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SYNTHESIS AND CHARACTERISATION OF METHYLATED AROMATIC  
POLYMERS BASED ON DURENE

A THESIS PRESENTED BY KEVIN HUGH PATTERSON, TO THE  
UNIVERSITY OF ST ANDREWS FOR THE DEGREE OF DOCTOR OF  
PHILOSOPHY.

JUNE, 1990.



Th 1222

I, Kevin Hugh Patterson, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any degree or professional qualification.

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DEDICATION

To the eclipsing binary R Arae,  
whoever it may be.

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ABSTRACT

In Chapter I the commercial sources of durene (1,2,4,5-tetramethylbenzene) are identified along with its current use and availability. Also structures of various polymers are evaluated and related to their physical properties.

In Chapter II the diacylation of methylated benzenes is reviewed. Preparation of difunctionalised derivatives based on the diacylation of mesitylene, durene and isodurene by substituted acylating agents is described. In particular the synthesis of bis(4-fluorobenzoyl)durene (Bis-F), bis(4-chlorobenzoyl)durene (Bis-Cl), bis(4-nitrobenzoyl)durene (Bis-NO<sub>2</sub>), bis(3-nitrobenzoyl)durene (Bis-mNO<sub>2</sub>), bis(4-fluorobenzoyl)isodurene (1,3-Bis-F) and bis(4-fluorobenzoyl)mesitylene (Bis-mesF) is achieved using an excess of acylating agent as solvent.

In Chapter III the polymerisation of the derivatives Bis-F, Bis-Cl and Bis-mesF from Chapter II is achieved with a range of diphenols including hydroquinone (HQ), 4,4'-dihydroxybenzophenone (DHBP), 2,2-bis(4-hydroxyphenyl)propane (Bis-A), bis(4-hydroxyphenyl)sulphone (Bis-S), 4,4'-thiodiphenol (TDP) and 4,4'-biphenol (PDP). Also in some polymerisations, a second dihalide monomer, either 4,4'-difluorobenzophenone (DFBP) or 4,4'-difluorodiphenylsulphone (DFS), was incorporated. Overall 10 new polymers were synthesised whose glass transition temperatures ranged from 178°C to 245°C. Only 4 of these new polymers had molecular weights sufficient to give reasonable mouldings and two of these, involving

combinations of the monomers Bis-F/DHBP and Bis-F/Bis-S, yielded mechanical strengths in the same order of that for unfilled poly(aryl-ether-sulphone) (PES). Of these 10 new polymers most were amorphous although some, involving the HQ, DHBP or PDP monomers, were semi-crystalline as made, making their preparation difficult. This limited crystallinity was soon lost upon moulding or reprecipitation resulting in this new series having only moderate solvent resistance to common organic solvents. Also their temperature of decomposition is low, starting around 340°C, probably owing to oxidation of the pendant methyl groups.

In Chapter IV possible applications for methylated polymers are examined and the controlled oxidation of the pendant methyl groups is attempted with limited success.

ABBREVIATIONS

Owing to the repeated use of various chemicals it is necessary to abbreviate their names to prevent excessive space being taken. Abbreviations are in three sections; chemical, polymer, and other, and are listed alphabetically in each section.

<u>CHEMICAL</u>	<u>ABBREVIATION</u>
Diacyldurene	A/B (acyl)
1,3-Bis(2,3,5,6-tetramethylbenzoyl)- -benzene	1,3-BDB
1,4-Bis(2,3,5,6-tetramethylbenzoyl)- -benzene	1,4-BDB
1,4-Bis[4-(4-fluorobenzoyl)- -(2,3,5,6-tetramethylbenzoyl)]-benzene	1,4-1,4-BDB
2,2-Bis(4-hydroxyphenyl)propane	Bis-A
Dibenzoyldurene	Bis-H
Bis(4-chlorobenzoyl)durene	Bis-Cl
Bis(4-fluorobenzoyl)durene	Bis-F
Bis(4-fluorobenzoyl)isodurene	1,3-Bis-F
Bis(4-nitrobenzoyl)durene	Bis-NO <sub>2</sub>
Bis(3-chlorobenzoyl)durene	Bis-mCl
Dibenzoylmesitylene	Bis-mesH
Bis(4-fluorobenzoyl)mesitylene	Bis-mesF
Bis(3-fluorobenzoyl)durene	Bis-mF
Bis(3-nitrobenzoyl)durene	Bis-mNO <sub>2</sub>
4,4'-Dihydroxyphenylsulphone	Bis-S
Bis(4-chlorophenyl)sulphone	CPS

<u>CHEMICAL</u>	<u>ABBREVIATION</u>
Bis(4-chlorophenyl) sulphoxide	CPSO
4,4'-Difluorobenzophenone	DFBP
4,4'-Difluorodiphenylsulphone	DFS
4,4'-Dihydroxybenzophenone	DHBP
Dimethylsulphoxide	DMSO
Diphenyl sulphone	DPS
1,2,4,5-Tetramethylbenzene	Durene
1,4-Bis(4-fluorobenzoyl)benzene	1,4-FBB
Hydroquinone	HQ
Concentrated sulphuric acid	c.H <sub>2</sub> SO <sub>4</sub>
Propan-2-ol (Isopropyl alcohol)	IPA
Benzoylmesitylene	mono-H
4-Chlorobenzoyl durene	mono-Cl
4-Fluorobenzoyl durene	mono-F
N-Methyl-2-pyrrolidone	NMP
4,4'-Biphenol	PDP
Pyromellitic dianhydride	PMDA
4,4'-Thiodiphenol	TDP
Trimethylsilyl	TMS
Tribenzoylmesitylene	Tris-mesH

<u>POLYMER</u>	<u>ABBREVIATION</u>
High density polyethylene	HDPE
Low density polyethylene	LDPE
Polyethylene	PE
Poly[aryl(ether-ether-ketone)]	PEEK
Poly[aryl(ether-ketone)]	PEK
Poly[aryl(ether-ketone-ketone)]	PEKK

POLYMER

Poly[aryl(ether-sulphone)]  
 Poly(ethyleneterephthalate)  
 Polyimide  
 Polypropylene

ABBREVIATION

PES  
 PET  
 PI  
 PP

OTHER

Inherent viscosity  
 Polymer heat of fusion  
 Amorphous  
 Boiling point  
 Differential Scanning Calorimetry  
 Gas-liquid Chromatography  
 Gel Permeation Chromatography  
 Melting point  
 Nuclear Magnetic Resonance  
 Permanantly semi-crystalline  
 Reaction Injection Moulding  
 Reduced viscosity  
 Semi-crystalline as made  
 Glass transition temperature  
 Thermal Gravimetric Analysis  
 Polymer melting peak  
 X-Ray Diffraction  
 Ultraviolet

ABBREVIATION

$\eta_{inh}$   
 $\Delta H_F$   
 a  
 b.p.  
 DSC  
 GLC  
 GPC  
 m.p.  
 NMR  
 psc  
 RIM  
 RV  
 scam  
 $T_g$   
 TGA  
 $T_m$   
 XRD  
 UV

## Chapter I: Introduction

The mechanical strength and solvent resistance of a polymer is dependent on a wide variety of factors. However, one of the most crucial factors is the chemistry of the polymer itself, as it is this that determines the nature of intermolecular forces.

The structure of a polymer can be considered in three levels, each level introducing a greater degree of complexity:

1) The primary structure, i.e. the sequence and type of functional groups on the polymer backbone. These determine its stiffness and polarity which fundamentally set the limits on the polymer's ultimate tensile strength. They also determine the chain strength as well as its chemical stability particularly at elevated temperatures.

2) The secondary structure, i.e. the shape of the chain. Whether it is linear, helical, etc., determines the strength of both intermolecular and intramolecular interactions.

3) The tertiary structure, i.e. the arrangement of one chain with respect to another. If the chains have a tendency to align themselves in a regular fashion, the polymer is likely to be crystalline. However, if the chain arrangement is more random, a less dense, less rigid amorphous structure will be the probable result.

In general, with polymers there is never 100% crystallinity but an internal mixture of a hard crystalline component and an amorphous rubber-elastic

component. Even high density polyethylene has only 70-90% crystallinity<sup>1</sup>. At room temperature polyethylene is impact resistant (tough) but becomes brittle below -70°C as its amorphous phase freezes<sup>2</sup>.

Polyethylene (PE) is one of the simplest polymers known (see figure 1), and is usually synthesised from ethylene by one of two means: high pressure emulsion polymerisation to produce low density polyethylene (LDPE) with many branches; and Ziegler-Natta polymerisation to produce high-density polyethylene (HDPE) with little or no branching.

Figure 1: Polyethylene (PE)



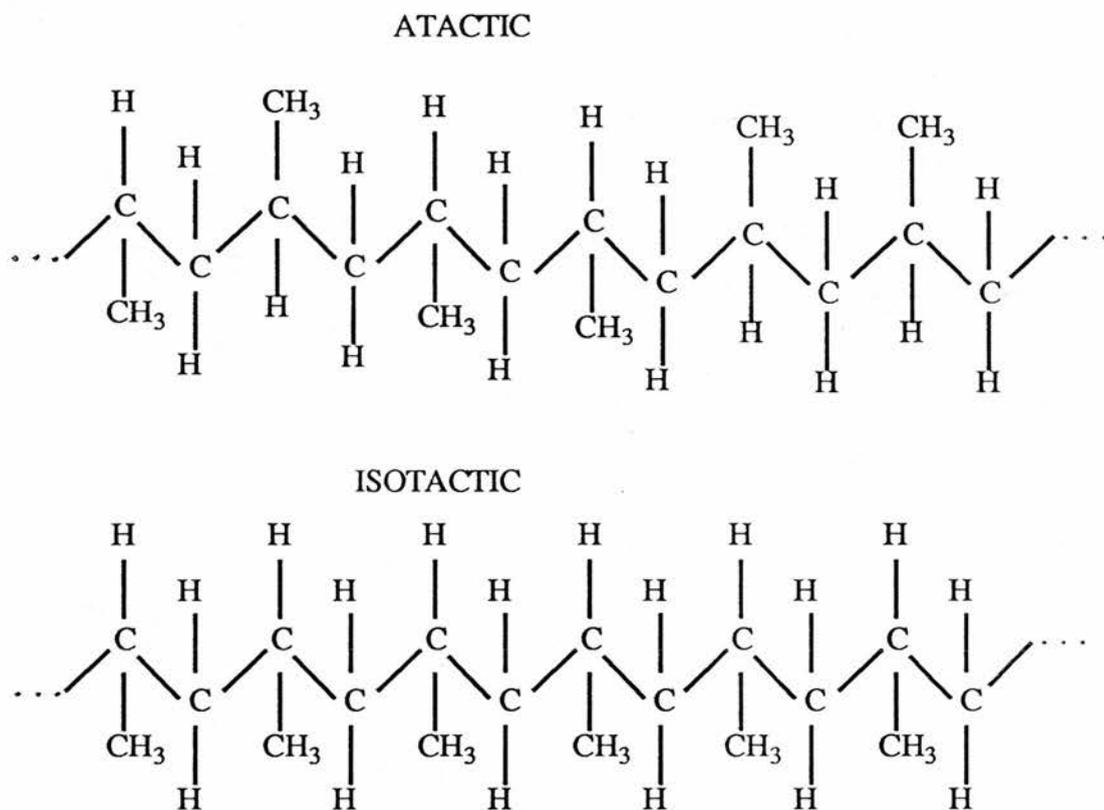
The degree of branching dramatically affects the properties of these two varieties. The more regular HDPE is able to be closely packed yielding a highly crystalline structure which is stronger, denser, more opaque, higher melting, and more solvent resistant than the more amorphous LDPE.

Polypropylene (PP), synthesised from propylene, has pendant methyl groups the arrangement of which affects the regularity of the polymer chain (see figure 2) and therefore the properties of the polymer as a whole<sup>1</sup>.

Atactic (random orientation of pendant methyl groups) polypropylene, where the polymerisation takes place without stereochemical control, is a rubbery solid of little

commercial value. Using Ziegler-Natta catalysts (as for HDPE) isotactic (pendant methyl groups on the same side of the polymer backbone) polypropylene can be produced which is a regular crystalline polymer with good mechanical strength.

Figure 2: Polypropylene (PP)

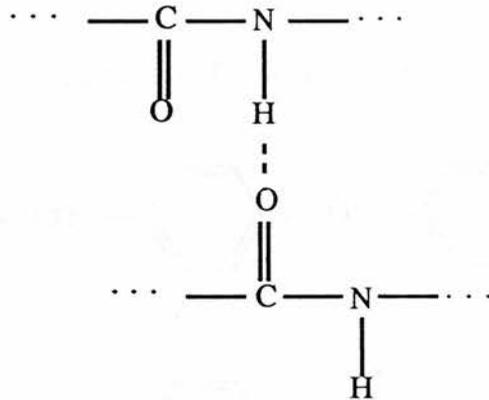


Nylon, a polyamide usually synthesised from a polycondensation of a diamine and a diacid, has extremely strong intermolecular forces (see figure 3) owing to the presence of hydrogen bonding between the chains.

This intermolecular attraction is so strong that, to achieve their optimum mechanical strength, polyamides

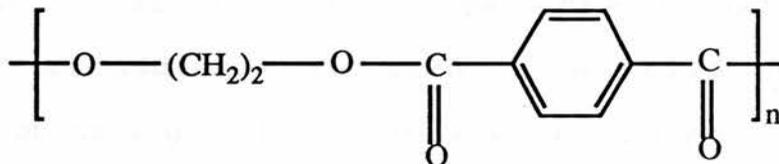
typically have molecular weights an order of magnitude lower than polyethylenes i.e.  $10^4$  as opposed to  $10^5$ .

Figure 3: Nylon



Introduction of aromatic rings into the polymer backbone, as in poly(ethyleneterephthalate) (PET), has the effect of "stiffening" it (see figure 4), and hence produces a material with a high tensile strength ( $57 \text{ MN m}^{-2}$ ) when compared to the aliphatic polymers LDPE ( $17.3 \text{ MN m}^{-2}$ ), HDPE ( $34.6 \text{ MN m}^{-2}$ ) and polypropylene ( $41.5 \text{ MN m}^{-2}$ ).

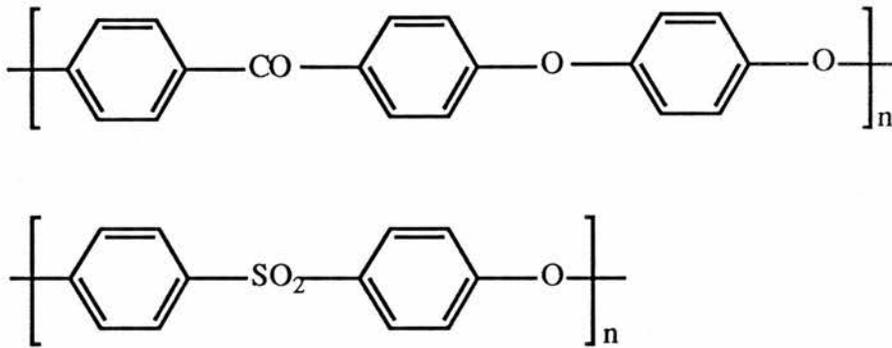
Figure 4: Poly(ethyleneterephthalate)



Poly[aryl(ether-ether-ketone)] (PEEK) and poly[aryl(ether-sulphone)] (PES) are rapidly becoming the engineering materials in common use today (see figure 5).

These almost totally aromatic polymers have very good mechanical strengths and solvent resistances, PEEK being soluble only in concentrated acids. PES has good solvent resistance to a more limited range of solvents which do however include JP5 (jet fuel).

Figure 5: PEEK and PES.



Until recently only low molecular weights were obtainable for PEEK, the problem being that it was too insoluble to be polymerised to high molecular weights<sup>3</sup>. Then in 1975 ICI discovered and patented a new high temperature polymerisation/solvent<sup>4</sup> system that inhibited premature precipitation of this and other crystalline polymers before high molecular weights were obtained.

Polymerisation is a chain-growth process and, whether it be by an addition reaction or a polycondensation reaction, obtaining high molecular weight polymer before it precipitates out of solution is a common problem. The usual route around this is to polymerise at the melting point of the polymer, but this may not be possible if temperature instability problems exist.

Aromatic polymers exhibit far better fire resistance than aliphatic polymers as the hydrogen:carbon ratio is very much lower in the former. This leads to carbonaceous charring upon ignition which terminates the combustion process<sup>5</sup>.

Introduction of a filler such as glass or carbon fibre can substantially increase the strength of a polymer. Glass fibre, typically of 100 $\mu$ m length and 2-10 $\mu$ m diameter, would increase the flexural strength of PEEK threefold. Conversely reducing the flexural strength, i.e. making the polymer more like a rubber, can be accomplished by the addition of a plasticiser, such as glycerol, to the polymer matrix. However, for proper mixing to occur the two components must be compatible i.e. have similar solubility parameters<sup>6</sup>.

Cross-linking a polymer<sup>7</sup>, by chemical bonding between polymer chains to convert it into a three-dimensional resin, has the effect of making it very hard and strong, but also more brittle. Once cross-linking has occurred the polymer generally cannot be remoulded and therefore becomes a thermoset rather than a thermoplastic. Commonly in moulding operations the uncrosslinked polymer is reaction injection moulded (RIM)<sup>1</sup> with a cross-linking agent e.g. an epoxy resin.

Polyimides (PI) are another class of highly aromatic polymers which are attracting considerable attention as engineering materials, particularly as they have good solvent resistance except to concentrated acids. As can be seen<sup>8-10</sup> in Table 1, the polyimide illustrated in figure 6

demonstrates a significant increase in high temperature use properties over the other polymers; however the use of polyimides at only 900 tonnes/year in 1982 was not widespread due to two reasons.

Figure 6: A polyimide of N-(3-aminophenyl)-4-(3-aminocarbanilino)-phthalimide and isophthaloyl chloride.

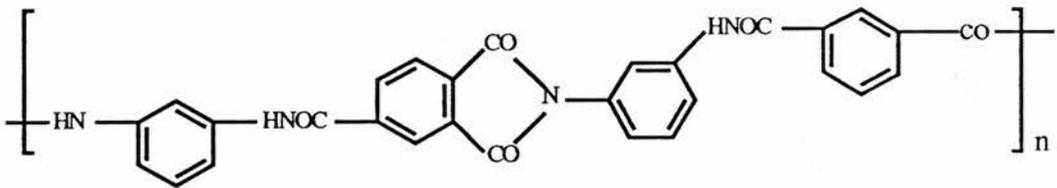


Table 1: Some polymer physical properties.

