (TGA) trace of these materials gives information on amount of cyclopentadiene lost, and may be correlated with the DSC peak assigned for this process.

Decomposition onset temperature was selected as the first temperature at which the percentage of the starting
weight had dropped below the steady value by 1% (or more).

The final temperature attained by the instrument (the highest possible) was approximately 940°C, the final weight (char yield) was recorded at this temperature.

The TGA traces depict both a main curve of percentage initial weight versus temperature, and the first derivative of the main curve which is a measure of rate of weight loss versus temperature. Maxima and inflection points in this type of curve are recorded on the traces.

Temperatures are rounded to the nearest °C, weights to the nearest %, and rates of weight loss to 0.1 %/minute.

4.2 POLYMER THERMAL STABILITIES UNDER NITROGEN

Figures 4.1 to 4.6 inclusive depict the TGA traces of the polymers heated under nitrogen at 2°C/minute. The results are summarised in table 4.1:

TABLE 4.1: Polymer Thermal Stabilities Under Nitrogen

<table>
<thead>
<tr>
<th>Polymer</th>
<th>To/°C</th>
<th>Tmax/°C</th>
<th>(dW/dt)Max/%-min⁻¹</th>
<th>Wf/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>432</td>
<td>471</td>
<td>2.4</td>
<td>26</td>
</tr>
<tr>
<td>II</td>
<td>419</td>
<td>438</td>
<td>2.5</td>
<td>38</td>
</tr>
<tr>
<td>III</td>
<td>406</td>
<td>466</td>
<td>1.7</td>
<td>32</td>
</tr>
<tr>
<td>IV</td>
<td>382</td>
<td>462</td>
<td>1.7</td>
<td>31</td>
</tr>
<tr>
<td>V</td>
<td>419</td>
<td>457</td>
<td>2.0</td>
<td>36</td>
</tr>
<tr>
<td>VI</td>
<td>406</td>
<td>455</td>
<td>1.9</td>
<td>37</td>
</tr>
</tbody>
</table>
Figure 4.1: TGA Trace, 2C/min. under Nitrogen

Figure 4.2: TGA Trace, 2C/min. under Nitrogen
Figure 4.3: TGA Trace, 2C/min. under Nitrogen

Figure 4.4: TGA Trace, 2C/min. under Nitrogen
Figure 4.5: TGA Trace, 2C/min. under Nitrogen

Figure 4.6: TGA Trace, 2C/min. under Nitrogen
where \( T_0 \) is the decomposition onset temperature as defined above, \( T_{\text{max}} \) the temperature at which maximum rate of weight loss was obtained, \( (dW/dt)_{\text{max}} \) the maximum rate of weight loss, and \( W_f \) the final weight or char yield at 940°C.

All the thermograms showed the same pattern of decomposition with one main maximum in the rate followed by a shoulder.

The polymaleimides began decomposing at the highest temperatures on average. However, when decomposition had begun they also showed the greatest rate of decomposition as measured by rate of weight loss. The polymaleimides are expected to be the most stable since they contain the least aliphatic content and highest proportion of aromatic.

The polymers with \( m \)-substituted benzene rings appeared to begin decomposing at lower temperatures than the corresponding \( p \)-isomers.

On average the largest final weights were observed for the polynadimides.

The above observations have been made on differences close to reproducibility between runs. Table 4.2 depicts an example of a comparison between results from two TGA experiments carried out on two different samples from the same batch of polymer of V. The two runs were carried out under nitrogen (flow rate 50cm³) at 2°C/minute on five milligramme samples.
TABLE 4.2: Reproducibility Between Runs

<table>
<thead>
<tr>
<th>T&lt;sub&gt;0&lt;/sub&gt;/°C</th>
<th>T&lt;sub&gt;max&lt;/sub&gt;/°C</th>
<th>(dW/dt)&lt;sub&gt;max&lt;/sub&gt;/%·min&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>W&lt;sub&gt;f&lt;/sub&gt;/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>419</td>
<td>457</td>
<td>2.0</td>
<td>36</td>
</tr>
<tr>
<td>429</td>
<td>454</td>
<td>2.1</td>
<td>28</td>
</tr>
</tbody>
</table>

Both T<sub>0</sub> and W<sub>f</sub> are subject to quite large errors despite attempts to keep sample size and shape constant, with a 10°C difference in T<sub>0</sub> values and an 8% difference between W<sub>f</sub> values. However, T<sub>max</sub> and (dW/dt)<sub>max</sub> values were much more reproducible. The reproducibility of results is affected by sample size, shape, division, homogeneity, and gas flow rate. These are probably larger factors contributing to reproducibility than are instrument accuracy.

No large differences in thermal stability were observed due to either imide type or substitution pattern in the chains.

The onset of decomposition of the polymaleimides and polycitraconimides under nitrogen occurs at temperatures in the same order as those observed for some thermally stable phosphorus-containing bis- and tris-maleimides and citraconimides previously reported<sup>5, 40, 41</sup>. Although slightly greater thermal stabilities in maleimides than those in citraconimides might be expected, no such differences were observed in these phosphorus-containing bis-imides. These materials have char yields in the order of 60%, higher than those with structures not containing the phosphorus heteroatom.
Very little difference in the thermal stabilities under nitrogen between bis-4-maleimidophenylmethane, bis-4-maleimidophenylether, bis-4-maleimidophenylsulphone, and bis-3-maleimidophenylsulphone have been observed. To values (reference 27) were in the order of \( \approx 440 \) to \( \approx 450^\circ C \), similar to those observed here, between \( \approx 420^\circ C \) to \( 430^\circ C \) for maleimides. Similarly, \( T_{\text{max}} \) values of between \( \approx 475^\circ C \) to \( 485^\circ C \) were similar to those obtained here of between \( 440^\circ C \) and \( 470^\circ C \) for maleimides. Char yields (\( W_r \) values) at \( 600^\circ C \) were between 54\% and 56\%, and these compare well with values of 54\% (I) and 53\% (II) for the two maleimides at \( 600^\circ C \) as may be seen in figures 4.1 and 4.2.

The \( T_0 \), \( T_{\text{max}} \), and \( W_r \) values for the poly(bis-maleimides) are similar to values reported previously.

### 4.3 POLYMER THERMAL STABILITIES UNDER AIR

Figures 4.7 to 4.12 inclusive depict the TGA traces of the polymers heated under air at 2\(^{\circ}C/\)minute. The results are summarised in table 4.3:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_0/\text{°C} )</th>
<th>( T_{\text{max}}/\text{°C} )</th>
<th>( (dW/dt)_{\text{max}}(1)/%\text{-min}^{-1} )</th>
<th>( T_{\text{max}}(2)/\text{°C} )</th>
<th>( (dW/dt)_{\text{max}}(2)/%\text{-min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>372</td>
<td>423</td>
<td>0,8</td>
<td>500</td>
<td>3,4</td>
</tr>
<tr>
<td>II</td>
<td>385</td>
<td>434</td>
<td>0,7</td>
<td>515</td>
<td>2,9</td>
</tr>
<tr>
<td>III</td>
<td>365</td>
<td>466</td>
<td>1,1</td>
<td>562</td>
<td>2,8</td>
</tr>
<tr>
<td>IV</td>
<td>363</td>
<td>459</td>
<td>0,9</td>
<td>551</td>
<td>3,1</td>
</tr>
<tr>
<td>V</td>
<td>363</td>
<td>462</td>
<td>1,0</td>
<td>549</td>
<td>2,5</td>
</tr>
<tr>
<td>VI</td>
<td>346</td>
<td>457</td>
<td>0,9</td>
<td>541</td>
<td>2,5</td>
</tr>
</tbody>
</table>
Figure 4.7: TGA Trace, 2C/min. under Air

Figure 4.8: TGA Trace, 2C/min. under Air
Figure 4.9: TGA Trace, 2°C/min. under Air

Figure 4.10: TGA Trace, 2°C/min. under Air
Figure 4.11: TGA Trace, 2°C/min. under Air

Figure 4.12: TGA Trace, 2°C/min. under Air
All materials began losing weight at lower temperatures under air than under nitrogen as expected. The traces showed two maxima in rate of weight loss with temperature. Neither of these corresponded to the single maximum observed under nitrogen, suggesting a different mechanism of decomposition in the two media. Except for the maleimides, an inflection point was observed during the increase in rate to the second maximum - these are marked on the figures.

Char yields of all materials at 940°C under air were close to zero.

The two maleimides began decomposing at slightly higher temperatures than the citraconimides and nadimides. However, once decomposition had begun, the maleimides reached a maximum rate of decomposition at lower temperatures than either of the other two types of imide. This was true of both maxima observed. By 600°C maximum weight loss had been attained. The two nadimides appeared to show the lowest rate of weight loss during the second maximum.

The two polymaleimides show similar decomposition onset temperatures and curve shape (with two maxima) as results previously reported for bis-4-maleimidophenyl methane. However, the To values are considerably lower than that of 445°C reported for m-bis-maleimidobenzene.

Greater thermo-oxidative stability in poly(bis-maleimide)s (as measured by TGA) as compared with that in poly(bis-citraconimide)s are not generally observed (eg references 5 and 41). This was also found to be the case
in the bis-maleimide and bis-citraconimide polymers described above.

4.4 WEIGHT LOSS IN BIS-NADIMIDE MONOMERS

4.4.1 General Features

Figures 4.13 and 4.14 depict the TGA traces of the bis-nadimide monomers V and VI respectively, run at 10°C/minute under nitrogen (50cm³/minute flow rate). Two weight loss processes are to be noted. The first shows an inflection point soon after its onset and represents a total weight loss in the order of 10%. The second process terminates with a final weight of approximately 35% starting weight and corresponds to thermal decomposition. Results are summarised in table 4.4. Tο(1) is the starting temperature of the inflection following the first process, and taken as the temperature at which the first process was complete.

TABLE 4.4: Weight Loss in Bis-Nadimide Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tο(1)/°C</th>
<th>Tmax(1)/°C</th>
<th>Tr(1)/°C</th>
<th>Tο(2)/°C</th>
<th>Tmax(2)/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>219</td>
<td>331</td>
<td>394</td>
<td>444</td>
<td>496</td>
</tr>
<tr>
<td>VI</td>
<td>215</td>
<td>320</td>
<td>388</td>
<td>430</td>
<td>497</td>
</tr>
</tbody>
</table>

The processes that can occur on heating nadimides are described in Chapter 1.

The region of temperature over which the first
Figure 4.13: TGA Trace of Monomer V, 10C/min. under Nitrogen

Figure 4.14: TGA Trace of Monomer VI, 10C/min. under Nitrogen
process occurs corresponds to the region of temperature over which the broad endotherm (retro Diels-Alder decomposition of nadimide end groups) followed by the exotherm (due to polymerisation) occur as shown in the corresponding DSC thermogram (10°C/minute) in Chapter 3. This weight loss is thus probably due to volatilisation of cyclopentadiene produced by retro Diels-Alder decomposition of nadimide end groups. Comparison of the TGA and DSC traces shows that weight loss due to cyclopentadiene occurs both before and during the course of the thermal polymerisation. The maximum rate of endotherm observed in the DSC trace of V was at 307°C. The maximum rate of weight loss was at 331°C. These two temperatures need not necessarily correspond since the endotherm is not only due to volatilisation of cyclopentadiene but due also to the retro Diels-Alder decomposition which produces the cyclopentadiene, some of which which is incorporated into the polymer structure. The same is true of VI where maximum rate of endotherm occurred at 297°C whereas maximum rate of weight loss was at 320°C.

From the weight losses obtained, the amount of cyclopentadiene lost per original bis-nadimide molecule may be calculated. Bis-nadimide V lost 11% of original weight, and bis-nadimide VI, 9%. The molecular weight of the bis-nadimides is 724.8 g/mole. That of cyclopentadiene is 66.1 g/mole. The average number of moles of cyclopentadiene lost per molecule of bis-nadimide, n, is thus given by equation 4.1:
\[ n = \left( \frac{PWL}{100} \right) \times 724.8 / 66.1 \]  \hspace{1cm} \text{Eqn 4.1}

where PWL is percent starting weight lost due to cyclopentadiene volatilisation.

Thus from V and VI the values of n are calculated as 1.2±0.1 and 1.0±0.1 respectively assuming uncertainty in PWL is ±1%. Thus approximately half of all nadimide end groups decompose losing cyclopentadiene from the system altogether. Further nadimide may have decomposed releasing cyclopentadiene that was then incorporated into the polymer structure either as the double Diels-Alder adduct or as cyclopentadiene monomer residues 1,4-polymerised into the chain. Cyclopentadiene evolution has been monitored as a volatile by-product but the amount of cyclopentadiene evolved has not been fully documented. Although the amounts released from the two bis-nadimides described here were similar, the amounts released may depend on polymerisation conditions. Thus the amounts documented here are quoted for between five and ten milligrammes heated under nitrogen at 10°C/minute, for the two structures given.

The temperatures of maximum rate of weight loss due to polymer decomposition (496°C and 497°C) do not correspond to those reported earlier (section 4.2 - 457°C and 455°C) being much higher. This demonstrates the substantial effect of a much higher heating rate on recorded temperatures.
4.4.2 Dependence of Weight Loss on Isothermal Temperature

Experiments were carried out under nitrogen on both the p-nadimide isomer (V) and the m-isomer (VI). A series of five TGA runs was carried out by taking the monomer sample to an isothermal temperature $T_i$ at a rate of 10°C/minute, and then holding at this isothermal temperature until constant weight was obtained. $T_i$ values were chosen such that the weight loss that has been associated with evolution of cyclopentadiene occurred, but not decomposition. Figure 4.15 is a typical trace where percentage of starting weight is plotted against time. This trace was obtained for V where $T_i$ was 350°C.