	Nylon 6/6	PET	LDPE	HDPE	PP	PI <sup>a</sup>	PEEK	PES
Density (g cm <sup>-3</sup> )	1.13	1.3	0.93	0.95	0.90	1.5	1.5	1.38
Tensile Strength (MN m <sup>-2</sup> )	83	57	17.3	34.6	41.5	130	91	84
Deflection Temperature (°C) at 1.81 MN m <sup>-2</sup>	75	50	90	121	140	360	160	203
Cost (£/kg)	1.1 (1982)	-	0.6 (1989)	0.6 (1989)	-	40 (1982)	50 (1989)	10 (1989)

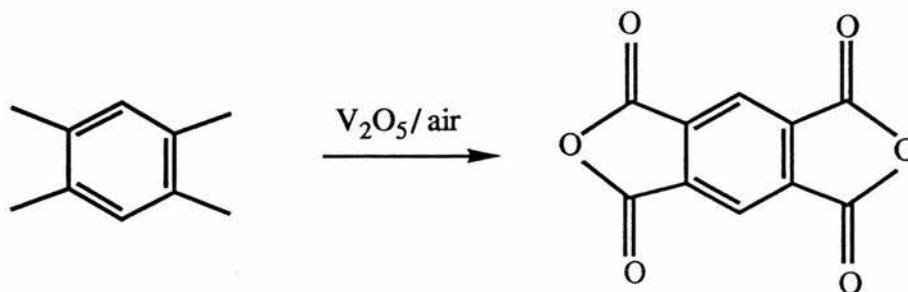
a - polyimide of N-(3-aminophenyl)-4-(3-aminocarbanilino)-phthalimide and isophthaloyl chloride.

Most polyimides are thermosets while the other polymers mentioned so far are thermoplastics. This is in part due to the polyimides' properties, i.e. they have processing temperatures which exceed their stability therefore requiring them to be synthesised upon moulding (RIM). The second reason is cost, at approximately £40/kg (1982) they are only economic in low volume speciality areas such as in aerospace/military applications of transmission gears, electric motors, and insulation of aircraft and missile cables.

PEEK at approximately £50/kg (1989) suffers from the same problems, while PES at approximately £10/kg (1989) only just becomes economic as a metal part replacement in commercial aircraft (which leads to a lighter structure and subsequent fuel savings).

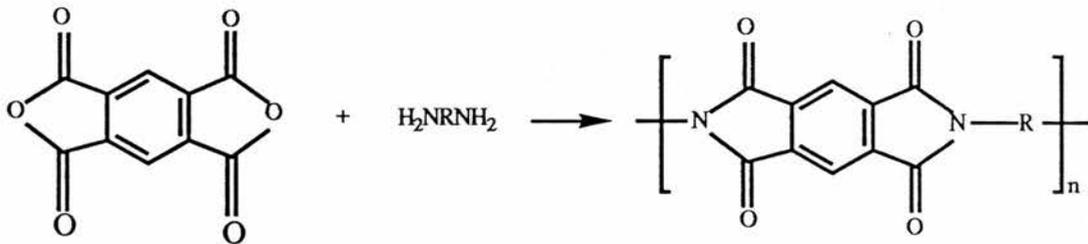
The high cost of polyimides arises from the difficulty in making the bis-anhydrides. Pyromellitic dianhydride (PMDA) is one such bis-anhydride and is obtainable (see figure 7) from the oxidation of durene (1,2,4,5-tetramethylbenzene).

Figure 7: Synthesis of PMDA.



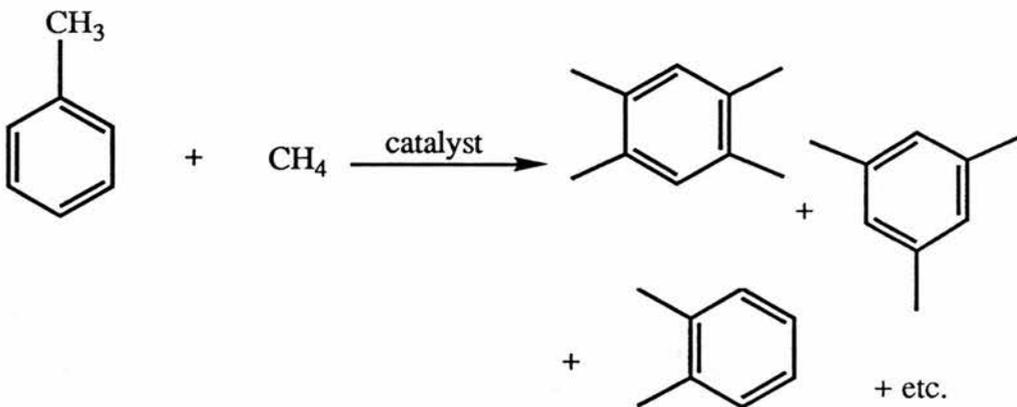
PMDA is then reacted with a suitable diamine to yield a polyimide (see figure 8) the properties of which are influenced by the choice of diamine.

Figure 8: Synthesis of polyimides from PMDA.



Durene in the past was prepared in commercial quantities by methylating aromatic hydrocarbons (see figure 9) and then separating it out of the resulting indiscriminate mix, most of which has little commercial value<sup>8</sup>.

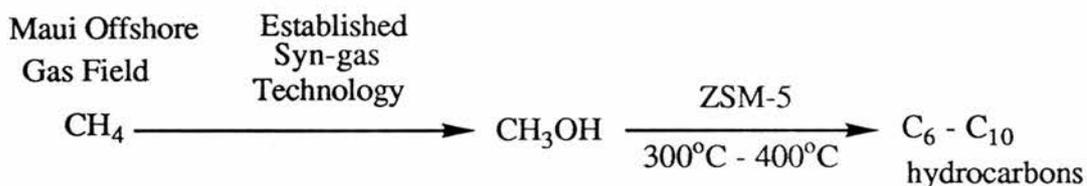
Figure 9: Synthesis of durene from methylated hydrocarbons.



Political and economic considerations however affect the direction of commercial research just as much as chemical pathway possibilities. Therefore these factors must be considered in the following preamble.

In February 1985 the Motonui gas-to-gasoline Syn-fuels plant opened in Taranaki, New Zealand. This plant used for the first time on a commercial scale the zeolite catalyst ZSM-5 to convert methanol to petrol (see figure 10).

Figure 10: Gas to Petrol.



Owing to size-shape selectivity in the catalyst<sup>11</sup>, a major side-product is durene. This is preferred over the trimethylated benzenes which are too small in size to be thermodynamically stable in the intracrystalline space. The other tetramethylated benzenes, although formed in the intracrystalline space, are too unsymmetric to escape down the narrow sieve exitways.

Durene is produced at the rate of 30 000 tonnes/year, an amount which under slightly higher temperatures can be increased to 70 000 tonnes/year. The durene presents some technical problems, to the main purpose of the plant (producing petrol), as it is a solid at room temperature (m.p 79°C) and tends to crystallise out in the pipelines. Also it has to be hydrocracked as the demand for its use has not yet arisen, owing to polyimides being thermosets rather than thermoplastics as previously mentioned. However, in principle, this process makes durene an

attractive commercial chemical feedstock for the first time.

Table 2: World oil prices 1972-1990.

Year	Price Oil \$US/barrel
1972	2
1975	20
1979	40
1985	15
1990	20

The Motonui plant is the first plant of its type in the world owing to a New Zealand government political/economic decision in 1980. At that time oil prices were rising (see Table 2) and a large gas reserve, rated in the world's top 20, was available locally off the Taranaki coast (Maui). This was coupled with the possible threat to national security as all oil had to be imported from the Middle East 9000 miles away past possibly unfriendly countries, along with the need to create jobs and a local skills base<sup>12,13</sup>.

However, falling oil prices due to worldwide energy conservation and increased oil exploration means that no other plants of its type have yet been built. The discovery of the McKee oil field (also in Taranaki) in 1985 threatens the viability of the Motonui plant unless a high-value use can be found for durene.

In August 1987 an ICI/NZ government group was formed to investigate the commercial exploitation of durene. The work described in this thesis was initiated as part of that investigation.

#### Objectives of the Project

Whereas durene had previously been used widely in polymer synthesis only as a source of PMDA, it was hoped to use durene in such a way that the four methyl groups would still be present in the final polymer. The aim was to attempt to functionalise durene at the two unmethylated positions on the benzene ring in such a way as to produce a difunctional monomer. It was accepted that the susceptibility of the methyl groups to oxidation at high temperatures might limit applications of such materials; however, it was hoped that the bulk of the pendant groups might alter the secondary or tertiary structure of the polymer relative to unmethylated analogues. It was also envisaged that the pendant methyl groups might eventually be used for crosslinking purposes by subsequent functionalisation, or by controlled oxidation to give polar materials for membrane applications.

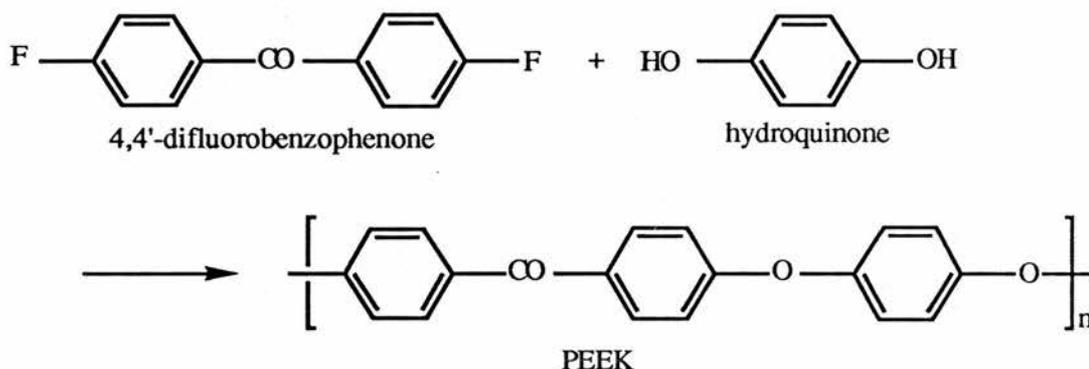
## Chapter II : Friedel-Crafts Diacylation of Durene

### 2.1 Introduction

Friedel-Crafts acylations generally occur between an acyl component and an aromatic substrate, with a catalyst, to yield an aromatic ketone.

Benzene, is found to be acylated only once under normal reaction conditions. Durene, however, with its four 'electron donating' methyl groups is capable of undergoing diacylation as will be shown in the following discussion.

Figure 11: Synthesis of PEEK

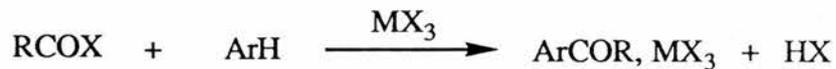


This leads to the possibility of difunctionalised derivatives which can be used in PEEK [poly(aryl-ether-ether-ketone)] type polymerisations (see figure 11), where durene, diacylated with suitable halogenated acyl components, may replace the 4,4'-difluorobenzophenone (DFBP).

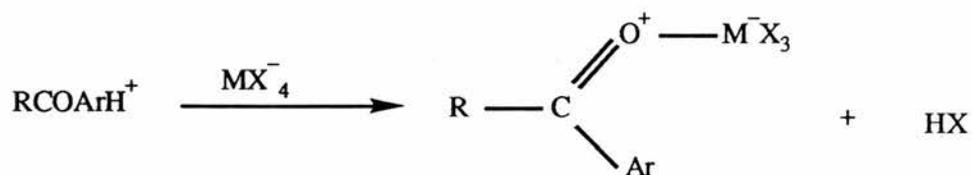
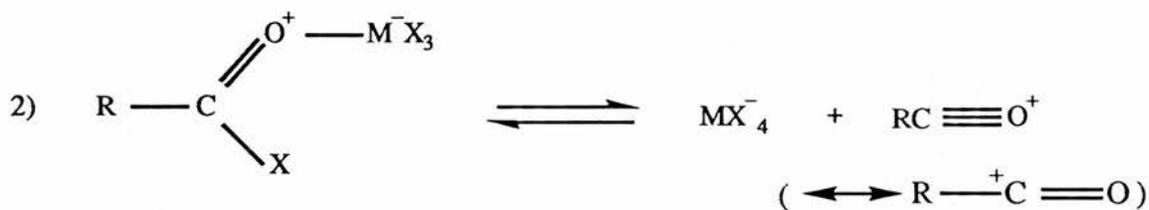
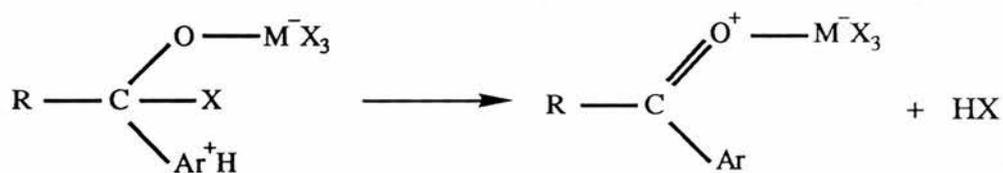
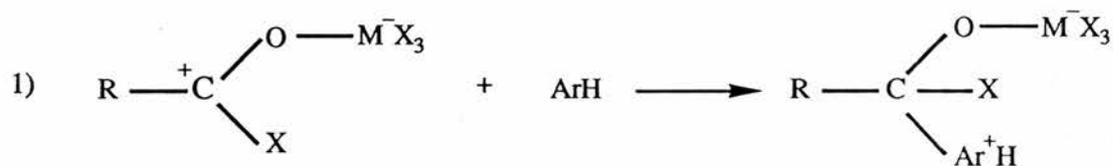
## 2.2 General Features of Friedel-Crafts Acylations

### 2.2.1 Mechanism

For a reaction of



the mechanism may be one of two types:-



It has been shown via X-ray diffraction studies on crystals, formed from benzoyl chloride - aluminium chloride mixtures in carbon disulphide, that intermediates of the type found in mechanism 1) exist, although it must be

remembered that these studies were, of necessity, conducted in the solid state rather than in solution<sup>16</sup>.

Also it has been established that carbon monoxide is quantitatively formed from the decomposition of several aliphatic anhydrides involved in acylation additions, a reaction expected from the type 2) mechanism intermediates<sup>17</sup>.



In general the type 1) mechanism predominates except in cases where the acyl component or the aromatic substrate is sterically hindered whereupon the type 2) mechanism is favoured<sup>14,15</sup>.

Both mechanisms are kinetically indistinguishable having second order kinetics of the type

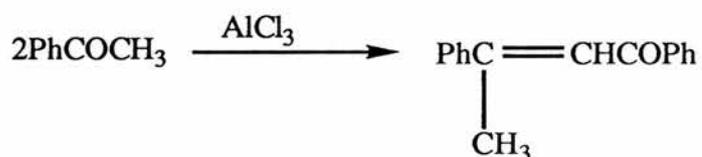
$$\text{rate} = k_2[\text{ArH}][\text{RCOX}] .$$

### 2.2.2 Solvents

With regard to solution behaviour, such acylations can take place in two extreme environments:- heterogeneous and homogeneous. The main effect on the acylation is in yield obtained. Poor solvents such as carbon disulphide tend to promote heterogeneous behaviour as neither aluminium chloride nor its complexes with the acyl chloride are appreciably soluble. Intermediate solvents such as methylene chloride fall in between the two extremes while good solvents such as nitrobenzene or a solution in the acylating agent itself tend to be homogeneous<sup>18</sup>.

### 2.2.3 Catalyst

Care has to be taken in using the right amount of catalyst. Aluminium chloride (the most common such catalyst) is a strong Lewis acid and if used in excess, uncomplexed by solvent or reagent, it may bring about undesirable side reactions such as dehalogenation<sup>19</sup> or dealkylation<sup>20</sup> of the substrate, resulting in carbonised material. If the reaction is prolonged, at high temperature, not only may these reactions manifest themselves but other side reactions such as aldol-type condensations may also occur<sup>21</sup>.



Water contamination of the catalyst, if slight, is known not to inhibit the reaction via catalyst hydration, but can in some situations aid the reaction by forming an even stronger acid and also releasing the heat required to initiate the reaction.

## 2.3 Benzene and Methylated Benzenes as Aromatic Substrates

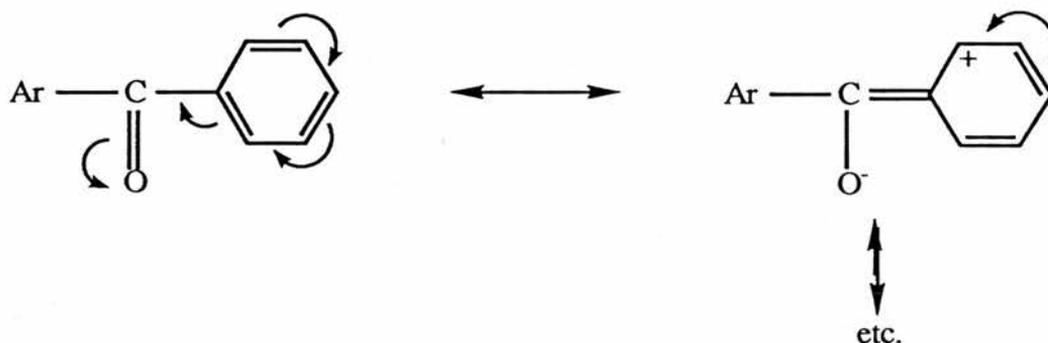
### 2.3.1 Benzene

In general only monoacylation occurs with this substrate, even in excess benzoyl chloride<sup>22</sup>, owing to the ring becoming deactivated through electron withdrawal by the acyl substituent (see figure 12). It has been reported that 1,3-dibenzoylbenzene and a little 1,3,5-

tribenzoylbenzene are formed from renewed treatment of benzophenone with benzoyl chloride and aluminium chloride in a ratio of 1:3:3 (catalyst:substrate:acylating agent) under extremely vigorous conditions (200-220°C/48hours). However the likelihood of the central ring of the diacylated compound being further acylated, when there are other singly acylated rings adjacent, is small. This coupled with the large amount of tarry material reported, renders this last claim to be of somewhat dubious value<sup>23</sup>.

Simultaneous acylation and alkylation may occur when both acyl and alkyl halides are present<sup>24</sup>.

Figure 12: Deactivation of acylated benzene.