Figure 4.15: A Typical TGA Trace Depicting the Amount of Volatile Evolution (Assumed to be Cyclopentadiene) versus Time at an Isothermal Temperature $T_i$, here this is 350°C.
Tables 4.5 and 4.6 show the results obtained from the TGA traces where \( W_f \) is the final weight reached as a percentage of starting weight, and \( n \) is the average number of moles of cyclopentadiene lost per molecule of bis-nadimide as calculated from \( W_f \) and equation 4.1.

**TABLE 4.5 Weight Loss Dependence upon Temperature in V**

<table>
<thead>
<tr>
<th>( T_i/°C )</th>
<th>( W_f/x )</th>
<th>( n )</th>
<th>Run Length/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>89</td>
<td>1.2</td>
<td>122</td>
</tr>
<tr>
<td>325</td>
<td>90</td>
<td>1.1</td>
<td>120</td>
</tr>
<tr>
<td>300</td>
<td>89</td>
<td>1.2</td>
<td>148</td>
</tr>
<tr>
<td>275</td>
<td>88</td>
<td>1.3</td>
<td>266</td>
</tr>
<tr>
<td>250</td>
<td>86</td>
<td>1.5</td>
<td>623</td>
</tr>
</tbody>
</table>

Average \( n \) 1.3

**TABLE 4.6 Weight Loss Dependence upon Temperature in VI**

<table>
<thead>
<tr>
<th>( T_i/°C )</th>
<th>( W_f/x )</th>
<th>( n )</th>
<th>Run Length/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>86</td>
<td>1.5</td>
<td>123</td>
</tr>
<tr>
<td>325</td>
<td>87</td>
<td>1.4</td>
<td>121</td>
</tr>
<tr>
<td>300</td>
<td>92</td>
<td>0.9</td>
<td>148</td>
</tr>
<tr>
<td>275</td>
<td>89</td>
<td>1.2</td>
<td>266</td>
</tr>
<tr>
<td>250</td>
<td>89</td>
<td>1.2</td>
<td>395</td>
</tr>
</tbody>
</table>

Average \( n \) 1.3

The \( n \) values show a fairly large scatter but show that the polymer composition did not appear to depend upon
temperature. The average values of \( n \) for the two bis-nadimides are the same.

The rate of weight loss was markedly slower in the 250°C runs than at higher temperatures as indicated by the time needed for the weight to settle at a constant value, i.e., run length.

4.5 SUMMARY

No large differences between the thermal stabilities or thermo-oxidative stabilities of the six pure bis-imides were observed. Despite their lower proportion of saturated hydrocarbon structure, the polymaleimides did not have greatly superior stability to the polycitraconimides or polynamidimides.

Measured parameters were similar to those previously observed for bis-maleimidophenyl methane, bis-maleimidophenyl sulphone, and bis-maleimidophenyl ether, and showed lower stabilities in air than under nitrogen as expected.

Weight loss occurred both before and throughout the thermal polymerisation of the two bis-nadimide monomers V and VI. This was assumed to be associated with evolution of cyclopentadiene vapour. Using this assumption, under the conditions used at a 10°C/minute heating rate it has been calculated that more than half of all nadimide end groups decomposed by retro Diels-Alder reaction evolving cyclopentadiene as a volatile. The amount evolved did not appear to depend upon temperature.
Chapter 5

Experimental
5.1 GENERAL EXPERIMENTAL

5.1.1 Reagents

Diethyl ether was stored over anhydrous calcium chloride and filtered before use. Toluene was stored over sodium wire. Dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), and ethanol were stored over 4Å molecular sieve. No precautions were taken to dry methanol or ethanol when used for precipitations.

Dimethyl formamide was distilled under reduced pressure before use in vapour pressure osmometry.

5.1.2 Analysis

All melting or liquifaction temperatures were measured visually by Koffler Hot-Stage Microscope Melting Point Apparatus.

Infrared spectra were run on a Perkin-Elmer Model 1750 Fourier Transform Infrared Spectrometer interfaced to a Perkin-Elmer 7300 Professional Computer.

Proton and all 13C NMR was carried out by Mr J.P. Bloxidge of the University of Surrey Chemistry Department using a Bruker WH90 Pulse Fourier Transform Nuclear Magnetic Resonance Spectrometer operating at 90 MHz for proton NMR. One proton NMR, that of the bis-4-(3-aminophenoxy)phenyl sulphone was carried out on a Varian EM-360 Proton Nuclear Magnetic Resonance Spectrometer running at 60MHz (Ho = 14.092 KG).
Elemental Analyses were run by Mr E. Hopwood and Mrs N. Walker of Microanalysis Section of the University of Surrey Chemistry Department.

The mass spectrum was run by Mr J. S. Delderfield of the University of Surrey Chemistry Department.

Temperature scanning DSC was carried out on a Du Pont 910 Differential Scanning Calorimeter interfaced to a Du Pont 9900 Computer/Thermal Analyser. The Du Pont Pressure Cell was used for pressure cell DSC work.

Isothermal DSC work was carried out on a Perkin-Elmer DSC7 Differential Scanning Calorimeter interfaced to a Perkin-Elmer 7500 Professional Computer.

Samples for DSC were weighed using a Sartorius 4503 MICRO microbalance with digital readout displaying to ±0.001mg.

Thermogravimetric analysis was carried out using a Du Pont 951 Thermogravimetric Analyser interfaced to either a Du Pont 1090 thermal Analyser or the Du Pont 9900 Computer/Thermal Analyser. Nitrogen flow was at 50ml/minute. Experiments under air flow were carried out using a compressed airline. Flow was regulated by tap at 50ml/minute flow rate. The air was passed from the line into a large glass tube containing cellulose wool plugs to remove any possible oil particles. Between the plugs silica gel drying agent was placed to ensure the supply of air to the thermogravimetric analyser was not damp.

Vapour Pressure Osmometry was carried out by Mr P. Curnock of the University of Surrey Chemistry Department using a Knauer Vapour Pressure Osmometer.
Analytical HPLC was carried out on a Waters HPLC apparatus. An ordinary phase column was used. The detector was of the Ultra-Violet type running at 280nM linked to a computing integrator. Solutions of the final pure products and the crude products for which analyses are presented in Chapter 2 were made up in HPLC-grade dichloromethane containing approximately 2% by volume of HPLC-grade tetrahydrofuran (THF), except for the analytical HPLC of the bis-4-maleimidophenyl methane which was carried out in HPLC-grade dichloromethane containing 5% by volume of HPLC-grade THF.

5.1.3 Polymerisation Tests

Typically a sample of monomer was placed in a Pyrex Quickfit (B19) Boiling Tube fitted with Dreshel-Head. Nitrogen was passed over the sample via the Dreshel-Head. The tube was heated by means of either a thermostat-controlled silicone-oil bath or tube furnace. A thermometer was placed in contact with the outside of the tube, and thus polymerisation temperatures quoted are only approximate. The approximate temperature-time conditions for each polymerisation test are given in Chapter 2.

5.1.4 Preparative Scale High Performance Liquid Chromatography

This was carried out using a Waters Preparative HPLC apparatus. The detector was of the differential
refractometer type. The mobile phase was HPLC-grade dichloromethane containing 2% by volume of HPLC-grade THF untreated for peroxides. The column was polar, (normal phase). Flow rate was normally 0.1 litres per minute but was switched to 0.2 litres per minute after elution of the main (first) peak. Solvent pressure varied between 5 and 15 atmospheres, chamber pressure was approximately 30 atmospheres.

The following method was used for all samples purified by preparative HPLC.

Before each run the mobile phase was allowed to circulate through the system (approximately 30 minutes) by placing the outlet tube in the solvent reservoir which was topped up to five litres before each run.

The crude samples of the bis-imides were loaded onto the column as a solution via a second solvent inlet - not by injection. The amount loaded onto the column was between one and ten grammes. The material was dissolved in the mobile phase (75ml). Collection vessels were changed several times during the elution of a compound shown by a single peak on the detector readout. Every portion was tested by analytical HPLC and only portions of greater than 99% purity were combined to give a solution of the product. This solution was taken and some of the solvent removed by reduced pressure distillation using a rotary evaporator leaving approximately 100 ml.

Iron(II) sulphate (ferrous sulphate) (four grammes) was dissolved in distilled water (80ml). The solution of the product (approximately 100ml) was shaken with the
aqueous iron (II) sulphate (40ml) in a separating funnel, the two layers carefully separated, and the aqueous solution (upper layer) discarded. This procedure was then repeated once. The dichloromethane-THF solution was shaken with distilled water (100ml), and the organic solution (lower layer) carefully separated off. The aqueous layer was discarded. This washing procedure was then repeated a further twice.

The solution of the product was allowed to dry over anhydrous sodium sulphate (five grammes) in a stoppered conical flask (approximately one day). The solution was decanted off the sodium sulphate into a sinter funnel and the solution vacuum filtered. The filtrate was taken and all solvent distilled off under reduced pressure using a rotary evaporator. The product was dried in a drying pistol (70°C, approximately 16 hours). It was this final product that was examined by analytical HPLC, IR and NMR spectroscopy, melting point test, microanalysis etc - the results are given in Chapter 2.

Following each run the system was flushed with pure HPLC-grade THF, followed by the dichloromethane-THF mixture to clean the column, ie remove any impurities retained.

5.1.5 Data Analysis for Kinetic Parameters

Data analysis for kinetics was not performed on either of the aforementioned computers interfaced to the two DSC instruments. Built in dedicated software was used
to convert the data to ASCII code files on the two computers. Data was then transferred via interface to a Hewlett-Packard HP86 Computer. Programs to send the data from either the Du Pont (scanning DSC experiments) or Perkin-Elmer (isothermal DSC data) computers were purpose-written, as was the program for the Hewlett-Packard to accept the data and save the information on disc.

All subsequent data analysis was performed on the Hewlett-Packard HP86 Computer using purpose-written software.

All the software for sending, accepting, and analysing data for kinetics was written by Dr J. M. Barton of the Materials and Structures Department, Royal Aircraft Establishment, Farnborough, Hampshire.

5.1.6 Polymerisation of Bis-Imines for Thermogravimetric Analysis

All samples polymerised were in the purest obtained state. The samples were polymerised under nitrogen (50cm³/minute) by DSC in aluminium open-top pans. A Du Pont 910 Differential Scanning Calorimeter interfaced to the Du Pont 9900 Computer/Thermal Analyser was used for this purpose.

The temperature-time programmes involved a 10°C/minute scan to a selected isothermal temperature (T). The material was held at this temperature for 15 minutes and the sample quenched by immediate removal from the DSC
cell. Isothermal temperatures (T) are given below in table 5.1:

TABLE 5.1 POLYMERISATION TEMPERATURES OF SAMPLES FOR TGA

<table>
<thead>
<tr>
<th>Compound</th>
<th>T/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-Maleimide I</td>
<td>230</td>
</tr>
<tr>
<td>Bis-Maleimide II</td>
<td>170</td>
</tr>
<tr>
<td>Bis-Citraconimide III</td>
<td>385</td>
</tr>
<tr>
<td>Bis-Citraconimide IV</td>
<td>385</td>
</tr>
<tr>
<td>Bis-Nadimide V</td>
<td>350</td>
</tr>
<tr>
<td>Bis-Nadimide VI</td>
<td>350</td>
</tr>
</tbody>
</table>

Samples were removed from the DSC pans by bending in half (open side out). This operation was carried out in a clean plastic bag to allow collection of fallen particles of resin preventing loss of yield.

The particles were ground as finely as possible with mortar and pestle.

5.2 SYNTHESIS

5.2.1 N-Phenylmaleimide

Maleic anhydride (49.03g, 0.5 moles) was placed in a 500ml three-neck round-bottom flask equipped with thermometer, nitrogen inlet/outlet, pressure-equalising dropping funnel, condenser, and mechanical stirrer.

N,N-dimethylformamide (100ml) was added, and the maleic anhydride dissolved by stirring. The flask was
flushed with nitrogen, and a steady stream passed over the stirred contents during the remainder of the experiment.

The contents of the reaction vessel were cooled to between 0 and 5°C by means of a surrounding ice-bath.

Aniline (46.50g, 0.5 moles) was slowly added from the dropping funnel to the cooled solution at such a rate that the temperature of the solution did not exceed 15°C. After completion of addition, the contents of the reaction vessel were allowed to warm to room temperature and stirred under nitrogen (60 minutes).

Sodium acetate (16.67g), acetic anhydride (76.57g, 0.75 moles), and further N,N-dimethylformamide (100ml) were added to the reaction mixture. The apparatus was flushed with nitrogen, and the solution warmed (55°C, 60 minutes under nitrogen).

The solution was allowed to cool to ambient temperature under nitrogen. It was then slowly poured into vigorously mechanically stirred distilled water (1500ml). The resulting precipitate was separated by vacuum filtration, dried in a vacuum oven, and recrystallised from ethanol yielding 65.35 grammes of canary-yellow needles, melting point 90 to 91°C.

5.2.2 N-Phenylpindimide

Nadic anhydride (82.08g, 0.5 moles) was placed in a one litre three-neck round-bottom flask equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, and a Dean and Stark trap with
condenser and nitrogen inlet/outlet.

Toluene (250ml) was added and the anhydride dissolved by stirring. The reaction vessel was flushed with nitrogen, and a steady stream allowed to pass over the stirred reactants during the remainder of the experiment.

Aniline (46.50g, 0.5 moles) was slowly added at such a rate as the temperature did not exceed 15°C. This resulted in a thick precipitate. N,N-dimethylformamide (100ml) was added and the precipitate allowed to dissolve. The solution was stirred under nitrogen (16 hours, ambient temperature).

To the solution was added p-toluenesulphonic acid (2.0 grammes) and the apparatus flushed with nitrogen. The solution was refluxed (22 hours), collecting 12.5ml of water in the Dean and Stark trap.