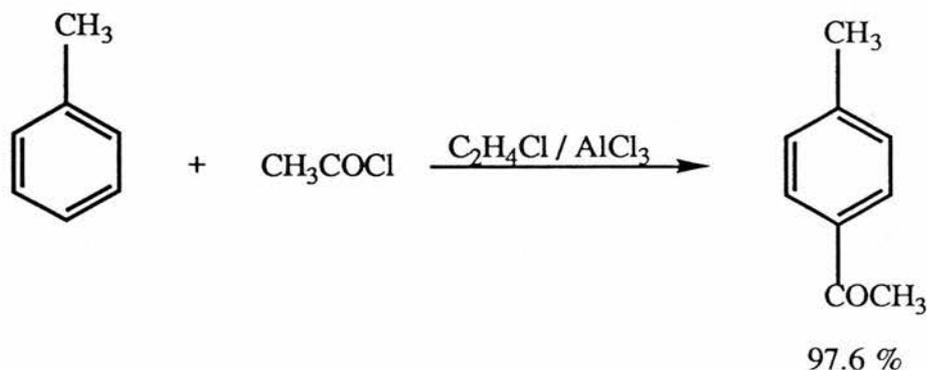
### 2.3.2 Toluene (methylbenzene)

Choice of solvent can dramatically affect the rate of benzoylation of toluene (25°C) by benzoyl chloride. For example the following relative rate constants were noted<sup>25</sup>: benzoyl chloride 30, methylene chloride 3.5, and 1,2,4-trichlorobenzene 1.

Although the last solvent promotes a homogeneous medium (disregarding benzoyl chloride which also promotes a homogeneous solution), it probably binds too tightly to the

catalyst thereby inhibiting catalyst availability to the acylating agent. This situation is utilised by benzoyl chloride only when it acts as both solvent and acylating agent

Figure 13: Acetylation of toluene



In general only the *p*-isomers occur (see figure 13), and diacylation has not been reported<sup>26</sup>.

Owing to the ortho- and para-directing effects of methyl groups, very little *m*-isomer occurs.

Under some conditions in which the acylating agent is highly reactive, large amounts of the *o*-isomer may occur<sup>27</sup>. The reason for this is not certain, as a large number of factors govern rates of acylation and ortho : para ratios; these include (a) steric acceleration; (b) steric hindrance; (c) interaction between the substituent and reagent; (d) electronic effects; and (e) solvent effects. However, a comparative study between benzene and toluene was made of these effects by Olah using substituted benzoyl chlorides (see table 3).

Use of electron donating methyl and fluorine groups ortho- or para- to the benzoyl cation decreases its reactiveness, although this is somewhat countered in the *o*-fluoro case, by its inductive strength, as it is in close proximity to the cation. Hammett<sup>28</sup> constants ( $\sigma^+$ ) for the electron donating effectiveness of methyl ( $\sigma^+ = -0.31$ ), chlorine ( $\sigma^+ = 0.11$ ) and fluorine ( $\sigma^+ = -0.07$ ) groups in the para position compared to hydrogen ( $\sigma^+ = 0.00$ ) indicate that the situation is quite evenly balanced for the halogens and would really require experimental evaluation for a given reaction type to determine reactivity in a given situation.

Table 3: Relative rates and isomer distribution in the aluminium chloride catalysed acetylation of toluene ( $k_t$ ) and benzene ( $k_b$ ) in nitromethane solution at 25°C.

Benzoyl Chloride	$k_t:k_b$	%ortho	%meta	%para
$C_6F_5COCl$	16.1	35.4	7.8	56.8
2,5- $F_2C_6H_3COCl$	96.2	12.3	1.6	86.1
[ $CH_3COCl$	141.0	2.5	2.0	95.5]
$C_6H_5COCl$	153.5	8.1	1.2	90.7
4- $CH_3C_6H_4COCl$	164.4	7.8	1.1	91.1
4- $FC_6H_4COCl$	170.0	8.0	1.1	90.7
2,4,6- $(CH_3)_3C_6H_2COCl$	196.0	2.3	0.6	97.1

When an acylating agent of a greater reactivity is chosen, (see section 2.2.1) the transition state of higher

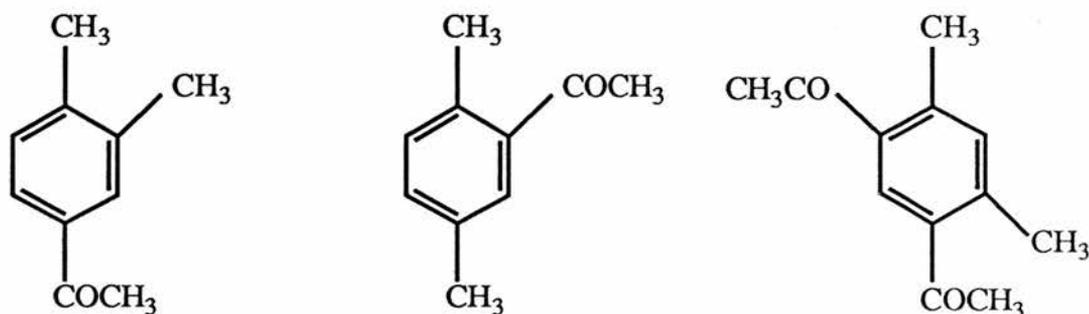
energy lies closer to the reactants (pi-complex) than the intermediates (sigma-complex) and hence is less sterically crowded (for similarly sized acylating agents); therefore o-acylation becomes kinetically more favoured. Also, as the transition state is earlier, the choice of substrate has less effect; hence  $k_t:k_b$  tends towards unity<sup>29,30</sup>.

Use of a titanium(IV) chloride catalyst reverses the relative reactivity of benzoyl chloride with respect to acetyl chloride when acylating toluene<sup>31</sup>. In the presence of aluminium chloride, acetyl chloride is the more reactive acylating agent<sup>32</sup>. The rates of both reactions decrease however, with use of the titanium chloride catalyst; it is just that the effect on the acetyl chloride rate is greater<sup>33</sup>. Hence aluminium chloride is still the more effective catalyst.

### 2.3.3 Xylene (dimethylbenzene)

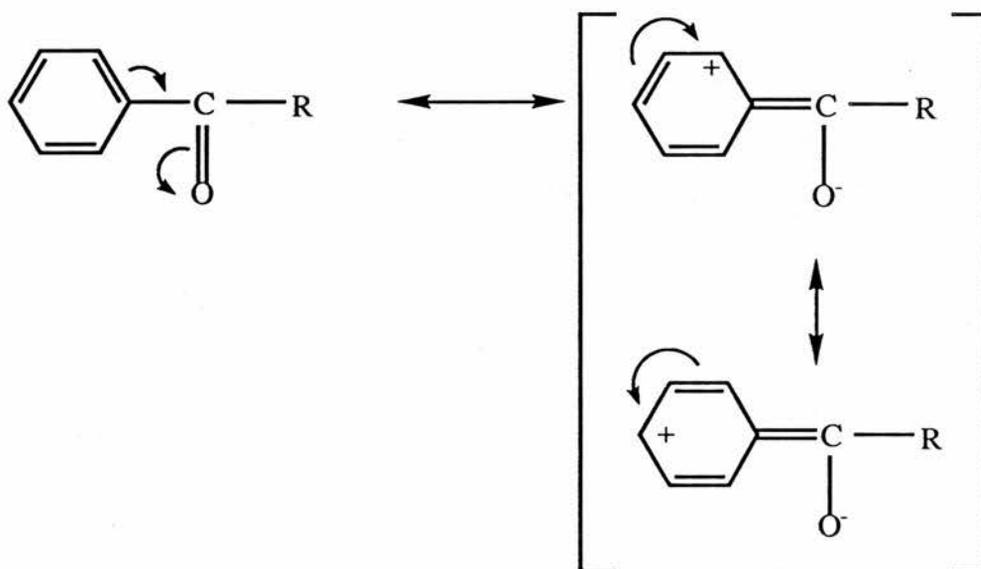
The *o*- and *p*-xylenes (see figure 14) yield only the singly acylated isomers while *m*-xylene undergoes diacylation to some extent, in excess acetyl chloride<sup>34</sup>.

Figure 14: Acylated xylenes



The interesting point here is the position of acylation. As in the case of toluene it is in the least sterically hindered position for *o*-xylene. Due to the positive inductive stabilisation offered by the methyl groups to the positions *o*- and *p*- to it, *m*-xylene can be diacylated. Only in the case of *m*-xylene do these two positions coincide for both methyl groups.

Figure 15: Deactivating effect of acyl groups.

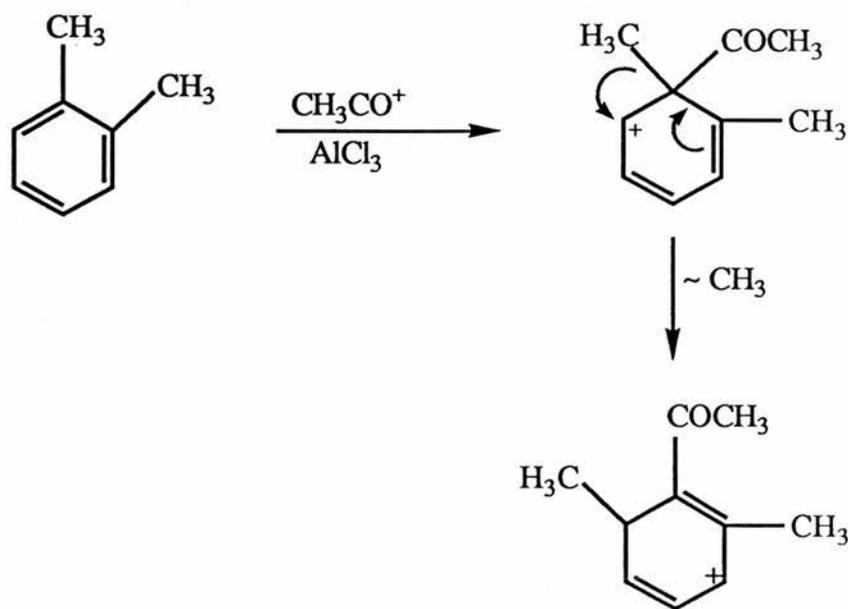


It is probably the activating effect of the second methyl group on *m*-xylene that allows diacylation in this case when compared to toluene. Steric factors for the second acylation would be essentially the same for both toluene and *m*-xylene as this acylation would prefer to occur *o*- to a  $\text{CH}_3$  group in both cases. Also the smaller directing effect of the first acyl group promotes the second acylation *m*- to it as it deactivates this site less than the *o*- and *p*- sites (see figure 15).

The diacylation of *m*-xylene is also less sterically hindered when compared to *o*- and *p*-xylene. For diacylation to occur in the *o*- and *p*-xylene cases, owing to the directing effects of both the methyl and acyl groups three adjacent sites on the benzene ring would prefer to be substituted, a sterically undesirable situation, although, as mentioned for toluene (see section 2.3.2), this sometimes depends on acylating agent reactivity. For example with *m*-xylene it has been reported that 1,3-dibenzoyl-2,4-dimethylbenzene forms as a minor product along with 1,3-dibenzoyl-4,6-dimethylbenzene (major)<sup>35</sup>.

When studying the acylation of the dimethylbenzenes the problem of methyl group migration becomes apparent, leading to isomerisation<sup>36</sup>. The *o*-xylene complex with aluminium chloride, for example, may isomerise to the more reactive *m*-xylene complex (see figure 16).

Figure 16: Methyl migration on xylene.



Hence in the acylation of *o*-xylene by acetic anhydride a large amount of 2,4-dimethylacetophenone (48%) occurs as well as 3,4-dimethylacetophenone (52%), although the yield of isomerised product can be limited to just 12% by decreasing the contact time between catalyst and substrate (see table 4).

Table 4: Product Ratio of 2,4-methylacetophenone and 3,4-methylacetophenone from the acylation of *o*-xylene by acetic anhydride.

<i>o</i> -xylene (moles)	Ac <sub>2</sub> O (moles)	AlCl <sub>3</sub> (moles)	CS <sub>2</sub> (ml)	Addn. Time (hours)	Reflux Time (hours)	Yield (%)	2,4- (%)	3,4- (%)
2.0	2.2	5.4	1150	2.25	2.5	81	52	48
0.125	0.1	0.28	50	0.5	1.0	96	88	12

It is interesting at this point to compare the yields of benzoylated product from the various substrates with benzoyl chloride (see table 5).

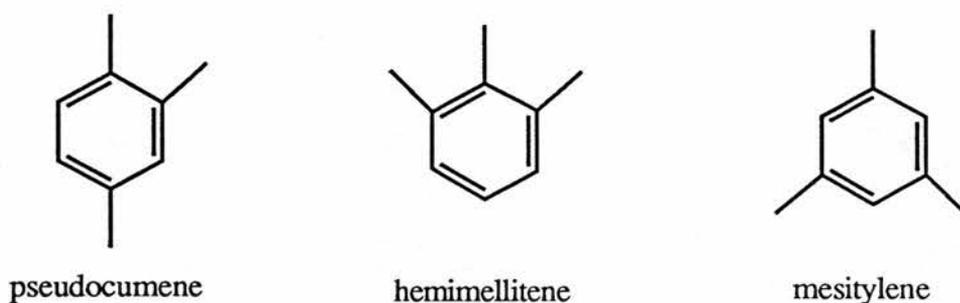
Table 5: Acylations by benzoyl chloride.

Substrate	Temp. (°C)	Time (hours)	Product	Yield (%)
benzene	80	8.5	benzophenone	14
chlorobenzene	132	5	2- and 4- chlorobenzophenone	13
toluene	110	48	2- and 4- methylbenzophenone	85
<i>o</i> -xylene	138	6	2,5- dimethylbenzophenone	82

Owing to the electron withdrawing nature of chlorine, chlorobenzene as a substrate gives a low yield (13%) when compared to *p*-xylene (82%).

#### 2.3.4 Trimethylbenzene

Figure 17: Trimethylbenzenes.



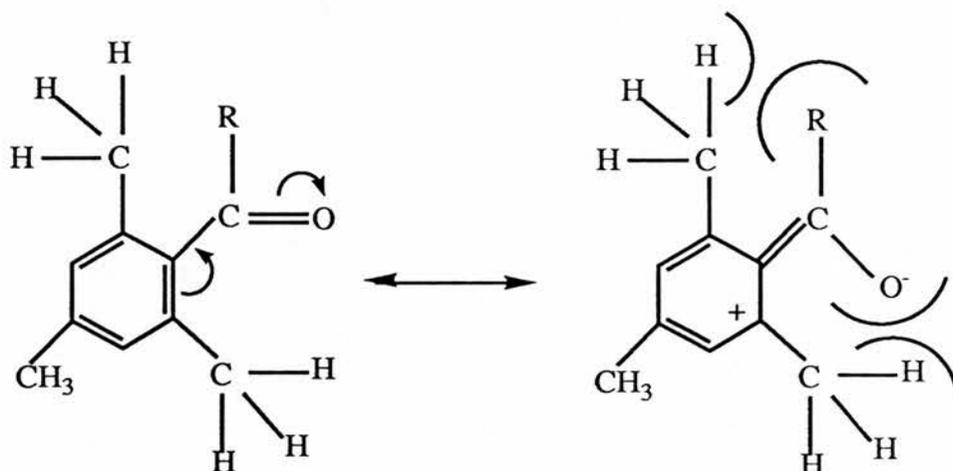
Of the three trimethylbenzenes (see figure 17) only mesitylene has been reported to be diacylated to any appreciable extent<sup>37-39</sup>. As before (see section 2.3.3 on *m*-xylene) this is due to steric/electronic effects, although in the case of mesitylene a third factor comes in - delocalisation inhibition.

Unlike *m*-xylene, the only position at which acylation can occur has to be between the methyl groups (see figure 18). Once this occurs deactivation of the ring is inhibited owing to the neighbouring methyl groups preventing the carbonyl group from becoming coplanar with the ring.

This type of hindrance has been previously noticed in the hydrolysis of 2,4,6-trimethylbenzoate esters (see

figure 19) which only proceeds in concentrated sulphuric acid ( $A_{AC1}$  mechanism) rather than in dilute sulphuric acid ( $A_{AC2}$  mechanism).

Figure 18: Delocalisation inhibition on mesitylene.



As the position of acylation is so sterically hindered it is probable that the mechanism (see section 2.2.1) of acylation is now type 2 where the electrophile is the linear  $R-CO^+$  rather than the trigonal  $R-C^+(X)-OM^+X_3$ .

Proton dissociation constants of the protonated substrates ( $SH^+$ ) make an interesting study as a measure of the electronic effects. The values in table 6 were measured by Mackor<sup>40</sup> in hydrofluoric acid i.e. mesitylene, on electronic effects alone, is a much more reactive substrate than benzene.

So, although acylation is sterically more difficult for mesitylene relative to *m*-xylene, the relative proton

acidities coupled with the inhibition of delocalisation for mono-acylated mesitylene, makes diacylation highly probable.

Figure 19: Acid hydrolysis of 2,4,6-trimethylbenzoate esters.

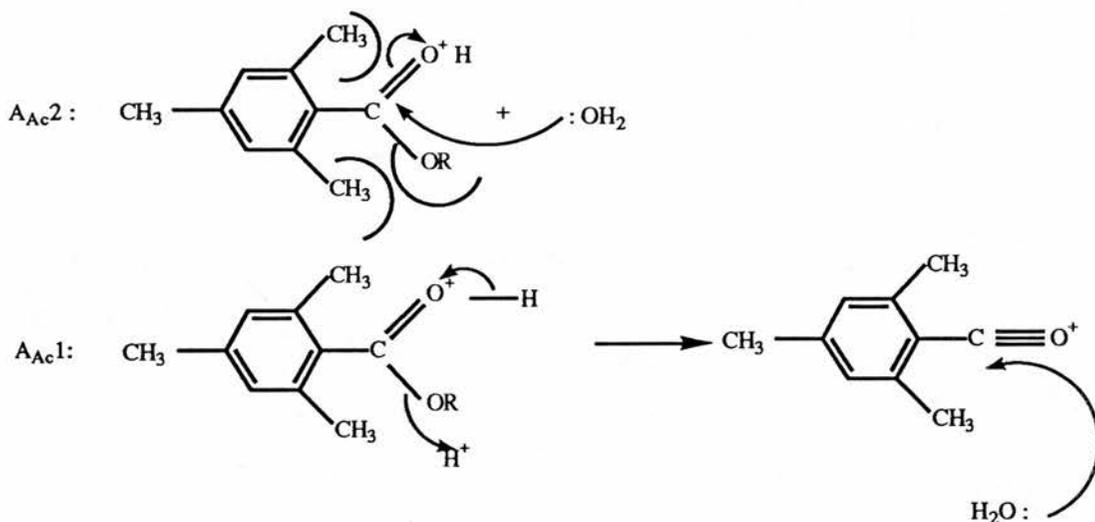


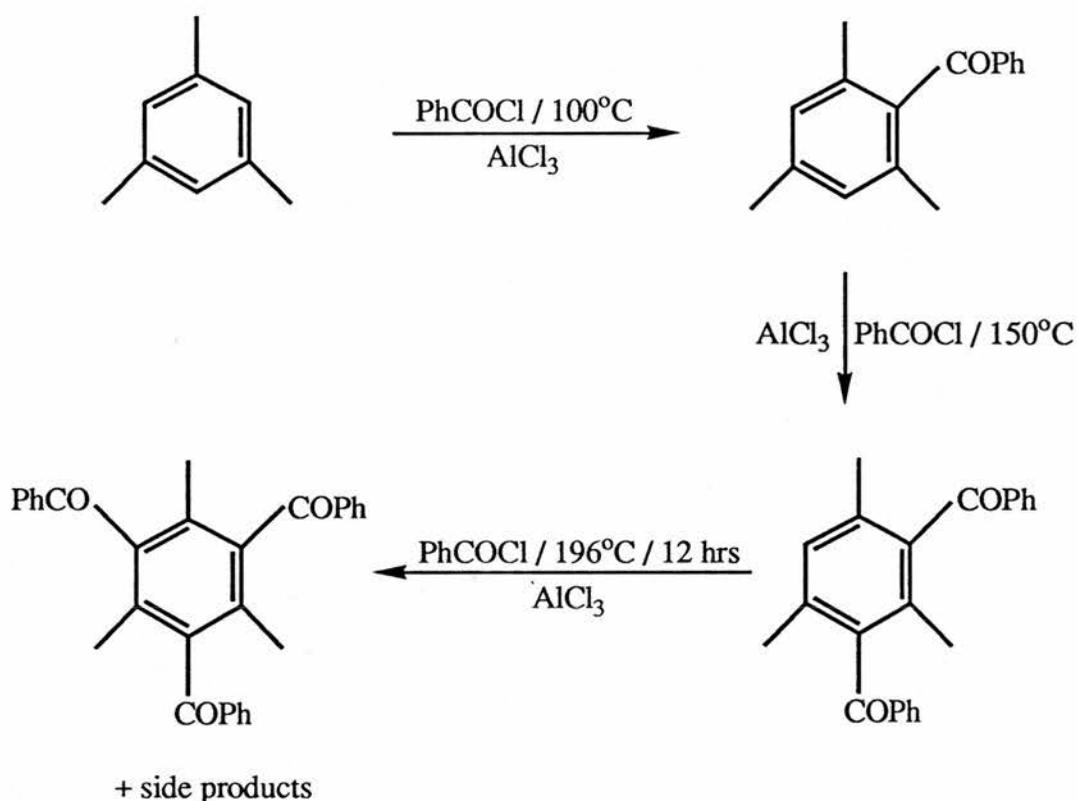
Table 6: Proton Dissociation Constants ( $\text{SH}^+$ ),  $T = 0^\circ\text{C}$ .

Substrate (protonated, $\text{SH}^+$ )	$-\log P_o$
benzene	1.35
toluene	1.55
m-, p-xylene	1.70
mesitylene	1.95

Louise<sup>37</sup> found that upon acylating mesitylene with benzoyl chloride as both acylating agent and solvent, there were three stages of acylation (see figure 20): below  $100^\circ\text{C}$

monoacylation, around 150°C diacylation, and at the boiling point of benzoyl chloride (196°C) triacylation. This last reaction, however, took 12-13 hours and then so much carbonised material was produced that it became a major operation to obtain a purified product.

Figure 20: Benzoylation of mesitylene.

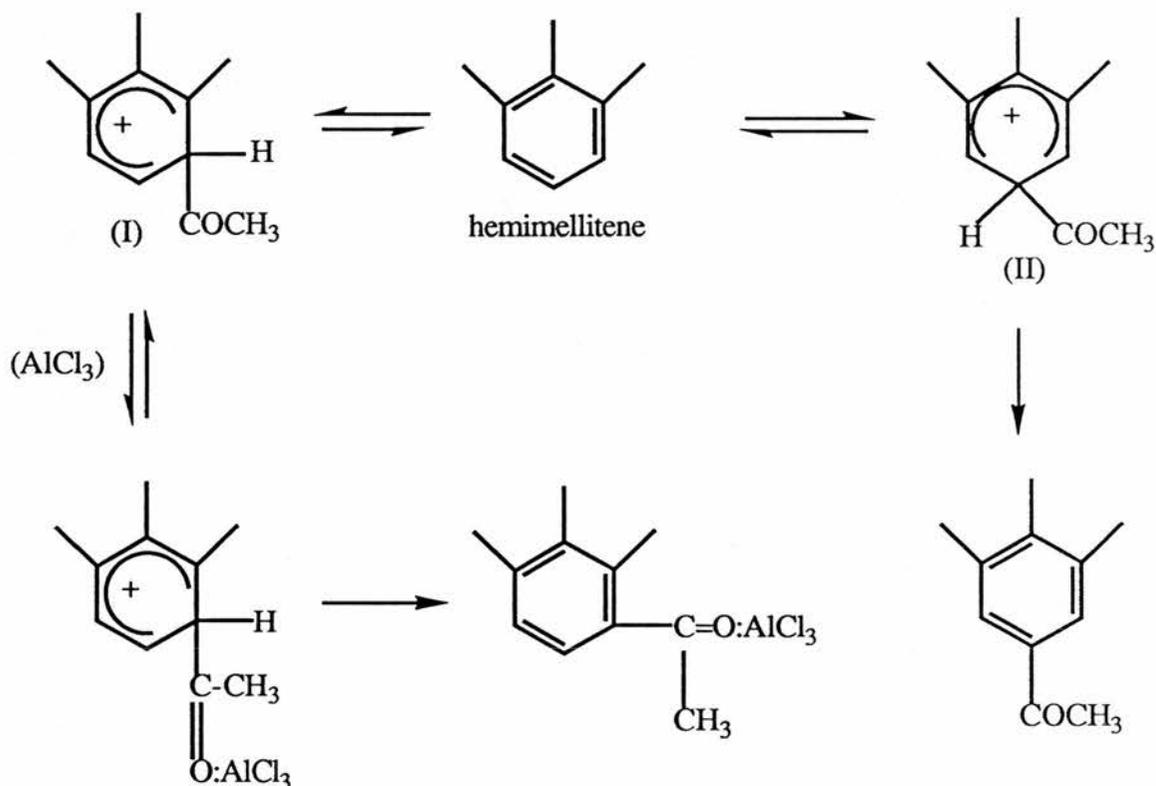


Gore and Hoskins<sup>41</sup> found however, that the dibenzoylation of mesitylene could be accomplished by benzoyl chloride in carbon disulphide (50°C).

The three methyl groups on mesitylene all constructively interact electronically to promote acylation, as they all lie either *o*- or *p*- to each of the

three vacant sites. Also, the smaller deactivating influence of the remaining activated sites by the acyl groups is limited as these sites would lie *m*- to the acylated position.

Figure 21: Acetylation of hemimellitene.



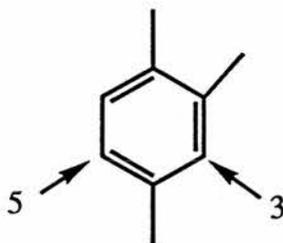
For hemimellitene (see figure 21) of the three vacant sites, two (I) are equivalent and more likely to be acylated on electronic grounds, while the third (II) is more likely to be acylated under steric constraints. It is found experimentally<sup>42</sup> that, in presence of excess catalyst, acylation is preferred next to the methyl groups (I) owing to the formation of an equilibrium (see figure

21) where the more reactive but less thermodynamically desired (I) is complexed with the free aluminium chloride.

Moreover, transacylation between reaction products has been shown not to be the cause of this situation.

Pseudocumene (1,2,4-trimethylbenzene), prefers to be acylated o- to the lone methyl group (at position 5, figure 22) thereby allowing two of its methyl groups to promote the reaction (see figure 22). The possibility of a second acylation of pseudocumene in the more sterically crowded position (position 3, figure 22) has not been reported in the literature.

Figure 22 : Acylation of pseudocumene.



Even slight variation of the experimental conditions can have a major effect on product yield. In table 7, the acetylation of mesitylene by the so called "Perrier<sup>43</sup> procedure" (which allows the catalyst and acylating agent to be mixed for a period before the addition of the substrate, as opposed to the "Bouveault<sup>44</sup> procedure" in which the catalyst and substrate are mixed, before addition of the acylating agent) in carbon disulphide, results in

varying mono-/di- ratios dependent on time, temperature, and catalyst-to-acyl component ratio<sup>45</sup>.

In general, the time/temperature components are mutually interacting, in that a lower temperature can be compensated for by reacting for a longer time. But the catalyst-to-reactant ratio is more critical, with larger catalyst proportions tending to promote the disubstitution but at the same time promoting side-reactions resulting in tarry by-products.

Table 7: Yield versus conditions for the acetylation of one mole of mesitylene.

AcCl (moles)	AlCl <sub>3</sub> (moles)	Temp. (°C)	Time (hours)	mono- (%)	di- (%)
1	1	40	0.5	92	1.4
2	3	50	0.25	50	50
2	3	50	0.5	34	66
3	6	50	1.0	-	95

#### 2.3.5 Tetramethylbenzene (durene and its isomers)

The main aim is to produce difunctionalised derivatives based on the diacylation of durene (see figure 23).

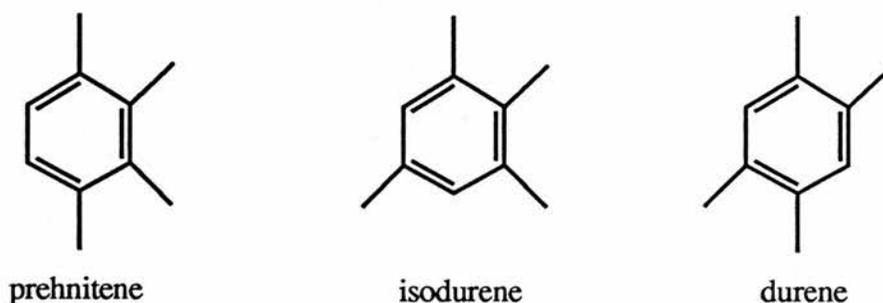
As previously discussed, benzene rings cannot be easily diacylated because deactivation of the ring usually follows the first acylation. However, owing to the increased activation, due to the methyl groups, and steric

restrictions on the deactivating influence of the first acyl group introduced, diacylation in this series should not only be possible but should proceed relatively quickly.

The mechanism of diacylation, because of steric restrictions, should involve the formation of the acylium ion ( $\text{RCO}^+$ ), and the kinetics ought to be second order - i.e. the reaction rate is a function of the concentration and reactivity of the acylium ion as well as of the substrate.

This should also be true of isodurene, particularly as three of the four methyl groups are *o*- or *p*- to the vacant sites and would therefore promote the reaction. Also the two vacant positions on isodurene are *m*- to each other which further limits the deactivating influence of the first acyl group on the second acylation.

Figure 23: Tetramethylbenzenes (prehnitene, isodurene, durene)



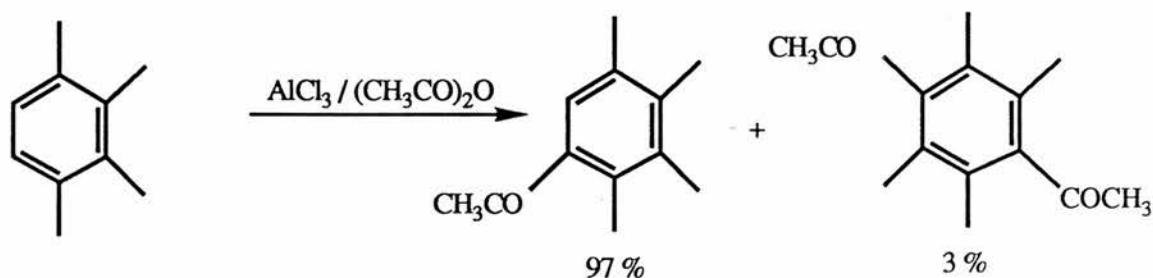
Prehnitene, however, lacks the steric restriction, so that while it is singly acylated three times faster by benzoyl chloride in nitromethane (25°C) than durene, it has not been found to be diacylated<sup>46,47</sup>.

There are two main methods for Friedel-Crafts

acylations (differing in the order of addition of the reactants) which have important consequences for durene. This is due, as mentioned previously (see section 2.3.3), to the possibility of methyl group migration, giving a mixture of isomers. Therefore it is preferable to add the durene to the acyl chloride/aluminium chloride mixture at the reaction temperature, as this allows the catalyst complex to form first<sup>48,49</sup>, i.e. the "Perrier procedure".

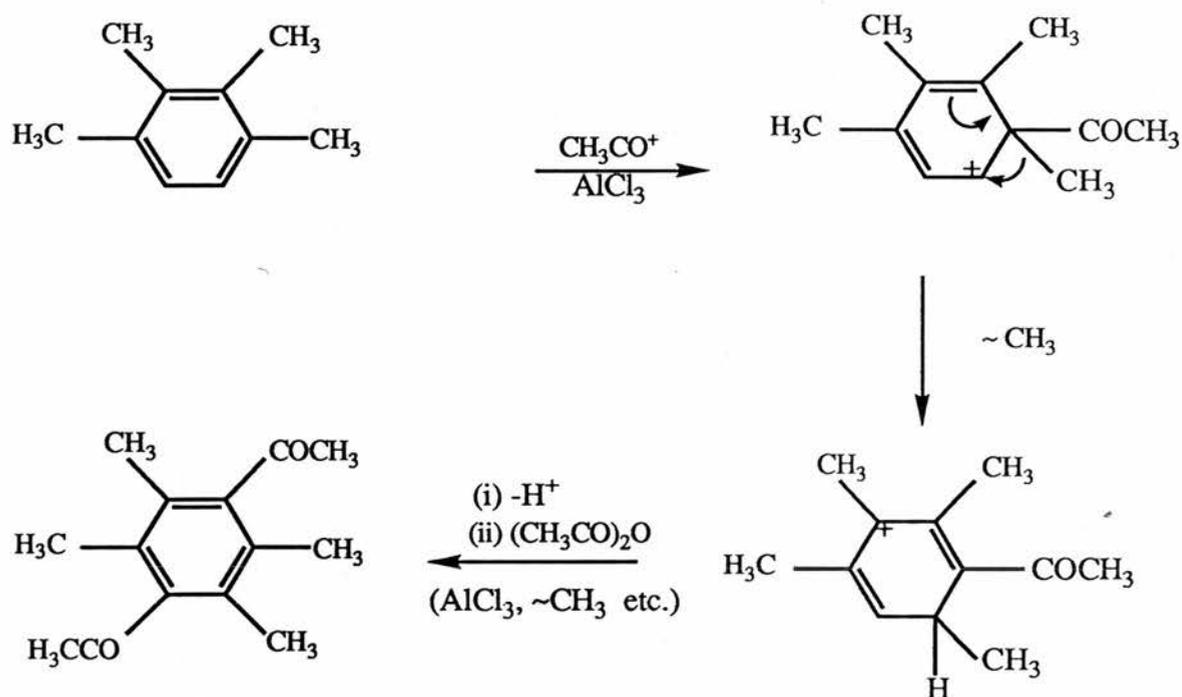
The Bouveault procedure in this series may lead to methyl group migration. Thus, for example, 3% of diacetyldurene is obtained as a by-product by the action of excess acetic anhydride and aluminium chloride on prehnitene<sup>50</sup> (see figures 24 and 25). Also, although dibenzoyldurene has been produced by the Bouveault procedure<sup>51</sup> analytical data for this product are lacking and the sublimation point quoted is only approximate (276°C) when compared to the product prepared by Cheng, et. al.<sup>49</sup>, by the Perrier method (269-270°C), so there is a possibility that methyl migration may also have occurred in this case<sup>52</sup>.

Figure 24: Acetylation of prehnitene.



Not only do methyl migrations occur but transacylations between reaction products may also take place, demonstrating the reversibility of Friedel-Crafts acylations. For example, acetylprehnitene (43-72%) may be formed from a mixture of acetylisodurene and prehnitene in a nitromethane solution<sup>53</sup> (at 20°C).

Figure 25: Methyl migrations during the acylation of prehnitene.



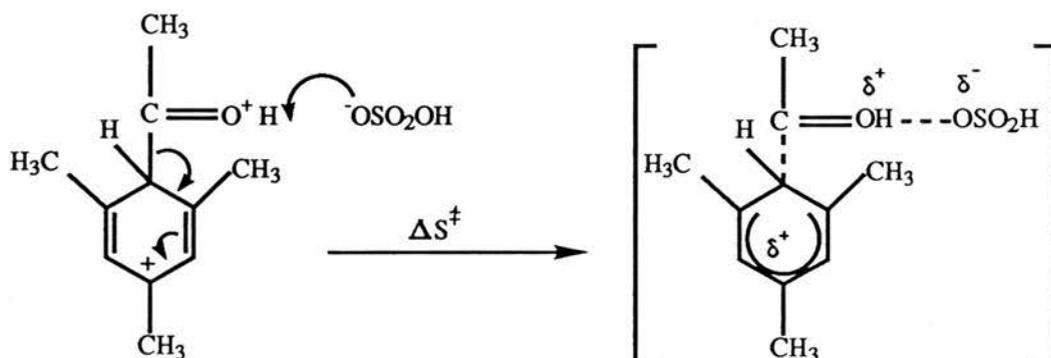
However, under slightly more vigorous conditions, with an excess of acetyl chloride and catalyst in carbon disulphide (50°C), diacetylisodurene is the major product starting from the prehnitene substrate alone under Bouveault conditions. Yet again this demonstrates the effect that higher temperatures and excess catalyst have on yielding the more substituted product, and the effect of the order of reactant addition on the isomer (or isomer

mixture) obtained<sup>54</sup>. In terms of reactant addition the Perrier procedure must be used if the yield of unrearranged products is to be maximised.

Studies of protiodeacylation of acetophenones and benzophenones in 89.8% sulphuric acid<sup>55-57</sup> indicate that the first deacylation step of diacylated mesitylene is 1000 fold slower than the second, and is due to the lowering of  $\Delta S^\ddagger$  by  $50 \text{ J K}^{-1} \text{ mol}^{-1}$  between the two deacylation steps.

This results primarily from the increase in ordering on the activation step (see figure 26) from the arriving hydrogen sulphate ion, which is found to be much more limited in the diacyl- than the monoacyl- case owing to the system already being "under tension". The increase in energy for a strained system to achieve the ordering necessary before the reaction can proceed can be significantly greater than for a less strained system. Hence the likelihood of the desired conformation being randomly achieved (entropy) is much less for the strained system (diacylmesitylene).

Figure 26: Protiodeacetylation of mesitylene.



These results on protiodeacylation, although they relate to the opposite side of the transition state energy barrier, indicate that the system is more highly strained when further acylated, but in such a way that the reverse reaction is less easily accomplished.