The contents of the reaction vessel were then allowed to cool, and the solution transferred to a one litre rotary-evaporator flask. The solvent was removed by reduced-pressure distillation by rotary evaporator. The resultant solid was washed on a vacuum-filter with distilled water (one litre), dried in a vacuum oven, and recrystallised from methanol yielding 92.51 grammes of white crystalline product melting at 144 to 145°C.

5.2.3 N-Phenylcitraconimide

A solvent mixture was made up by mixing toluene (50ml) and N,N-dimethylformamide (20ml).

A 250ml three-neck round-bottom flask was equipped
with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap, condenser, and nitrogen inlet/outlet.

Aniline (18.60g, 0.2 moles) was dissolved in the solvent mixture (50ml) under nitrogen.

The contents of the reaction vessel were cooled to between 0 and 5°C by means of an ice-bath. Citraconic anhydride liquid (22.40g, 0.2 moles) was added slowly at such a rate so as the temperature did not exceed 15°C. The solution was then allowed to warm to ambient temperature when it was stirred under nitrogen (60 minutes).

Further toluene (20ml) and N,N-dimethylformamide (20ml) were added together with p-toluenesulphonic acid (0.9g). The apparatus was flushed with nitrogen, and the solution then refluxed under nitrogen (330 minutes) collecting 4.4ml of water in the Dean and Stark trap. Solvent (mainly toluene) was distilled out of the reaction vessel via the Dean and Stark trap until the vapour temperature in the flask attained 151°C.

The solution was allowed to cool to ambient temperature, and then poured slowly into vigorously mechanically stirred distilled water (300ml). The precipitated solid was removed from the water by vacuum filtration.

The solid was dissolved in the minimum cold carbon tetrachloride (approximately 300ml). The yellow solution was shaken three times with aqueous sodium bicarbonate (each portion 300ml of 1M solution in distilled water), and once with distilled water (300ml). The carbon
Tetrachloride was allowed to dry over anhydrous calcium sulphate (16 hours).

The carbon tetrachloride solution was decanted from the calcium sulphate, and three spatulas of activated charcoal added to the solution in a 500ml round-bottom flask. The mixture was refluxed (30 minutes). The cooled suspension was vacuum filtered. The filtrate was taken and all the carbon tetrachloride removed by reduced pressure distillation by means of a rotary evaporator.

The yellow-white solid was recrystallised from an n-heptane/ethanol mixture (1:1 by volume). The crystals were washed on the filter with a little carbon tetrachloride (approximately 5ml), and the compound dried in a pistol yielding 24.22 grammes of yellow-white product, melting between 95 and 96°C.

5.2.4 Purification of Bis-4-maleimidophenylmethane

A column of radius 1cm and length approximately 35cm containing a sinter was filled to a height of 15cm with neutral activated alumina.

The crude material (5.00 grammes) was dissolved in dichloromethane (50ml). The solution was carefully added to the column and allowed to pass through into a 250ml conical flask as a collection vessel below. When the solution level reached that of the alumina, further dichloromethane (30ml) was carefully added to the column. The top-up procedure was repeated a further twice. All the liquid was collected in the same vessel.
The dichloromethane solution was taken and the solvent removed by reduced pressure distillation using a rotary evaporator.

The resultant yellow solid was recrystallised from methyl ethyl ketone yielding 2.14 grammes of yellow product melting between 159 and 160°C.

5.2.5 Bis-4-(4-Maleimidophenoxy)phenyl Sulphone (I)

Synthesis of Crude Material

Bis-4-(4-aminophenoxy)phenyl sulphone (72.97g, 0.17 moles) was placed in a 500ml three-neck round-bottom flask equipped with thermometer, powder-dropping funnel, mechanical stirrer, condenser, and nitrogen inlet/outlet. The apparatus was flushed with nitrogen and the powder stirred. The remainder of the reaction procedure was carried out under a steady flow of nitrogen. N,N-dimethylformamide (220ml) was added and the diamine dissolved by stirring.

The solution was cooled to between 0 and 5°C by means of an ice-bath, and maleic anhydride (33.11g, 0.34 mole previously ground) added from the solid-dropping funnel at such a rate as to keep the temperature less than or equal to 15°C.

The stirred solution of the bis-maleimide acid was allowed to warm to ambient temperature, and stirred under nitrogen (60 minutes).

Anhydrous sodium acetate (11.26g) and acetic
anhydride (51.74g, 0.51 moles) were added to the solution, and the apparatus flushed with nitrogen. The stirred solution was heated under a slow stream of nitrogen (55°C, 60 minutes).

The solution of the crude bis-maleimide was allowed to cool to ambient temperature.

The contents of the reaction vessel were poured into vigorously mechanically stirred methanol (500ml), resulting in a tan-coloured precipitate. The suspension was vacuum filtered, and the product washed on the filter with distilled water (1500ml). The product was dried in a vacuum oven, yielding a weight of 92.79 grammes of tan powder, the crude product.

**Bis-Maleimide I - Intermediate Material**

The crude bis-maleimide (10.00g) was added to a beaker containing methanol (200ml). The solid was crushed and stirred well (15 minutes), and then isolated by vacuum filtration. The solid was washed with methanol (100ml) on the filter, followed by carbon tetrachloride (100ml), and allowed to dry further on the filter.

The solid was then stirred with acetone (100ml), removed from the liquid by vacuum filtration, and washed on the filter with diethyl ether (100ml previously dried over calcium chloride, and filtered.)

The whole of the above procedure was repeated once further, and the solid dried in a pistol yielding 5.47 grammes of yellow-tan powder.
This material had the correct microanalysis within analysts quoted experimental error, but was only 96.5% pure as guaged by analytical HPLC. This is the material referred to as crude or 96.5% pure material in Chapter 3 where the DSC analysis of this material was described. Material purified in this way was further purified by preparative scale high performance liquid chromatography to give the pure material.

5.2.6 Bis-4-(3-Aminophenoxy)phenyl Sulphone

All manipulations involving potassium aminophenoxide solutions or solution of the diamine product up to but not including the first precipitation of the diamine, must carried out with great care under nitrogen in order to avoid oxidation of the m-aminophenoxide or the diamine.

A one litre three-neck round-bottom flask was equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap, condenser, and nitrogen inlet/outlet.

Into the flask was placed m-aminophenol (105.92g; 0.97 moles). The flask was flushed thoroughly with nitrogen (30 minutes), dimethyl sulphoxide (200ml) and toluene (220ml) added, and the m-aminophenol dissolved under nitrogen by stirring.

Aqueous potassium hydroxide solution (127.31g of 0.00755 mol/g standardised solution, a total of 0.96 moles of potassium hydroxide) was placed in the dropping funnel.

The solution was warmed to 50°C and all of the
aqueous potassium hydroxide solution added carefully in portions to the warm liquid under nitrogen.

The temperature was raised and the solution refluxed. Water was removed via the toluene-water azoetoche and collected as the lower layer in the Dean and Stark trap, which was emptied frequently into a stoppered container.