## 2.4. Results

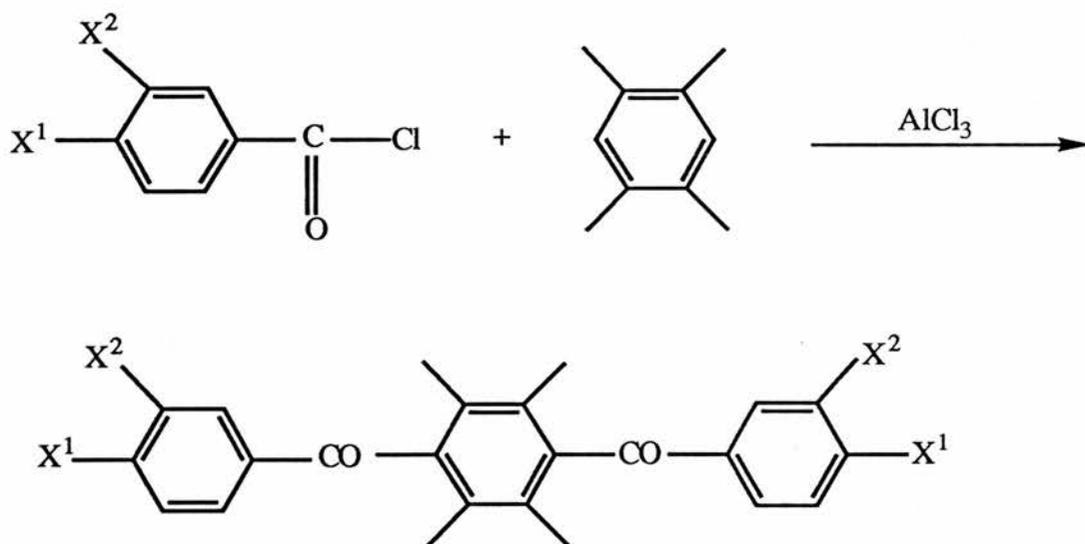
### 2.4.1 Difunctionalisation of Durene With Halogenated Acylating Agents

The diacylation of durene by acetyl chloride in carbon disulphide proceeded, in moderate yield (60%), at 50°C using a substrate : acylating agent : catalyst ratio of 1 : 4.3 : 6.8, as also did the corresponding reaction with benzoyl chloride (despite reports to the contrary<sup>58</sup>), but in lower yield (18%). However 4-fluorobenzoyl chloride or 4-chlorobenzoyl chloride could only achieve mono-acylation in the same solvent (yields 18% and 71% respectively), as expected, when using the same procedure<sup>59</sup>.

Although the addition of an inductively electron withdrawing halogen group on the acylating agent would increase its reactivity, the remote position of the halogen group (para) coupled with its electron donating ability more than counters this, resulting in it having a greater stability than benzoyl chloride (see table 3). Therefore at 50°C neither 4-fluorobenzoyl chloride nor 4-chlorobenzoyl chloride was reactive enough to complete a second acylation of durene.

It was not until this procedure was attempted using the acylating agent as solvent in a substrate : catalyst : acylating agent ratio of 1 : 6 : 10, therefore making higher temperatures accessible (120°C-160°C), that diacylation became possible (yields of 66% for bis(4-fluorobenzoyl)durene (Bis-F) and 53% for bis(4-chlorobenzoyl)durene (Bis-Cl) being obtained) although some carbonaceous material formed (see figure 27). Recovery of the excess acylating agent was only possible, and then with some difficulty owing to the viscous nature of the reaction mixture, by vacuum distillation, typical recovery yields being 40-50% of the unused material.

Figure 27: Dibenzoylation of durene at 120-160°C; X<sup>1</sup>, X<sup>2</sup> = H, F, Cl or NO<sub>2</sub>.



Furthermore, unchanged acylating agent proved a problem in the workup owing to its low solubility (and slow hydrolysis) in aqueous phases; this required rather a large

volume of sodium carbonate solution to be used.

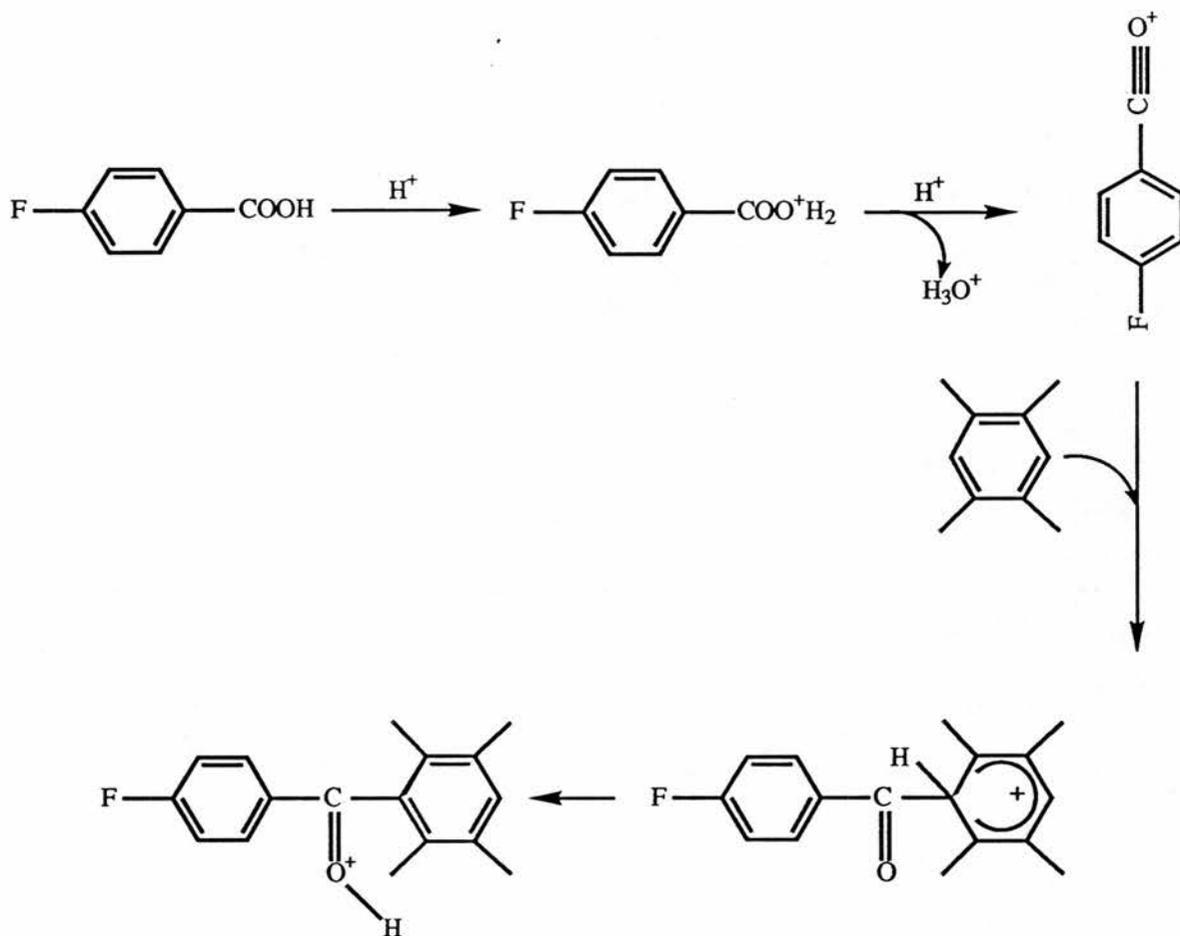
An attempt to use nitrobenzene as an alternative solvent in the diacylation failed probably owing to it strongly complexing with the aluminium chloride catalyst, thereby preventing the acylating agent from forming a complex (see section 2.2.1).

Methylene chloride proved to have too low a boiling point (40°C) for the diacylation yielding only the singly acylated 4-chlorobenzoyl-durene (yield 34%).

As previously mentioned when discussing mesitylene (see section 2.3.4), the formation of carbonised material is common at elevated temperatures, due to the action of free aluminium chloride (see section 2.2.3). This resulted in the diacylated durene having an off-white appearance, which could only be removed by treatment with activated carbon and further recrystallisation from a propan-2-ol/toluene mixture.

Use of trifluoromethanesulphonic (triflic) acid<sup>60</sup> (at 25°C) both as solvent and catalyst (see figure 28) goes part of the way in determining whether a truly homogeneous reaction was taking place (cf. carbon disulphide which was strictly heterogeneous) Only singly acylated durene (mono-F) was formed from 4-fluorobenzoic acid (yield 50%), probably owing to the temperature being too low to promote diacylation. Higher temperatures were not used owing to the likelihood of side reactions in this strong acid medium leading to carbonaceous material.

Figure 28: Ketone formation in a strong acid medium (triflic acid).



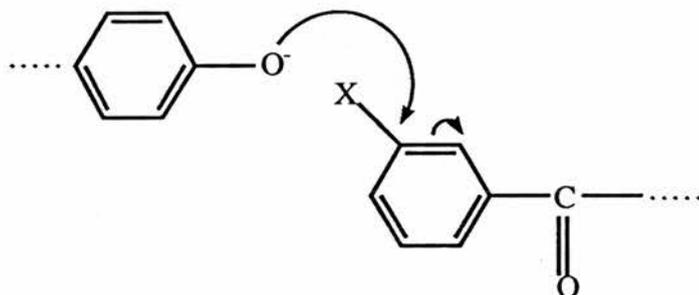
Although the possibility of the monoketone-aluminium chloride complex's insolubility inhibiting Friedel-Crafts diacylation still exists, overall it appears from the reactions studied thus far that temperature inhibition from the use of low boiling point solvents is the more likely restraint, as the methylene chloride and triflic acid systems, which are both homogeneous throughout the reaction, only mono-acylate, while the mesitylene system shows distinct, temperature related, steps of acylation, provided an excess of acylating agent and catalyst is used.

#### 2.4.2 Other Diacylated Methylated Benzenes

The other diacylated durenes were all synthesised at 120°C-160°C using the acylating agent as solvent. The yields obtained were all in the 36-71% range.

Bis-(3-chlorobenzoyl)-durene (Bis-mCl) and bis-(3-fluorobenzoyl)-durene (Bis-mF) make an interesting study especially when comparing NMR shifts (see section 2.5). They are both relatively unreactive in a polymerisation situation as the carbonyl group cannot act as an "electron sink" to stabilise the anionic intermediate (see figure 29).

Figure 29: Delocalisation inhibition.



The nitro analogues, bis-(4-nitrobenzoyl)-durene (Bis-NO<sub>2</sub>, yield 36%) and bis-(3-nitrobenzoyl)-durene (Bis-mNO<sub>2</sub>, yield 71%), were synthesised primarily as an expansion to the project whereby if the fluoro analogues failed or could produce no satisfactory polymers the nitro analogues could be used.

Likewise bis(4-fluorobenzoyl)isodurene (1,3-Bis-F,

yield 8.9%) was synthesised relatively easily using the same "neat" procedure. The low yield is probably a reflection of the difficulty of removing this very soluble monomer from the crystallising solvent, a problem that could probably be easily overcome upon repetition of the process. This diketone is of interest as a monomer in its own right, and may act as a possible "chain disruptor" preventing crystallinity in the resulting polymer by putting a "kink" into the chain.

The non-durene analogue 1,4-bis(4-fluorobenzoyl)benzene (1,4-FBB) was synthesised from terephthaloyl chloride, benzene and aluminium chloride by an adaptation of a literature method<sup>61</sup>.

If a bis-(acid chloride) is reacted with excess durene under Perrier conditions in carbon disulphide (50°C) only mono-acylation of the durene takes place<sup>62</sup>, and thus 1,4-bis(2,3,5,6-tetramethylbenzoyl)benzene (1,4-BDB, yield 89%) and 1,3-bis(2,3,5,6-tetramethylbenzoyl)benzene (1,3-BDB, yield 66%) were synthesised in high yield as expected from terephthaloyl chloride and isophthaloyl chloride respectively. The former (1,4-BDB) was diacylated with 4-fluorobenzoyl chloride under "neat" conditions to produce a monomer with 5 aromatic rings, 1,4-bis[4-(4-fluorobenzoyl)-(2,3,5,6-tetramethylbenzoyl)]benzene (1,4-1,4-BDB), in moderate yield (22%).

The attempted sulphonylation of durene by 4-fluorobenzene-sulphonyl chloride, as both acylating agent and solvent, resulted in only decomposed material, despite

the use of temperatures 50°C below the acylating agent's decomposition temperature (190°C).

#### 2.4.3 Diacylation of Mesitylene

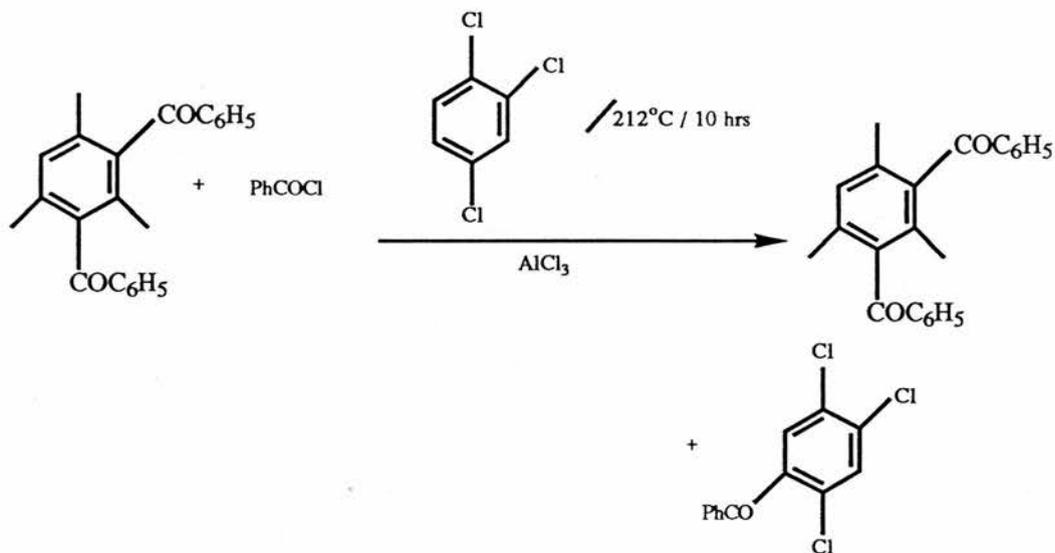
The acylation of mesitylene was also investigated in association with S.E. Gardner<sup>63</sup>. A starting mixture in 1,1,1-trichloroethane of mesitylene : benzoyl chloride : aluminium chloride in a ratio of 1 : 1.56 : 1.11, refluxed at 75°C for 3 hours, yields only the singly acylated benzoylmesitylene in moderate yield (73%). However, under Perrier conditions, with carbon disulphide as the solvent, and a reactant mixture ratio of 1 : 4.27 : 5.30, refluxing for only 1.5 hours (50°C) yielded dibenzoylmesitylene albeit in poor yield (3%).

This was probably due to a higher catalyst : substrate ratio being used in the second case. Certainly it comes as no surprise that benzoyl chloride can diacylate mesitylene at this temperature given that durene, a less reactive substrate, is also diacylated by benzoyl chloride under similar conditions (see section 2.4.1, yield 17%).

Care in choice of alternative solvents must be made. While, in this study, attempting to acylate dibenzoylmesitylene with benzoyl chloride in 1,2,4-trichlorobenzene, with dibenzoylmesitylene : benzoyl chloride : aluminium chloride in a ratio of 1 : 12.4 : 16.3, it was found that 2,4,5-trichlorobenzophenone was the major product (see figure 30). The more substituted 1,2,4,5-tetrachlorobenzene might be expected to be a less

reactive solvent. However, a high yield would be unlikely, given the possibility of complexes being formed between the solvent and the catalyst, thereby inhibiting catalyst availability to the acylating agent.

Figure 30: Attempted acylation of dibenzoylmesitylene.



When the acylation of dibenzoylmesitylene was attempted under Perrier conditions, using the benzoyl chloride as solvent in a dibenzoylmesitylene : benzoyl chloride : aluminium chloride ratio of 1 : 4.67 : 7.4, also under vigorous conditions (196°C/16 hours), a mixture of both tribenzoyl- and dibenzoylmesitylene was obtained along with much carbonised material (yield = trace), confirming the experimental work of Louise<sup>37</sup>.

The lower reactivity of the 4-fluorobenzoyl chloride compared to benzoyl chloride was confirmed when attempting to diacylate mesitylene under Perrier conditions, in carbon disulphide (50°C), with a mesitylene : 4-fluorobenzoyl

chloride : aluminium chloride ratio of 1 : 4.27 : 5.30. After 1.5 hours the only major reaction product was 4-fluorobenzoic anhydride.

It required the use of elevated temperatures (150°C/1 hour), with the acylating agent as solvent, and a reactant ratio of 1 : 5.42 : 9.11, to bring about the formation of bis(4-fluorobenzoyl)mesitylene (Bis-mesF, yield = 49%).

#### 2.4.4. Monomer Purification

For a monomer to be of polymerisable grade in a polycondensation it must be as pure as possible (e.g. 99.5%+) because:

1) exact molar equivalence of the two comonomers must be present for high molecular weights to be obtained;

2) small amounts of a reactive impurity could result in unpredictable side reactions which could degrade the polymer or "end-cap" the growing molecule;

3) even small amounts of a foreign material can form nuclei for fracture formation/propagation in a moulded polymer resulting in a vastly diminished impact strength.

As a reliable method had been found at this point to produce the main monomer - bis-(4-fluorobenzoyl)-durene - and an ample supply of its main starting material - 4-fluorobenzoyl chloride - was at hand, it was unnecessary at this stage to develop the method further.

Another interesting aspect worth noting is that the relative solubility of bis-(4-fluorobenzoyl)-durene (Bis-F) is approximately four times that of the chloro-analogue bis-(4-chlorobenzoyl)-durene (Bis-Cl) in propan-2-ol or

toluene. This is probably due to the more polarised nature of the C-F bond compared to the C-Cl bond.

As mentioned, the mono-acylated compounds (4-chlorobenzoyl)-durene (mono-Cl) and the fluoro analogue (4-fluorobenzoyl)-durene (mono-F) were synthesised (yields of 68% and 18% respectively) with relative ease in carbon disulphide with a substrate : acylating agent : catalyst ratio of 1 : 4.3 : 6.8. They also proved to be much more soluble in ethanol than their diacylated counterparts. In principle these have some value as "end-capping agents" for the polymerisation i.e. when the required molecular weight is achieved in the polymerisation vessel an end-capper is added to terminate the reaction. [This has the advantage not only of limiting the average molecular weight of the polymer but also increasing its temperature stability for moulding, as replacing phenate end groups with a more stable functionality prevents further polymerisation upon moulding and limits decomposition reactions] However there exists a practical difficulty in dispersion of such a reagent into a mixture of increasing viscosity.