After complete dehydration (approximately seven hours, total of 92cm³ water collected - theory ≈91cm³) some potassium m-aminophenoxide had crystallised out. Solvent (mainly toluene) was then distilled out of the reaction vessel via the Dean and Stark trap until the liquid reflux temperature in the flask attained 160°C. By this time the potassium m-aminophenoxide had completely redissolved. The solution was allowed to cool to room temperature, and stirred under nitrogen (ambient temperature, 14 hours).

Whilst the solution was at ambient temperature, a powder-dropping funnel containing p-dichlorodiphenyl sulphone (132.88g, 0.46 moles) was substituted for the pressure-equalising dropping funnel keeping a positive pressure of nitrogen in the apparatus so as not to allow contact of air with the solution.

The temperature of the solution was then raised to 100°C and held at this value. The powder-drop was heated by means of a hot-air blower until some of the p-dichlorodiphenyl sulphone had melted. All of the p-dichlorodiphenyl sulphone was added to the dimethyl sulphoxide solution in portions as a melt. After completion of the addition, the solution was refluxed
under nitrogen (160°C, five hours).

The contents of the reaction vessel were cooled under nitrogen to ambient temperature, when the crystallisation of a white compound (probably potassium chloride) was observed.

To four litres of distilled water containing one percent by weight of sodium hydroxide, was added sodium sulphite (40g). The solution was deoxygenated by bubbling nitrogen through it (20 minutes). To this aqueous solution (vigorously mechanically stirred) were slowly added the cooled contents of the reaction vessel, yielding a white precipitate which was isolated by vacuum filtration. The solid was washed on the filter with distilled water (deoxygenated as before) until the washings were at pH7.

The white solid was restirred in distilled water (four litres deoxygenated as before) containing sodium sulphite (40g, but no sodium hydroxide). The solid was isolated by vacuum filtration, and washed on the filter with a further portion of distilled water (one litre deoxygenated as before).

The product was dried in a pistol under vacuum in the presence of anhydrous calcium chloride at ambient temperature. The yield of white solid was 185 grammes (=92.5%).

The product was purified in four portions as follows.

The crude diamine (50.00g) was added to dilute hydrochloric acid (90ml, approximately 3M) in a one litre three-neck round-bottom flask. Anti-bumping granules and a little distilled water were added to the flask, which was
set up for steam distillation by equipping with steam inlet, steam head, condenser, and heating mantle. With no steam passing through, the contents of the flask were heated to reflux, and distilled water added until all the solid had dissolved as the dihydrochloride. To the boiling aqueous solution was added activated charcoal (four grammes) and steam passed through the boiling suspension (four hours).

The heating was stopped and the suspension immediately vacuum filtered to remove charcoal whilst the liquid was still hot. The filtrate was allowed to cool to ambient temperature in a beaker. When the solution had cooled, dilute aqueous sodium hydroxide solution (140ml, approximately 2M) was carefully added to the stirred dihydrochloride solution, precipitating the free amine.

The white solid was isolated by vacuum filtration. The solid was washed on the filter with distilled water until the pH of the washings had decreased to pH7.

The diamine was dried in a vacuum desiccator (16 hours) over anhydrous calcium chloride.

The solid was recrystallised under nitrogen from ethanol without hot filtration or charcoal treatment. Part of the material was obtained as a tar at the bottom of the flask, part as buoyant platelet crystals which were easily separated by swirling the liquid in the flask, and then decanting the crystals and solvent from the settled tar into a Buchner funnel. The tar was taken and redissolved in the minimum fresh ethanol under nitrogen and the solution allowed to cool whence further crystals and tar
were obtained, and the crystals isolated as before. This procedure was repeated until no more crystals were obtained.

The white platelet crystals were dried in a pistol under vacuum at ambient temperature in the presence of anhydrous calcium chloride (one week).

The above purification procedure was repeated a further twice with 50 grammes of the crude product. Yields of 24.32 grammes, 21.05 grammes, and 21.30 grammes were obtained.

The remaining 35 grammes of crude material was purified in the same way (reagent quantities were the same except only 65ml of 3M hydrochloric acid was used to form the dihydrochloride, and diamine was reprecipitated with only 100ml of aqueous 2M sodium hydroxide).

The total yield of white platelet crystals was 83.41 grammes, all portions melted at 134 to 135°C.

5.2.7 Bis-4-(3-Maleimidophenoxy)phenyl Sulphone (II)

The diamine (as synthesised above in section 5.2.6; 30.00g, 0.07 moles) was placed in a 250ml three-neck round-bottom flask equipped with thermometer, pressure-equalising dropping-funnel, mechanical stirrer, condenser, and nitrogen inlet/outlet. The apparatus was thoroughly flushed with nitrogen.

N,N-dimethylformamide (45ml) was added to the diamine which was dissolved by stirring under nitrogen. The solution was cooled to between 0 and 5°C by means of an
Maleic anhydride (13.62g, 0.14 moles) was dissolved in N,N-dimethylformamide (45ml) and the solution slowly added to the cooled diamine solution under nitrogen so as the temperature did not exceed 15°C.

The solution of the bis-maleimic acid was allowed to warm to ambient temperature, and then stirred under nitrogen (60 minutes).

Anhydrous sodium acetate (4.62g) and acetic anhydride (21.30g, 0.2 moles) were added, the apparatus flushed with nitrogen, and the stirred solution warmed under nitrogen (55°C, 60 minutes).

The solution was allowed to cool to ambient temperature, and the contents of the reaction vessel added drop by drop to vigorously mechanically stirred methanol (1350ml). The yellow crude bis-maleimide precipitated, and was isolated by vacuum filtration to give 29.73 grammes of crude product, liquifying between 90 and 100°C.

Pure material was obtained by purification by preparative scale HPLC.

5.2.8 Bis-4-(4-Citraconimidophenoxy)phenyl Sulphone (III)

A solvent mixture was made up by mixing toluene (80ml) and N,N-dimethylformamide (50ml).

Bis-4-(4-aminophenoxy)phenyl sulphone (41.81g, 0.097 mole) was placed in a 250ml three-neck round-bottom flask equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap,
condenser, and nitrogen inlet/outlet. The apparatus was thoroughly flushed with nitrogen.

To the diamine was added all of the solvent mixture previously made up, and the diamine dissolved under nitrogen with stirring.

The contents of the reaction vessel were cooled to between 0 and 5°C by means of an ice-bath. From the dropping funnel citraconic anhydride (21.68g, 0.194 moles) was slowly added so as the temperature of the solution did not exceed 15°C. The solution was allowed to warm to ambient temperature, and then stirred under nitrogen (60 minutes).

To the solution was added p-toluenesulphonic acid (0.45g) and the reaction heated to reflux temperature. Water was collected in the Dean and Stark trap as the lower layer. When the cyclodehydration was complete (after five hours, 4.0ml water collected - theoretical ≈ 3.5ml) solvent was distilled out of the reaction vessel (80ml) via the Dean and Stark trap. The solution was then allowed to cool to ambient under nitrogen. The solution of the crude bis-citraconimide was added portion by portion to methanol (a total of 500ml) in a Waring blender. The portions of the liquid containing chopped precipitated bis-citraconimide were all collected together in a beaker, and the product isolated by vacuum filtration. The product was ground by use of a mortar and pestle, and stirred in methanol (500ml). The solid was separated by vacuum filtration, and dried in a vacuum dessicator. 42.22 grammes of grey-white crude product were obtained.
The pure material was obtained by preparative HPLC.