### 2.5 Nuclear Magnetic Resonance (NMR) Results and Discussion

The following discussion will show firstly that the structures indicated from the experimental work are consistent with the values obtained from NMR chemical shifts, and that no transmethylation, or contamination of the monomers with singly acylated material has occurred. Hence reasonably pure, linear (in the case of durene), polymerisation-grade monomers are confirmed. Secondly it

will show that, owing to steric interactions between pendant methyl groups on the durene ring and the carbonyl carbons, delocalisation effects are distorted between the carbonyl carbon and the methylated ring. However, it will be shown that this distortion occurs in a consistent manner, and this effect although it distorts the electron distribution on the adjacent non-methylated ring does so in only a minor way. Thus, the electronic reactivity of the terminal halogens of the monomers towards nucleophilic substitution, ought not to be significantly affected.

#### 2.5.1 $^{13}\text{C}$ NMR of products

$^{13}\text{C}$ -NMR was used primarily as an identification technique for the compounds synthesised. It established that no methyl migration occurred for these compounds.

Owing to the complications due to steric repulsion between the ketone and methyl groups (see section 2.3.4), it is difficult to calculate theoretical chemical shifts based on simple standard values<sup>64</sup>. Hence the predicted values of the carbons are based upon those obtained from dibenzoyldurene (Bis-H), as it is this distortion from the simple standard values<sup>64</sup> that will be the focus of the following discussion. This discussion will attempt to show that delocalisation inhibition occurs to varying degrees in any case where ring methyl groups are adjacent to carbonyl groups, and that the extent of such a distortion depends solely on the number and position of such groups.

The spectrum of dibenzoyldurene (Bis-H, see table 10 and figure 31.1, X=H) consists of 8 peaks, carbons 5 and 6 being equivalent to 3 and 2 respectively. First, the

carbonyl carbon (7) will be the most downfield (201.26ppm). Second, in comparing the calculated values<sup>64</sup> for the non-methylated ring carbons with spectrum values the following correlation (see table 8) is obtained with moderate consistency, demonstrating that the electron distribution on this ring is not substantially distorted by the steric interactions of the adjacent ring with the carbonyl carbon. Thirdly, the most upfield peak (16.56ppm) will correspond to the methyl carbons (10). The remaining two carbons (8,9) must correspond to 140.62ppm and 130.50ppm. As there are twice as many "9" carbons as there are "8" carbons, and the "8" carbons will relax more slowly owing to their closer proximity to the carbonyl group, carbon "9" will therefore have a much greater intensity and this corresponds to the peak at 130.50ppm.

Table 8: Calculated <sup>13</sup>C-NMR values for Bis-H.

Carbon	Observed Benzene	-COC <sub>6</sub> H <sub>5</sub> correction	Calculated Result	Observed
1	128.5	+9.4	137.9	137.11
2 (6)	128.5	+1.7	130.2	129.60
3 (5)	128.5	-0.2	128.3	128.91
4	128.5	+3.6	132.1	133.65

If standard values based on simple molecules<sup>64</sup> had been used for these last two values (8,9), the difference would have been substantial (-2.1ppm and -6.1ppm respectively). Hence it can be seen that ring electron distribution on the methylated ring is substantially distorted probably by delocalisation inhibition. Therefore, all the carbon chemical shifts for the methylated

derivatives will be predicted on the basis of those values determined from Bis-H, with the non-methylated ring values being further corrected by appropriate substituent constants based upon simple molecules (see table 9).

Table 10 contains a summary of all the results and figure 31.1-31.10 lists all the corresponding structures.

Table 9:  $^{13}\text{C}$ -NMR correction from benzene 128.5ppm (ref. TMS)<sup>64</sup>

carbon	F	Cl	NO <sub>2</sub>	CH <sub>3</sub>
ipso	+34.8	+6.2	+20.0	+8.9
ortho	-12.9	+0.4	-4.8	+0.7
meta	+1.4	+1.3	+0.9	-0.1
para	-4.5	-1.9	+5.8	-2.9

From the top of table 10 it can be seen that for the 31.1 and 31.2 type structures (Bis-H, F, Cl, NO<sub>2</sub>, mF, mCl, mNO<sub>2</sub> and 1,4-FBB) apart from 1,4-FBB, a high level of consistency is found for carbons 7-10. This result is of course expected given that the differences between these structures are remote from the carbons concerned.

1,4-FBB shows only slight deviation in its carbon 8 (-1.3ppm) from the predicted value<sup>64</sup>, which indicates that once the methyl groups are removed, the distortion on electron distribution via steric interaction no longer exists.

Partial removal of this restriction via removal of one of the carbonyl group functionalities (31.3, 31.4 and 31.5 structures) again distorts the picture. Carbons 8 and 9 chemical shift values deviate significantly (+4.1ppm) from

those predicted for mono-F (from Bis-H and corrected for from the simple values for the removal of a carbonyl group<sup>64</sup>) (see table 8). But the distortion is consistent as can be seen with the series of mono-F, mono-Cl, 1,4-BDB and 1,3-BDB (carbon 8 =  $139.5 \pm 0.2$  ppm, carbon 9 =  $134.2 \pm 0.2$  ppm).

The spectrum of structure 31.6 (1,4-1,4-BDB) of course suffers no such inconsistencies with its calculated data as the restrictions on its carbonyl groups attaining planarity remain.

However, observation of the spectra of structures 31.7, diacyldurene (A/B(acyl)), 31.8 (1,3-Bis-F), 31.9 (mono-mesH) and 31.10 (Bis-mesH,F) indicate the difficulty in predicting the extent of the distortion on methylated ring values as the restrictions on the carbonyl groups remain with respect to the central methylated ring, but the position of acylation and/or the acylated group varies.

For the other structures where large corrections have had to be made for electronic effects such as carbon 4 on Bis-F (+34.8ppm), and Bis-NO<sub>2</sub> (+20.0ppm), the difference between calculated and observed values has been significantly greater at -2.2ppm and -2.8ppm respectively. This has shown up with carbon 4 on 1,4-FBB (-2.0ppm), 1,4-1,4-BDB (-2.2ppm) and mono-F (-2.4ppm) but not surprisingly on carbon 3 or 4 of Bis-mF (-0.5ppm and +0.2ppm) or Bis-mNO<sub>2</sub> (+0.1ppm and -0.8ppm). Perhaps this is a further indication of the effect of cumulative error for large corrections which are maximised for carbons ipso and para to the groups in question. All other carbon 1-4

Table 10:  $^{13}\text{C}$ -NMR chemical shift values.

Carbon Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Bis-Ha	calc.	137.9	130.2	128.3	132.1		~200	142.7	136.6	~16				
	obs.	137.11	129.60	128.91	133.65		201.26	140.62	130.50	16.56				
Bis-Fb	calc.	132.6	131.0	116.0	168.5		201.3	140.6	130.5	16.6				
	obs.	133.61	132.34	116.15	166.33		199.52	140.43	130.58	16.54				
Bis-Cl <sup>b</sup>	calc.	135.2	130.9	129.3	139.9		201.3	140.6	130.5	16.6				
	obs.	135.31	130.94	129.32	140.22		199.84	140.21	130.60	16.56				
Bis-NO <sub>2</sub> <sup>b</sup>	calc.	142.9	130.5	124.1	153.7		201.3	140.6	130.5	16.6				
	obs.	141.02	130.48	124.29	150.90		199.07	140.00	130.96	16.66				
1,4-FBB <sup>a</sup>	calc.	133.4	131.6	115.4	166.9		~200	141.5	130.0					
	obs.	133.30	132.86	115.95	164.90		194.07	140.23	129.55					
Bis-mFb	calc.	138.5	116.7	163.7	120.8	130.3	201.3	140.6	130.5	16.6				
	obs.	139.20	115.74	163.15	120.98	130.68	199.77	140.32	130.74	16.55				
Bis-mCl <sup>b</sup>	calc.	138.4	130.0	135.1	134.1	130.2	201.3	140.6	130.5	16.6				
	obs.	138.62	129.12	135.42	133.87	130.33	199.73	140.19	130.69	16.57				
Bis-mNO <sub>2</sub> <sup>b</sup>	calc.	138.0	124.8	148.9	128.9	129.8	201.3	140.6	130.5	16.6				
	obs.	138.37	123.83	149.00	128.12	130.38	198.80	139.86	131.01	16.66				

Carbon Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
mono-Fa,b	calc.	132.6 <sup>b</sup>	131.0 <sup>b</sup>	116.0 <sup>b</sup>	168.5 <sup>b</sup>		201.3 <sup>b</sup>	139.1 <sup>a</sup>	136.8 <sup>a</sup>	16.6 <sup>b</sup>	134.9 <sup>a</sup>	16.6+ <sup>b</sup>	133.3 <sup>a</sup>	
	obs.	134.30	132.30	115.93	166.08		199.92	139.63	133.99	16.22	129.61	19.46	132.23	
mono-Cl <sup>b,c</sup>	calc.	135.2 <sup>b</sup>	130.9 <sup>b</sup>	129.3 <sup>b</sup>	139.9 <sup>b</sup>		199.9 <sup>c</sup>	139.6 <sup>c</sup>	134.0 <sup>c</sup>	16.2 <sup>c</sup>	129.6 <sup>c</sup>	19.5 <sup>c</sup>	132.2 <sup>c</sup>	
	obs.	135.90	130.84	129.14	140.04		200.16	139.48	134.30	16.22	129.63	19.42	132.03	
1,4-BDB <sup>a,c</sup>	calc.	141.5 <sup>a</sup>	130.0 <sup>a</sup>				199.9 <sup>c</sup>	139.6 <sup>c</sup>	134.0 <sup>c</sup>	16.2 <sup>c</sup>	129.6 <sup>c</sup>	19.5 <sup>c</sup>	132.2 <sup>c</sup>	
	obs.	140.63	129.78				201.08	139.38	134.35	16.34	129.61	19.46	132.12	
1,3-BDB <sup>a,c</sup>	calc.	137.7 <sup>a</sup>	131.9 <sup>a</sup>		128.1 <sup>a</sup>		199.9 <sup>c</sup>	139.6 <sup>c</sup>	134.0 <sup>c</sup>	16.2 <sup>c</sup>	129.6 <sup>c</sup>	19.5 <sup>c</sup>	132.2 <sup>c</sup>	
	obs.	138.15	130.59		129.46		200.70	139.30	134.28	16.24	129.46	19.41	132.06	
1,4-1,4-BDB <sup>b</sup>	calc.	132.6	131.0	116.0	168.5		201.3	140.6	130.5	16.6				
	obs.	133.61	132.29	116.18	166.34		199.25	140.13	130.71	16.55				
(C) <sup>a,c</sup>	calc.	141.5 <sup>a</sup>	130.0 <sup>a</sup>				199.9 <sup>c</sup>	139.6 <sup>c</sup>	134.0 <sup>c</sup>	16.2 <sup>c</sup>				
	obs.	140.55	130.00				200.45	140.66	130.61	16.69				
A/B(acyl) <sup>a,b</sup>	calc.	~30 <sup>a</sup>	(J,9.3)	(J,22.0)	(J,256.8)		201.3 <sup>b</sup>	140.6 <sup>b</sup>	130.5 <sup>b</sup>	16.6 <sup>b</sup>				
	obs.	32.67					208.61	143.37	128.52	16.10				

Carbon Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1,3-Bis-Fb,a	calc. 132.6 <sup>b</sup>	131.0 <sup>b</sup>	116.0 <sup>b</sup>	168.5 <sup>b</sup>			201.3 <sup>a</sup>	136.1 <sup>a</sup>	137.7 <sup>a</sup>	16.6 <sup>b</sup>	143.2 <sup>a</sup>	135.5 <sup>a</sup>	16.6+ <sup>b</sup>	16.6- <sup>b</sup>
mono-mesHb,a	obs. 133.74	132.26 (J,9.1)	116.13 (J,21.9)	166.27 (J,256.6)			198.96	138.10	134.16	16.66	133.20	131.96	17.62	15.20
Bis-mesHb,a	calc. 137.1 <sup>b</sup>	129.6 <sup>b</sup>	128.9 <sup>b</sup>	133.7 <sup>b</sup>			201.3 <sup>b</sup>	136.4 <sup>a</sup>	138.9 <sup>a</sup>	16.6+ <sup>b</sup>	126.8 <sup>a</sup>	140.8 <sup>a</sup>	16.6+ <sup>++b</sup>	
Bis-mesFb,d	obs. 136.89	129.58	128.40	133.14			200.11	136.55	138.02	18.92	127.96	133.71	20.79	
	calc. 132.6 <sup>b</sup>	131.0 <sup>b</sup>	128.9 <sup>b</sup>	133.7 <sup>b</sup>			201.3 <sup>b</sup>	136.2 <sup>a</sup>	140.6 <sup>a</sup>	16.6 <sup>b</sup>	142.5 <sup>a</sup>	16.6+ <sup>b</sup>	126.6 <sup>a</sup>	
	obs. 133.47 (J,2.3)	132.22 (J,9.8)	116.21 (J,21.7)	166.82 (J,255.0)			198.34	137.67	130.52	16.87	135.12	19.35	129.79	

a - predicted value if simple standard values were applied<sup>64</sup>

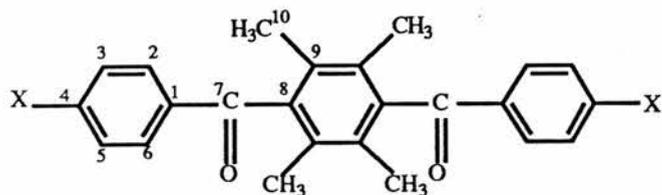
b - predicted value from simple substituent constants<sup>64</sup> applied to Bis-H

c - predicted value from simple substituent constants<sup>64</sup> applied to mono-F

d - predicted value from simple substituent constants<sup>64</sup> applied to Bis-mesH

calc. = calculated value, obs. = observed chemical shift

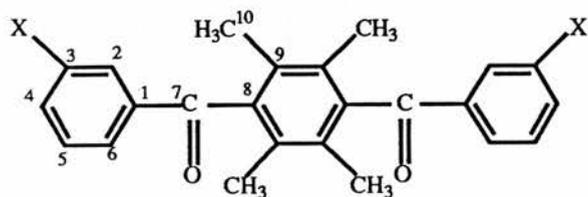
Figure 31:  $^{13}\text{C}$  NMR Structure Assignments



1.

X=H, F, Cl or  $\text{NO}_2$

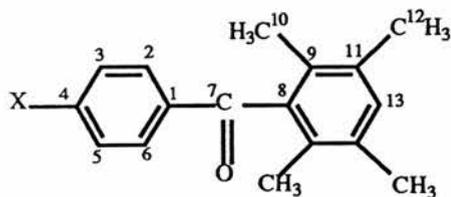
Bis-H, F, Cl,  $\text{NO}_2$



2.

X=F, Cl or  $\text{NO}_2$

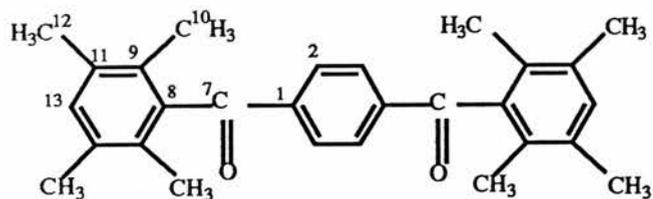
Bis-mF, mCl, m $\text{NO}_2$



3.

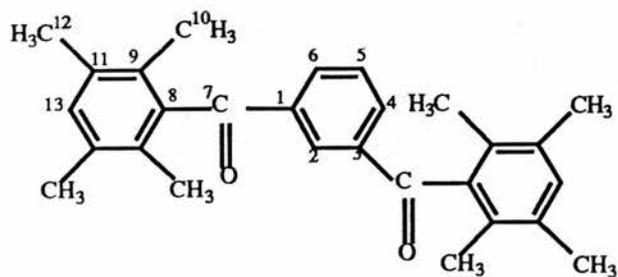
X=F or Cl

mono-F, Cl



4.

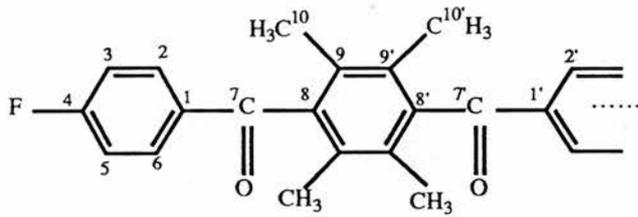
1,4-BDB



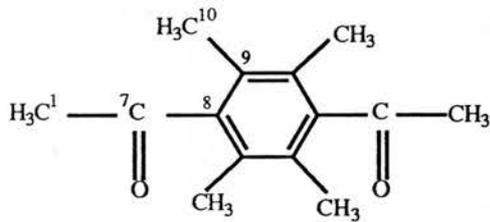
5.

1,3-BDB

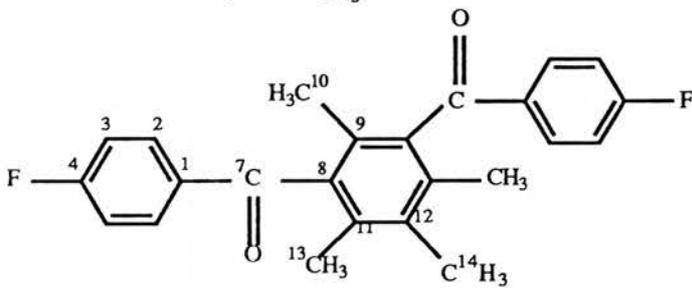
Figure 31 continued:  $^{13}\text{C}$  NMR Structure Assignments



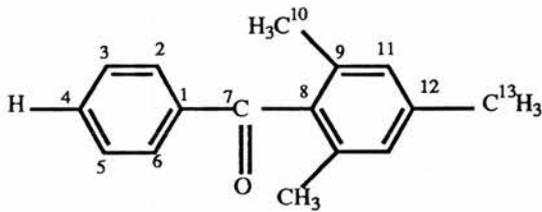
6.  
1,4-1,4-BDB



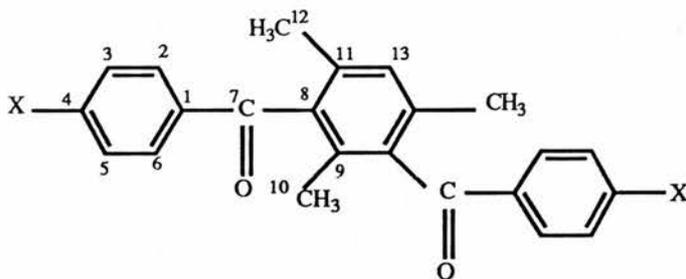
7.  
A/B(acyl)



8.  
1,3-Bis-F



9.  
mono-mesH



10.  
X=H or F  
Bis-mesH, mesF

values however show a high degree of consistency with those values predicted throughout the series in table 10 ( $\pm 1\text{ppm}$ ), which indicates that the steric constraints on the carbonyl groups ability to delocalise electrons from the neighbouring ring appears to be consistent.