5.2.9 Bis-4-(3-Citraconimidophenoxy)phenyl Sulphone (IV)

A 500ml three-neck round-bottom flask was equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap (approximately 20ml capacity), condenser, and nitrogen inlet/outlet. Into this reaction vessel was placed bis-4-(3-aminophenoxy)phenyl sulphone (as synthesised in 5.2.6, 50.00g, 0.116 moles). The trap was filled with toluene. The apparatus was flushed with nitrogen.

A solvent mixture was made up by mixing toluene (75ml) and N,N-dimethylformamide (75ml). To the diamine under nitrogen was added solvent mixture (125ml), and the diamine dissolved by stirring.

Citraconic anhydride (25.95g, 0.232 moles) was mixed with the remaining solvent mixture (25ml), and this was slowly added to the stirred solution under nitrogen at such a rate so as the temperature did not exceed 30°C. The reaction mixture was allowed to warm to ambient temperature, and stirred under nitrogen (60 minutes).

To the reaction flask was added p-toluenesulphonic acid (0.50g) and further toluene (50ml), and the apparatus flushed with nitrogen.

The stirred solution was heated, and allowed to reflux (four hours) allowing water to collect in the trap. After complete dehydration (4.8ml water collected - theoretical ≈ 4.2ml) the solution was allowed to cool to
ambient temperature.

The solution was added slowly to vigorously mechanically-stirred methanol (four litres). A yellow solid precipitated, and was obtained by vacuum filtration, and dried (16 hours) under vacuum at 60°C in a pistol.

The product was dissolved in dichloromethane (75ml), the solution vacuum filtered, and the filtrate added dropwise to vigorously mechanically stirred isopropanol (1250ml).

The precipitated solid was isolated by vacuum filtration, and dried under vacuum (70°C).

The solid was redissolved in dichloromethane (75ml), boiled with activated charcoal (15 minutes), hot filtered, and the filtrate added dropwise to vigorously mechanically stirred methanol (one litre). The yellow precipitated solid was obtained by vacuum filtration, and dried under vacuum in a pistol in the presence of phosphorus pentoxide yielding 7.85 grammes of the crude material liquifying between 104 and 108°C.

This material had the correct microanalysis, but was highly impure as shown by HPLC. Preparative HPLC was utilised to purify the crude material synthesised as above.

5.2.10 Bis-4-(4-Nadimidophenoxy)phenyl Sulphone (V)

A 250ml three-neck round-bottom flask was equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap, condenser, and
nitrogen inlet/outlet. In the flask was placed bis-4-(4-aminophenoxy)phenyl sulphone (29.83g, 0.069 moles). The apparatus was flushed with nitrogen.

A solvent mixture was made up by mixing toluene (105ml) with N,N-dimethylformamide (40ml). Some solvent mixture (75ml) was added to the diamine under nitrogen, which was stirred.

Nadic anhydride (22.65g, 0.138 moles) in solvent mixture (70ml) was added to the diamine solution under nitrogen slowly so as the temperature of the solution in the flask did not exceed 30°C. The solution was stirred under nitrogen without applied heating (60 minutes).

To the contents was added p-toluenesulphonic acid (0.3g), the apparatus reflushed with nitrogen, and the reaction mixture heated to reflux temperature.

After complete dehydration (20 hours, 3.5ml water collected - theoretical 2.5ml) the mixture was allowed to cool. At this point some material had precipitated from the solution. The contents of the flask were added slowly to vigorously mechanically stirred methanol (300ml) yielding a coffee-coloured precipitate. This was isolated by vacuum filtration and washed on the filter with a further portion of methanol (300ml).

The coffee-coloured powder was dried under vacuum in a pistol (100°C, several weeks in the presence of phosphorus pentoxide), yielding 48.98 grammes of the material which melted at 210 to 214°C.

The material as synthesised without any further purification was found to be pure as guaged by both
microanalysis and HPLC (>99%).

5.2.11 Bis-4-{3-Nimidophenoxy}phenyl Sulphone (VI)

Bis-4-{3-aminophenoxy}phenyl sulphone (10.00g, 0.023 moles) was placed in a 250ml three-neck round-bottom flask equipped with thermometer, pressure-equalising dropping funnel, mechanical stirrer, Dean and Stark trap, condenser, and nitrogen inlet/outlet. The apparatus was flushed with nitrogen.

A solvent mixture was made up by mixing toluene (35ml) and N,N-dimethylformamide (15ml).

To the contents of the flask was added some of the solvent mixture (25ml), and the diamine dissolved by stirring under nitrogen. To the stirred solution was then added nadic anhydride (7.59g, 0.046 moles) in the remainder of the solvent mixture (25ml) at such a rate so as the temperature of the mixture did not exceed 30°C - an induction period was observed for this reaction and cooling was aided by means of an ice-water bath.

After completion of addition, the solution was stirred under nitrogen without applied heating (60 minutes).

Toluene (10ml) and p-toluenesulphonic acid (0.10g) were added. At this point some of the intermediate bis-nadic acid precipitated. The apparatus was flushed with nitrogen, and the reaction mixture heated to reflux when all material dissolved. The stirred solution was refluxed under nitrogen (nine hours, 1.2ml of water were
collected - theoretical ≈0.8ml) after which the solution was allowed to cool to ambient temperature, and stirred under nitrogen (approximately 12 hours).

The solution was added slowly to vigorously mechanically stirred methanol (300ml), resulting in a white precipitate. This was obtained by vacuum filtration, and washed on the filter with further methanol (100ml), and dried in a vacuum dessicator yielding 14.14 grammes of crude off-white solid.

The material was recrystallised as follows. The solid was dissolved in the minimum refluxing chloroform, activated charcoal added, and the suspension boiled (30 minutes). The suspension was hot filtered, the filtrate transferred to a conical flask, and the solution set boiling on a hotplate. Methanol was carefully added dropwise until flakes of the material appeared that would not redissolve on further boiling. (Initially flakes of the product would appear on addition of drops of methanol, but these would redissolve on further heating.) The conical flask was removed and the solution allowed to cool to ambient temperature. (Product did not begin to crystallise out until below 30°C).

The material was obtained by vacuum filtration. It was recrystallised as described above a further twice. This was necessary in order to obtain material pure enough to give the correct microanalysis within experimental error.