From the carbon-fluorine coupling constants for Bis-F, 1,4-FBB, Bis-mF, mono-F, 1,4-1,4-BDB and Bis-mesF a high level of consistency is observed for all except  $J_{F4}$  of 1,4-FBB where the identification of both peaks was uncertain due to a low signal to noise ratio owing to the insolubility of this species in deuterated-chloroform. Taking an average of the remaining values with comparison values for fluorobenzene in brackets it is calculated that

$$\text{ipso carbon } J_{CF} = 254 \pm 5 \text{ Hz (245)}$$

$$\text{ortho carbon } J_{CF} = 22.0 \pm 0.3 \text{ Hz (21.0)}$$

$$\text{meta carbon } J_{CF} = 9.9 \pm 1.2 \text{ Hz}$$

### 2.5.2 $^1\text{H}$ NMR

The  $^1\text{H}$  NMR spectra were analysed in a similar way to the  $^{13}\text{C}$  NMR spectra, i.e. dibenzoyldurene (Bis-H) was again used as the standard from which the ring methyl resonances were analysed. The large differences between predicted<sup>64</sup> and observed peaks for methyl hydrogens were not so evident this time owing to the remoter positions of these hydrogens (as compared to the carbons) from the carbonyl groups. As discussed in the previous section, it was the steric interaction of these groups that probably caused the variation in electronic effects on the methylated ring.

From diagram 32.1 (X=H) it can be seen that there must be 4 proton signals. First, the methyl hydrogen (6) will be the most upfield (2.04ppm). Second, in comparing the calculated values for the unmethylated ring hydrogens the following correlation is obtained (table 11).

Table 11: Calculated <sup>1</sup>H-NMR values for Bis-H.

Hydrogen	Observed Benzene	-COC <sub>6</sub> H <sub>5</sub> corrections	Calculated Result	Observed	Difference
1	7.24	+0.65	7.89	7.87	-0.02
2	7.24	+0.30	7.54	7.48	-0.06
3	7.24	+0.30	7.54	7.62	+0.08

Table 13 contains a summary of all the results and figure 32.1-32.8 a list of all the structures. All the calculated values on the non-methylated ring hydrogens are based on simple molecules<sup>64</sup> (see table 12).

Upon observation of table 13 it can be seen that starting from the top (excepting 1,4-FBB) a high level of consistency is observed i.e. 2.04 ± 0.1ppm for the methylated rings methyl hydrogens (6), until the isodurene structure 1,3-Bis-F. This is again easily accounted for by the carbonyl-methyl group steric interaction which has been consistent through the table 13 series at 0.2ppm below the predicted value of 2.25ppm (toluene) for the 32.1 and 32.2 type structures (Bis-H to Bis-mNO<sub>2</sub>, except 1,4-FBB) and 0.3ppm below for the 32.3, 32.4 and 32.5 type structures (mono-F to 1,3-BDB), where one carbonyl group has been removed. Where a degree of restriction of the methyl groups has been removed, as with hydrogen 7 of

structures 32.3, 32.4 and 32.5 (mono-F to 1,3-BDB), the chemical shift value has reverted back almost to that of toluene (2.25ppm). This strange effect can again be noticed for the chemical shift values of hydrogens 6,7 and 8 of structure 32.8 (1,3-Bis-F) which range widely (2.25, 2.11 and 2.86ppm) in response to the varying degrees of freedom of the methyl groups.

Table 12:  $^1\text{H}$ -NMR correction from benzene 7.24ppm (ref. TMS) <sup>64</sup>.

Hydrogen	F	Cl	NO <sub>2</sub>	CH <sub>3</sub>
ortho	-0.30	0.00	+1.00	-0.10
meta	0.00	0.00	+0.30	-0.10
para	-0.20	0.00	+0.45	-0.10

The next significant departure comes from hydrogen 2 of 1,4-FBB, which deviates so much (+0.37ppm) from the first four molecules of table 13 that it could be suspected that some minor intramolecular electronic polarisation is occurring between this hydrogen and the pendant methyl groups for the first four structures. However, this would appear unlikely given that the deviation between predicted and observed values for Bis-H is so small. The reappearance of such deviations for 1,3-BDB where the likelihood of intramolecular interaction is higher (see section 2.5.1) does not rule out this possibility.

The  $J_{\text{FH}}$  coupling constants show a high degree of consistency through table 13. The range of coupling constants, however, along with the closeness of chemical

shifts made the Bis-mF  $^1\text{H}$  NMR spectrum very difficult to analyse.

Taking an average of these couplings together with comparison values in brackets for typical aromatic ring fluorine-hydrogen couplings, the following results were obtained:

$$\begin{aligned} \text{ortho hydrogen } J_{\text{HF}} &= 8.7 \pm 0.6 \text{ Hz (6-10)} \\ \text{meta hydrogen } J_{\text{HF}} &= 5.3 \pm 0.4 \text{ Hz (5-6)} \\ \text{para hydrogen } J_{\text{HF}} &= 1.4 \text{ Hz (2)} \end{aligned}$$

The adjacent proton couplings (CH-CH) showed a more moderate level of consistency, averaging out at  $8.2 \pm 1.5$  Hz. The typical value for benzene is 9 Hz although a range of 6-10 Hz is expected for substituted benzenes. The similarity of this coupling constant with that for the  $o$ -H-F coupling constant (8.7 Hz) resulted in most of the ortho protons being observed as undistorted triplets rather than double doublets.

The only case of a CH-C-CH type coupling being separable (i.e. observable) was for 1,3-BDB and again as expected the value for this at 1.8 Hz is a little lower than the typical value for meta hydrogen coupling for an unsubstituted ring (3 Hz).

For table 13:-

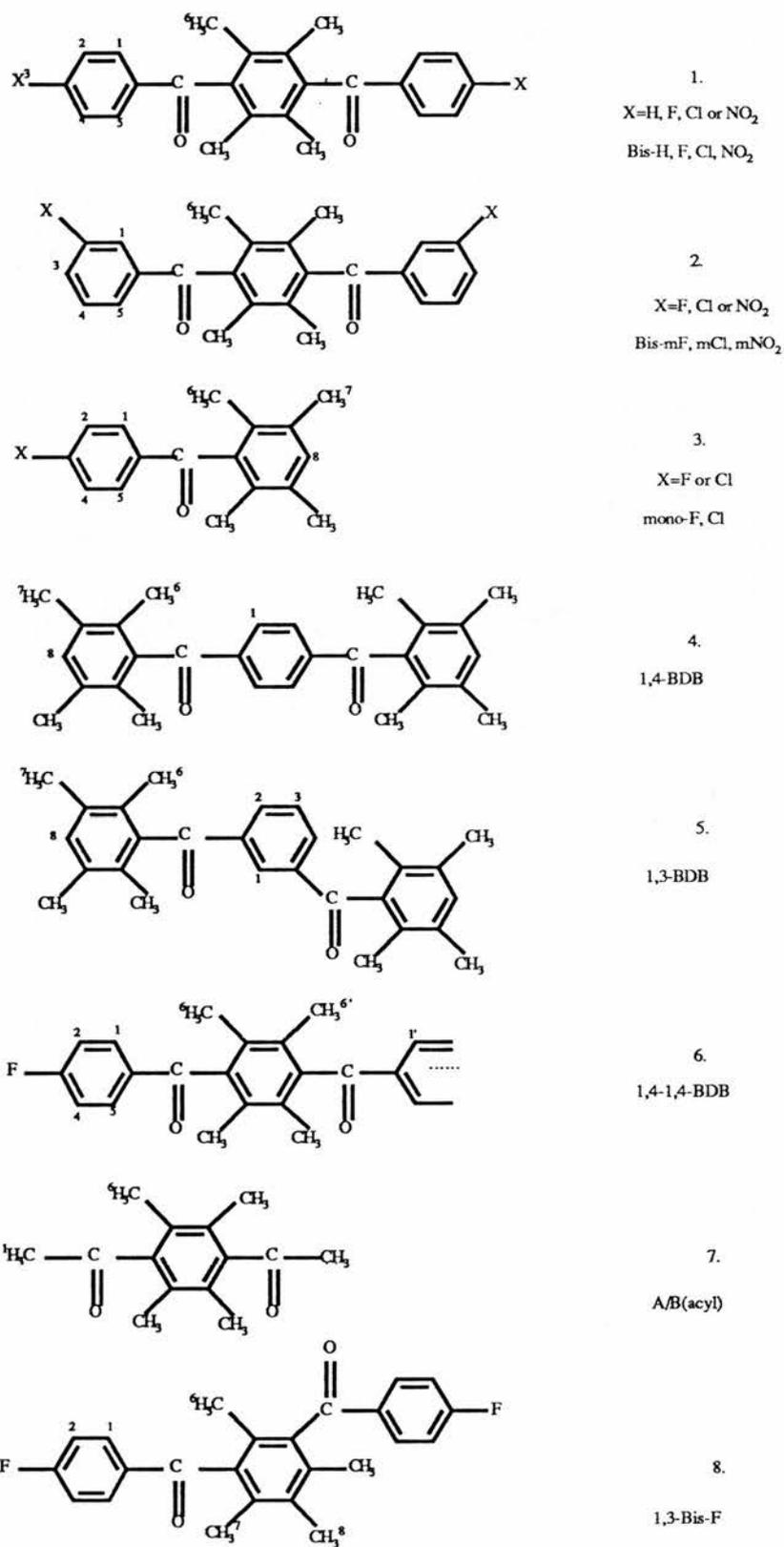
- a - predicted value if simple standard values were applied<sup>64</sup>
- b - predicted value from simple substituent constants<sup>64</sup> applied to Bis-H
- c - predicted value from simple substituent constants<sup>64</sup> applied to mono-F
- d - predicted value from simple substituent constants<sup>64</sup> applied to Bis-mesH

calc. = calculated value, obs. = observed chemical shift

Table 13:  $^1\text{H-NMR}$  chemical shift values.

$^1\text{H}$ Number		1	2	3	4	5	6	7	8
Bis-H <sup>a</sup>	calc.	7.89	7.54	7.54			2.25		
	obs.	7.87	7.48	7.62			2.04		
Bis-F <sup>b</sup>	calc.	7.87	7.18				2.04		
	obs.	7.90	7.15				2.04		
Bis-Cl <sup>b</sup>	calc.	7.87	7.48				2.04		
	obs.	7.83	7.46				2.04		
Bis-NO <sub>2</sub> <sup>b</sup>	calc.	8.17	8.48				2.04		
	obs.	8.04	8.34				2.04		
1,4-FBB <sup>a</sup>	calc.	7.89	7.24				8.19		
	obs.	8.03	7.55				8.01		
Bis-mF <sup>b</sup>	calc.	7.57		7.32	7.48	7.67	2.04		
	obs.	7.55		7.28	7.42	7.56	2.05		
Bis-mCl <sup>b</sup>	calc.	7.87		7.62	7.48	7.87	2.04		
	obs.	7.89		7.60	7.43	7.69	2.04		
Bis-mNO <sub>2</sub> <sup>b</sup>	calc.	8.87		8.62	7.78	8.32	2.04		
	obs.	8.77		8.52	7.74	8.16	2.05		
mono-F <sup>b,a</sup>	calc.	7.87 <sup>b</sup>	7.18 <sup>b</sup>				2.04 <sup>b</sup>	2.04 <sup>+b</sup>	7.14 <sup>a</sup>
	obs.	7.84	7.08				1.98	2.24	7.03
mono-Cl <sup>b,c</sup>	calc.	7.87 <sup>b</sup>	7.48 <sup>b</sup>				1.98 <sup>c</sup>	2.24 <sup>c</sup>	7.03 <sup>c</sup>
	obs.	7.73	7.38				1.96	2.23	7.03
1,4-BDB <sup>a,c</sup>	calc.	8.19 <sup>a</sup>					1.98 <sup>c</sup>	2.24 <sup>c</sup>	7.03 <sup>c</sup>
	obs.	7.88					1.97	2.25	7.05
1,3-BDB <sup>a,c</sup>	calc.	8.54 <sup>a</sup>	8.19 <sup>a</sup>	7.84 <sup>a</sup>			1.98 <sup>c</sup>	2.24 <sup>c</sup>	7.03 <sup>c</sup>
	obs.	8.14	8.02	7.53			1.94	2.22	7.02
1,4-1,4-BDB <sup>b</sup>	calc.	7.87	7.18				2.04		
	obs.	7.89	7.16				2.03		
('H) <sup>a,c</sup>	calc.	8.19 <sup>a</sup>					1.98 <sup>c</sup>		
	obs.	7.96					2.03		
A/B(acyl) <sup>a,b</sup>	calc.	2.40 <sup>a</sup>					2.04 <sup>b</sup>		
	obs.	2.45					2.11		
1,3-Bis-F <sup>b</sup>	calc.	7.87	7.18				2.04 <sup>+</sup>	2.04	2.04 <sup>++</sup>
	obs.	7.87	7.14				2.25	2.11	2.86

Figure 32: <sup>1</sup>H-NMR Structure Assignments



## 2.6 Experimental

### Chemical reagent sources

Durene, isodurene, mesitylene, anhydrous aluminium chloride and all the acylating agents were obtained from Aldrich p.l.c. or ICI Wilton and used without further purification.

### Instruments

Infrared spectra were obtained from a Perkin-Elmer 1330 Infrared Spectrophotometer using Nujol mulls. A Finnigan-Mat Incos 50 Mass Spectrometer was used to obtain 'low resolution' mass spectra. NMR spectra were obtained as described in section 3.8.10

### Method A

#### Diacetyldurene (A/B[acyl])<sup>48</sup> (Perrier procedure)

Acetyl chloride (3.97g, 51mmol) and aluminium chloride (13.55g, 101.6mmol) were mechanically stirred and refluxed (50°C) with carbon disulphide (60ml) for 15 minutes. Powdered durene (2g, 14.9mmol) was then slowly added over 5 minutes and the mixture gently refluxed for 1 hour. The carbon disulphide was distilled off, and the red residue allowed to cool to leave a dark brown slurry. This was carefully added to iced water (200ml) (violent reaction). The mixture was extracted with dichloromethane (200ml), washed with sodium carbonate (5-10%, 200ml), distilled water (200ml) and a saturated sodium chloride solution (200ml). The extract was dried with anhydrous sodium sulphate and evaporated to dryness. The light brown residue was recrystallised from benzene to yield white

crystals of diacetyldurene which melted at 176°C (lit.<sup>48</sup> mp. 178°C). Yield, 1.96g (60%). (Found: C, 77.1; H, 8.2. Calculated for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: C, 77.0; H, 8.3%).  $\nu_{\max}$  1620 cm<sup>-1</sup> (CO).

Dibenzoyldurene (Bis-H)

Method A was used, the reactants being benzoyl chloride (9.01g, 63.7mmol), aluminium chloride (13.55g, 101.6mmol) and durene (2.00g, 14.9mmol), in carbon disulphide (60ml). The resulting white crystals, recrystallised from benzene, sublimed at 269°C (lit.<sup>49</sup> mp. 269-270°C); yield, 0.91g (18%). m/z 342 (44%, M<sup>+</sup>), 265 (38, M-C<sub>6</sub>H<sub>5</sub>), 237 (6, M-C<sub>6</sub>H<sub>5</sub>CO), 222 (28, M-C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>), 105 (42, M-C<sub>6</sub>H<sub>5</sub>COC<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>), 77 (40, M-C<sub>6</sub>H<sub>5</sub>COC<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>CO); (Found: C, 84.0; H, 6.4. Calculated for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>: C, 84.2; H, 6.5%).  $\nu_{\max}$  1620 cm<sup>-1</sup> (CO).

(4-Chlorobenzoyl)-durene (mono-Cl)

Method A was used, the reactants being 4-chlorobenzoyl chloride (11.29g, 64.5mmol), aluminium chloride (13.55g, 101.6mmol) and durene (2.00g, 14.9mmol), in carbon disulphide (60ml). The resulting white crystals, recrystallised from benzene, melted at 167°C (lit.<sup>59</sup> 170.0-171.5°C); yield, 2.89g (71%). (Found: C, 74.7; H, 6.3. Calculated for C<sub>17</sub>H<sub>17</sub>ClO: C, 74.9; H, 6.3%).  $\nu_{\max}$  1620 cm<sup>-1</sup> (CO).

(4-Fluorobenzoyl)-durene (mono-F)

Method A was used, the reactants being 4-fluorobenzoyl chloride (10.16g, 64.5mmol), aluminium chloride (13.55g, 101.6mmol) and durene (2.00g, 14.9mmol), in carbon disulphide (60ml). The resulting white crystals,

recrystallised from benzene, melted at 117.5–118.5°C; yield, 0.70g (18%). (Found: C, 79.7; H, 6.9. Calculated for  $C_{17}H_{17}FO$ : C, 79.7; H, 6.7%).  $\nu_{\max}$  1620  $cm^{-1}$  (CO).

#### Method B

#### 1,4-bis(2,3,5,6-tetramethylbenzoyl)benzene (1,4-BDB)<sup>62</sup>

##### (Bouveault procedure)

Terephthaloyl chloride (5.0g, 24.6mmol) and durene (12.9g, 96.3mmol) were dissolved in carbon disulphide (50ml) and then added dropwise to a suspension of aluminium chloride (9.3g, 69.7mmol) in carbon disulphide (20ml). The bright orange mixture was refluxed for three hours, and worked up as in method A, to yield white crystals, recrystallised from benzene, which melted at 244–245°C (lit.<sup>62</sup> mp. 247°C); yield, 8.82g (89%).  $\nu_{\max}$  1620  $cm^{-1}$  (CO).

#### 1,3-bis(2,3,5,6-tetramethylbenzoyl)benzene (1,3-BDB)

##### (Bouveault procedure)

Method B was used, the reactants being isophthaloyl chloride (5.0g, 24.6mmol), durene (12.9g, 96.3mmol) and aluminium chloride (9.3g, 69.7mmol) and the solvent carbon disulphide (70ml). The resulting white crystals, recrystallised from benzene, melted at 169.0°C; yield, 6.58g (66%).  $m/z$  398 (77%,  $M^+$ ), 383 (22,  $M-CH_3$ ), 237 (44,  $M-COC_6H(CH_3)_4$ ), 161 (100,  $M-C_6H_4COC_6H(CH_3)_4$ ), 133 (56,  $M-COC_6H_4COC_6H(CH_3)_4$ ); (Found: C, 84.5; H, 7.7.  $C_{28}H_{30}O_2$  requires C, 84.4; H, 7.6%).  $\nu_{\max}$  1620  $cm^{-1}$  (CO).