Final recovery from four grammes of crude material recrystallised was 1.99 grammes of white solid melting at
210 to 215°C. This material had the correct microanalysis within experimental error, and was 97.2% pure as guaged by HPLC. All DSC, TGA, polymerisation was carried out on this recrystallised material. No further purification was carried out.
Summary

Compounds Synthesised

Six bis-imides were synthesised; two bis-maleimides (the all 4-substituted isomer I and the 4,3-substituted isomer II), two corresponding bis-citraconimides (the all 4-substituted isomer III and the 4,3-substituted isomer IV), and the two corresponding bis-nadimides (the all 4-substituted isomer V and the 4,3-substituted isomer VI). V was obtained pure as synthesised, VI could be recrystallised.

Bis-Maleimides and Bis-Citraconimides

The bis-maleimides and bis-citraconimides were obtained impure as synthesised. A recrystallisation procedure could not be found for any of these compounds, which could not be purified by reprecipitation or solvent washing methods either. Preparative HPLC was found to be a highly successful method of purifying these four compounds. Bis-4-maleimidophenylmethane was purified successfully by passing a solution through a neutral activated alumina column.

The major impurity found in the bis-citraconimide III was found to be the citraconimide-itaconimide mixed-imide structural isomer. This showed that under the reaction conditions used, citraconic-itaconic isomerisation had occurred.
Some melting points of the crude materials were the same as those of the pure, some were considerably lower or higher. The all 4-substituted bis-maleimide I, in which no melting point could be observed when impure, melted sharply when pure. The impure materials appeared to be less crystalline than the corresponding pure.

Within the pure materials it was found that:
The m-isomers had considerably lower liquifaction temperatures than the corresponding p-isomers. Citraconimides had slightly lower liquifaction temperatures than the maleimides. The m-isomers appeared to be much less crystalline than the corresponding p-isomers, and had much broader liquifaction ranges.

Within the pure materials it was found that the bis-maleimides polymerised at much lower temperatures than the bis-citraconimides.

By DSC a second exothermic reaction at higher temperatures was observed in the pure bis-maleimides. This was not observed for the bis-citraconimides, although this may have been due to both reactions occurring within the same temperature range, i.e. the second exotherm peak was obscured by the first.

The purity was shown to critically affect the thermal polymerisation reactivity of the synthesised bis-maleimides and citraconimides. This was also demonstrated for the well-known bis-4-maleimidophenylmethane. The reactivity of pure bis-maleimides was much greater than that of impure, and no second exotherm was observed in the crude materials. The lower reactivity of the crude bis-
maleimide II was duplicated by doping the pure material with approximately 2% hydroquinone, a known inhibitor. The effect of impurity on the two bis-citraconimides differed.

Scanning and isothermal DSC methods yielded Arrhenius parameters useful in predicting relative polymerisation reaction rates and their variation with temperature. The overall order of reaction for this process, contrary to some previous literature reports, was found to vary continuously throughout the course of the reaction. It is believed that this is consistent with a system constantly increasing in viscosity. The Arrhenius parameters and average overall reaction orders could not be related to detailed chemical mechanism.

**Bis-Nadimides**

Thermally induced processes in the bis-nadimides V and VI appeared more complex than those in bis-maleimides and bis-citraconimides. The thermal behaviour was affected by increases in pressure. The increased pressure possibly reduced cyclopentadiene loss by volatilisation from the bis-imide.

As measured by TGA, the weight loss associated with volatilisation of cyclopentadiene in retro Diels-Alder reaction did not vary as a simple function of temperature.
DSC rescans of bis-citraconimide polymers depicted step transitions probably due to glass transitions. However, no such indications were so obvious for the poly(bis-maleimide)s or poly(bis-nadimides)s.

No great differences between the polymers were observed in thermal or thermo-oxidative stability by TGA under nitrogen or air flow, although stabilities under air were lower than those under nitrogen as expected.
Suggestions for Future Work

1. Fundamental work needs to be carried out to elucidate the detailed structure of thermally polymerised maleimides. Simple monomaleimides (eg N-phenylmaleimide) could be used as model compounds for this purpose. It might be possible to use Gel Permeation Chromatography or HPLC to separate fragments in the thermally polymerised samples. Low molecular weight fragments could be examined by NMR, IR, and other techniques to elucidate their structure. This might yield information on the thermal polymerisation mechanism.

2. Further investigation of the DSC behaviour of highly pure maleimides and their second thermally-induced reactions is required. The effect of different chains between imide groups could be examined, as well as some monomaleimide structures.

3. The mechanical properties of the bis-maleimide resins need to be elucidated to determine their potential as practical matrix resins for composites.

4. Separation of the different components in the crude bis-maleimides to isolate and identify the inhibiting impurity would be of interest.

5. Synthesis and characterisation of the Michael Addition products of the bis-maleimides and bis-aminophenoxyphenyl sulphones reported here might yield potentially useful polyaspartimides crosslinkable for composite applications.
6. The DSC methods used to determine polymerisation rates and kinetics could be used to examine other known purified bis-maleimide and bis-citraconimide systems to determine whether the findings (e.g., order of reaction) apply to systems other than the four arylene ring compounds examined in this thesis.

7. The effect of purity on thermo-oxidative stability could be examined by thermogravimetric analysis.
References


Appendix

Melt-Polymerisation Behaviour of some Reported Bis-Imides

MP = Melting Point
To = Thermal Polymerisation Onset Temperature by DSC
T\text{Max} = Temperature of DSC Exotherm Peak Maximum
T_F = Temperature of End of Thermal Polymerisation by DSC
Ref. = Reference number

All Heating Rates 10°C/min.

<table>
<thead>
<tr>
<th>Structure</th>
<th>MP/°C</th>
<th>To/°C</th>
<th>T\text{Max}/°C</th>
<th>T_F/°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-R_1-M</td>
<td>195</td>
<td>200</td>
<td>250</td>
<td>370</td>
<td>41</td>
</tr>
<tr>
<td>C-R_1-C</td>
<td>180</td>
<td>200</td>
<td>250</td>
<td>380</td>
<td>41</td>
</tr>
<tr>
<td>C-R_1-D</td>
<td>222</td>
<td>232</td>
<td>250,305</td>
<td>381</td>
<td>41</td>
</tr>
<tr>
<td>D-R_1-D</td>
<td>265</td>
<td>270</td>
<td>295</td>
<td>340</td>
<td>41</td>
</tr>
<tr>
<td>M-R_2-M</td>
<td>122-125</td>
<td>195</td>
<td>275</td>
<td>330</td>
<td>27</td>
</tr>
<tr>
<td>M-R_3-M</td>
<td>157-160</td>
<td>185</td>
<td>245</td>
<td>325</td>
<td>27</td>
</tr>
<tr>
<td>M-R_4-M</td>
<td>246-250</td>
<td>260</td>
<td>263</td>
<td>330</td>
<td>27</td>
</tr>
<tr>
<td>M-R_5-M</td>
<td>203-205</td>
<td>220</td>
<td>285</td>
<td>350</td>
<td>27</td>
</tr>
</tbody>
</table>

WHERE:

\[
\begin{align*}
\text{N} & \quad = \quad \text{M} \\
\text{H} & \quad = \quad \text{C} \\
\text{Cl} & \quad = \quad \text{D}
\end{align*}
\]