Method C

Bis(4-fluorobenzoyl)durene (Bis-F)

Cheng et al.'s method<sup>49,65</sup> was adapted as follows:- aluminium chloride (337g, 2.53 moles) was added slowly to 4-fluorobenzoyl chloride (665g, 4.19 moles), the mixture being heated to ca. 80-100°C during the addition and being maintained within this temperature range until the aluminium chloride had completely dissolved. Powdered durene (56.2g, 0.42 moles) was slowly added to the stirred solution over 5 minutes resulting in a dark brown, viscous solution. The mixture was then stirred at 120-160°C for 1 hour, the excess 4-fluorobenzoyl chloride being distilled off under reduced pressure, ca 250g, being recovered. The product was added to crushed ice and acidified (pH 1-3, conc.HCl), then extracted with dichloromethane (1.2 l), the aqueous layer being re-extracted and the combined extracts reduced to ca. half volume, washed with sodium carbonate solution (5-10%, 5 l), distilled water (2 l) and then with a saturated sodium chloride solution (2 l). After a further evaporation (to ca. 400ml), the extract was dried with anhydrous sodium sulphate and evaporated to dryness. The brown residue was recrystallised from benzene to yield off-white crystals. These were further purified to polymerisation grade material by recrystallising from 190ml of toluene and 670ml of propan-2-ol following decolourisation by activated carbon. The resulting white crystals (yield 105g, 66%) had a melting point of 230°C. (Found: C, 76.0; H, 5.2. C<sub>24</sub>H<sub>20</sub>F<sub>2</sub>O<sub>2</sub> requires C, 76.2; H, 5.3%).  $\nu_{\max}$  1620 cm<sup>-1</sup> (CO).

Bis(4-chlorobenzoyl)durene (Bis-Cl)

Method C was used, the reactants being aluminium chloride (226g, 1.69 moles), 4-chlorobenzoyl chloride (493g, 2.8 moles) and durene (37.7g, 0.28 moles). The resulting off-white crystals were purified to polymerisation grade material by recrystallising from 950ml of toluene and 670ml of propan-2-ol following decolourisation by activated carbon. The resulting white crystals (yield 61.6g, 53%) had a melting point of 236-237°C. (Found C, 70.2; H, 4.9.  $C_{24}H_{20}Cl_2O_2$  requires C, 70.1; H, 4.9%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Bis(4-nitrobenzoyl)durene (Bis-NO<sub>2</sub>)

Method C was used, the reactants being aluminium chloride (12.00g, 89.0mmol), 4-nitrobenzoyl chloride (27.71g, 149.3 mmol) and durene (2.00g, 14.9mmol). The resulting light brown crystals, recrystallised from benzene, (yield 2.40g, 36%) had a melting point of 276°C. (Found C, 67.1; H, 4.7; N, 6.5.  $C_{24}H_{20}N_2O_6$  requires C, 66.7; H, 4.7; N, 6.5%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Bis(3-fluorobenzoyl)durene (Bis-mF)

Method C was used, the reactants being aluminium chloride (12.00g, 89.0mmol), 3-fluorobenzoyl chloride (23.68g, 149.3 mmol) and durene (2.00g, 14.9mmol). The resulting white crystals, recrystallised from benzene, (yield 4.00g, 69%) had a melting point of 236°C. (Found C, 76.4; H, 5.4.  $C_{24}H_{20}F_2O_2$  requires C, 76.2; H, 5.3%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Bis(3-chlorobenzoyl)durene (Bis-mCl)

Method C was used, the reactants being aluminium chloride (11.03g, 82.7mmol), 3-chlorobenzoyl chloride (24.00g, 137.1mmol) and durene (1.84g, 13.7mmol). The resulting white crystals, recrystallised from benzene, (yield 3.12g, 53%) had a melting point of 200°C. (Found C, 70.1; H, 4.7.  $C_{24}H_{20}Cl_2O_2$  requires C, 70.1; H, 4.9%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Bis(3-nitrobenzoyl)durene (Bis-mNO<sub>2</sub>)

Method C was used, the reactants being aluminium chloride (12.00g, 89.0mmol), 3-nitrobenzoyl chloride (27.71g, 149.3 mmol) and durene (2.00g, 14.9mmol). The resulting light brown crystals, recrystallised from benzene, (yield 4.74g, 71%) had a melting point of 315°C. (Found C, 66.5; H, 4.8; N, 6.4.  $C_{24}H_{20}N_2O_6$  requires C, 66.7; H, 4.7; N, 6.5%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Bis(4-fluorobenzoyl)isodurene (1,3-Bis-F)

Method C was used, the reactants being aluminium chloride (12.00g, 89.0mmol), 4-fluorobenzoyl chloride (23.68g, 149.3 mmol) and isodurene (2.00g, 14.9mmol). The resulting white crystals, recrystallised from benzene, (yield 0.52g, 8.9%) had a melting point of 143°C. (Found C, 76.0; H, 5.2.  $C_{24}H_{20}F_2O_2$  requires C, 76.2; H, 5.3%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

1,4-Bis[4-(4-fluorobenzoyl)-2,3,5,6-

tetramethylbenzoyl]benzene (1,4-1,4-BDB)

Method C was used, the reactants being aluminium chloride (8.96g, 66.5mmol), 4-fluorobenzoyl chloride (17.68g, 111.5 mmol) and 1,4-bis(2,3,5,6-

tetramethylbenzoyl)benzene (4.50g, 11.2mmol). The resulting white crystals, recrystallised from benzene, (yield 1.56g, 22%) had a melting point of 328°C. m/z 642 (16%,  $M^+$ ), 359 (14,  $M-COC_6(CH_3)_4COC_6H_4F$ ), 283 (20,  $M-C_6H_4COC_6(CH_3)_4COC_6H_4F$ ), 255 (12,  $M-COC_6H_4COC_6(CH_3)_4COC_6H_4F$ ), 123 (69,  $M-C_6(CH_3)_4COC_6H_4COC_6(CH_3)_4COC_6H_4F$ ), 95 (17,  $M-COC_6(CH_3)_4COC_6H_4COC_6(CH_3)_4COC_6H_4F$ ); (Found C, 78.3; H, 5.2.  $C_{42}H_{36}F_2O_4$  requires C, 78.5; H, 5.6%).  $\nu_{max}$  1620  $cm^{-1}$  (CO).

Benzoylmesitylene (mono-mesH) [with S.E. Gardner]<sup>63</sup>

Mesitylene (3.00g, 25.0mmol), benzoyl chloride (5.50g, 39.1mmol), aluminium chloride (3.7g, 27.8mmol) and 1,1,1-trichloroethane (50ml) were stirred together at 25°C for 1 hour, and then refluxed (75°C) for 3 hours. The resulting solution was then worked up as in method A to yield benzoylmesitylene (yield 4.1g, 73%).  $\delta_H$  2.10 (6H, s, 2 x  $CH_3$ ), 2.35 (3H, s,  $CH_3$ ), 7.01 (2H, s, mes-H), 7.35-7.75 (3H, m, m,p-H), 7.80-8.01 (2H, d, o-H).

Method D

Dibenzoylmesitylene (Bis-mesH) [with S.E. Gardner]<sup>63</sup>

Mesitylene (3.4g, 28.3mmol) was added dropwise to a solution of benzoyl chloride (17g, 120.9mmol), aluminium chloride (20g, 150.0mmol) and carbon disulphide (50ml). The solution was refluxed with stirring for 1.5 hours (50°C). After cooling, the mixture was added to crushed ice/water acidified to pH 1-3 with concentrated hydrochloric acid. The carbon disulphide layer was left to evaporate slowly overnight. The residue was made up to 100ml with dichloromethane and washed with 5-10% sodium carbonate

solution and water. The organic layer was dried (sodium sulphate), evaporated and recrystallised from ethanol to yield off-white crystals of dibenzoylmesitylene (yield 0.3g, 3%, mp. 114°C, lit.<sup>41</sup> mp. 117°C).  $\delta_{\text{H}}$  1.91 (3H, s, CH<sub>3</sub>), 2.20 (6H, s, 2 x CH<sub>3</sub>), 7.15 (1H, s, mes-H), 7.40-7.80 (6H, m, m,p-H), 7.95-8.06 (4H, d, o-H).

Attempted Preparation of Tribenzoylmesitylene (Tris-mesH)

[with S.E. Gardner]<sup>63</sup>

Method A was used, the reactants being aluminium chloride (10.00g, 75.0mmol), benzoyl chloride (8.00g, 56.9mmol) and dibenzoylmesitylene (1.50g, 4.6mmol). A higher temperature of 212°C over a longer time (13 hours) in a different solvent (1,2,4-trichlorobenzene) was used. The resulting solution was very dark and after dissolving in dichloromethane/water (pH 1-3), was filtered to remove the carbonaceous material that had formed, before working up in the usual way. The product was recrystallised from ethanol to yield impure brown crystals (mp. 68-70°C) that were identified by NMR spectroscopy as 2,4,5-trichlorobenzophenone. <sup>1</sup>H-NMR gave a multiplet with range 7.50-8.00ppm, i.e. devoid of methyl resonances as was <sup>13</sup>C-NMR.  $\delta_{\text{C}}$  128.82 (s), 130.02 (d), 130.28 (s), 130.41 (d), 131.51 (d), 134.20 (d), 134.99 (s), 135.72 (s), 138.07 (s), 192.77 (CO).

Method E

Tribenzoylmesitylene (Tris-mesH) [with S.E. Gardner]<sup>63</sup>

Dibenzoylmesitylene (10.00g, 30.5mmol), benzoyl chloride (20.00g, 142.3mmol) and aluminium chloride

(30.00g, 22.5mmol) were refluxed (196°C) and stirred for 16 hours. The blackened product was worked up as in the above method to yield a black tar. This was recrystallised from hexane to yield a black solid. The supernatant solution yielded yellow crystals.

Thin layer chromatography and  $^1\text{H-NMR}$  indicated that the black solid contained a higher proportion (3:1) of tribenzoyl- as opposed to dibenzoylmesitylene. This was purified further by column chromatography (Fisons (FSD) silica gel, 60-120 mesh, 0.125-0.250mm) with a 3 : 1 mixture of dichloromethane : hexane to yield brown crystals of impure tribenzoylmesitylene (yield = trace, mp. 194-196°C, lit.<sup>37</sup> mp. 214-216°C).  $\delta_{\text{H}}$  2.00 (9H, s, 3 x CH<sub>3</sub>), 7.50-7.80 (9H, m, m,p-H), 7.95-8.10 (6H, d, o-H). m/z 432 ( $\text{M}^+$ ).

Attempted Preparation of Bis(4-fluorobenzoyl)mesitylene (Bis-mesF) [with S.E. Gardner]<sup>63</sup>

Method D was used, the reactants being mesitylene (3.4g, 28.3mmol), 4-fluorobenzoyl chloride (19.2g, 120.9mmol) and aluminium chloride (20g, 150mmol) refluxed in carbon disulphide (50ml). The reaction product was a white solid identified as 4-fluorobenzoic anhydride (yield 3.05g, 41%, mp. 109-111°C, lit.<sup>66</sup> mp. 108-110°C.  $\delta_{\text{H}}$  7.15-7.50 (4H, dd, H-m-CO), 8.20-8.45 (4H, dd, H-o-CO).  $\delta_{\text{C}}$  116.29 (o-m-CO, J, 22.8), 125.03 (o-CO), 133.32 (o-o-CO, J, 9.8), 163.13 (o-F, J, 286.5), 168.45 (CO).

Bis-1,3-(4-fluorobenzoyl)mesitylene (Bis-mesF) [with S.E. Gardner]<sup>63</sup>

Method E was used, the reactants being aluminium chloride (12.00g, 90.0mmol), 4-fluorobenzoyl chloride (24.00g, 151.3mmol) and mesitylene (2.00g, 16.6mmol), and the solution was heated to 150°C and stirred for 1 hour. After working up as before, the resulting light brown crystals (yield 3.0g, 49%) had a melting point of 88-91°C.  $\delta_{\text{H}}$  1.85 (3H, s, CH<sub>3</sub>), 2.15 (6H, s, 2 x CH<sub>3</sub>), 7.12-7.30 (2H, dd, H-m-CO), 7.85-8.10 (2H, dd, H-o-CO). m/z 364 (M<sup>+</sup>).

1,4-Bis(4-fluorobenzoyl)benzene (1,4-FBB)

Hergenrother et. al.'s method<sup>61,67,68</sup> was adapted and used. Powdered aluminium chloride (2.40g, 17.8mmol) was added to a stirred solution of terephthaloyl chloride (1.52g, 7.5mmol) and fluorobenzene (9.43g, 97.2mmol) at room temperature. After the exothermic reaction had subsided the temperature was raised to 95°C for 3 hours where the colour of the solution changed from yellow to dark green. The solution was left to cool, then poured into cold water acidified to pH 3 by hydrochloric acid. A white solid precipitated, was filtered and subsequently washed with methanol, and oven dried (100°C). Recrystallisation from N,N-dimethylacetamide yielded 1.69g (70%) of a grey crystalline solid (m.p. 228°C). m/z, 322 (39%, M<sup>+</sup>), 227 (42, M-C<sub>6</sub>H<sub>4</sub>F), 199 (14, M-COC<sub>6</sub>H<sub>4</sub>F), 123 (100, M-C<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>4</sub>F), 95 (72, M-COC<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>4</sub>F), 75 (46, M-FHCOC<sub>6</sub>H<sub>4</sub>COC<sub>6</sub>H<sub>4</sub>F); (Found C, 75.2; H, 3.6. Calculated for C<sub>20</sub>H<sub>12</sub>F<sub>2</sub>O<sub>2</sub>: C, 74.53; H, 3.75%).  $\nu_{\text{max}}$  1620 cm<sup>-1</sup> (CO).

Attempted preparation of bis(4-fluorobenzoyl)durene (Bis-F) using triflic acid<sup>60</sup>

Durene (0.56g, 4.2mmol) and 4-fluorobenzoic acid (2.33g, 16.6mmol) were dissolved in triflic acid (50g). The deep orange-red solution was allowed to stand at room temperature for 24 hours, and was then poured into water and worked up as in method A to yield white crystals, recrystallised from benzene, (0.56g) with a melting point of 117-118°C. These were confirmed by <sup>13</sup>C NMR to be (4-fluorobenzoyl)durene (yield 50%).

Attempted preparation of bis(4-fluorobenzenesulphonyl)durene<sup>14</sup>

Method C was used with a temperature maximum of 140°C. The reactants were aluminium chloride (9.08g, 67.4mmol), 4-fluorobenzenesulphonyl chloride (22g, 113.0mmol) and durene (1.51g, 11.2mmol). The resulting material was black in composition and had only small multiple <sup>13</sup>C NMR peaks typical of decomposition.

Attempted preparation of bis(4-chlorobenzoyl)durene (Bis-Cl) in nitrobenzene

Method A was followed, the reactants being aluminium chloride (13.55g, 101mmol), 4-chlorobenzoyl chloride (11.29g, 64.5mmol) and durene (2.00g, 14.9mmol) in nitrobenzene (60ml). The mixture was heated between 120-160°C for 1 hour. Problems with separation between the aqueous (pH 3, HCl) and organic (CH<sub>2</sub>Cl<sub>2</sub>) layer led to the use of high temperature (150°C) vacuum distillation removal of the nitrobenzene. The remaining brown solid was identified as decomposed material.

Attempted preparation of bis(4-chlorobenzoyl)durene (Bis-Cl) using nitrobenzene and Method C

Method C was followed, the reactants being aluminium chloride (12.00g, 89mmol), 4-chlorobenzoyl chloride (13.06g, 74.6mmol) and durene (2.00g, 14.9mmol) heated together in nitrobenzene (9.13g, 7.6ml) between 120-160°C for 1 hour. A further 5ml (5.98g) of nitrobenzene was added to increase solution mobility after the durene was added at 80°C. The mixture was separated as in method C and reduced to a black liquid the contents of which failed to crystallise owing to their being the starting material unreacted, as identified by <sup>13</sup>C-NMR.

Attempted preparation of bis(4-chlorobenzoyl)durene (Bis-Cl) using methylene chloride and Method A

Method A was followed the reactants being aluminium chloride (12.00g, 89mmol), 4-chlorobenzoyl chloride (13.06g, 74.6mmol) and durene (2.00g, 14.9mmol) all refluxed together in methylene chloride (15.18g) at 40°C for 1 hour. The dark red solution was worked up as before to yield white crystals of (4-chlorobenzoyl)durene (1.45g, 34%) as the sole product.

## **Chapter III: Polymer Synthesis**

### **3.1 Introduction**

The primary aim with the difunctional durenene-type derivatives, that have been synthesised in chapter 2, is to produce novel aromatic polymers by nucleophilic displacement polycondensations.

The type of polymer to be synthesised should ideally contain some or all of the following properties: high mechanical strength, good solvent resistance, high temperature stability, low creep resistance at moderate temperatures, and low melt viscosity. A polymer with all these properties in excess would be a very useful and durable engineering material, but for reasons to be discussed, commercial polymers used thus far have had to be a compromise of these features, as the various factors which determine them compromise each other.

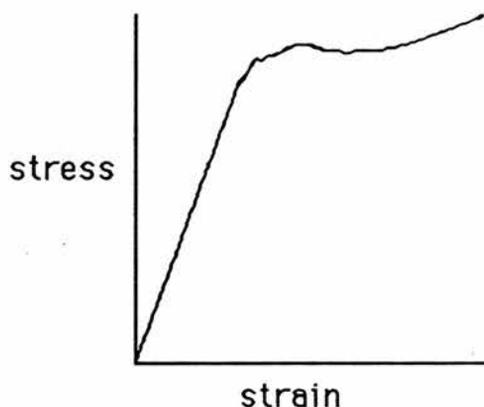
For example, the ICI polymers PEEK (poly[aryl-ether-ether-ketone]) and PES (poly[aryl-ether-sulphone]), marketed commercially as Victrex, are both excellent engineering materials with differing properties (see figure 33)<sup>67</sup>. PES has the better working temperature range with a glass transition temperature ( $T_g$ ) of 225°C compared to PEEK for which  $T_g=143^\circ\text{C}$ . PEEK, however, has the better solvent resistance, being soluble only in concentrated acid, whereas PES shows only moderate solvent resistance to most chlorinated solvents. It will soon become apparent why this is the case.

a) Good mechanical strength arises principally from materials of high molecular weight, as this leads to very

long chains which result in very high intermolecular attractive forces [per molecule] as well as greater chain entanglement; hence only a high strain will result in load failure. However, this very long chain length also allows a high degree of flexural mobility, so that such thermoplastics have the property of bending without breaking, i.e. they have a low crack propagation impulse (see graph 1)<sup>6</sup>.

However, if the molecular weight is too high, the melt flow will be too low for it to give a good consistency in the mould, and this could result in flaws in the finished product along which mechanical failures could be initiated or could propagate. Hence this demand for a good melt flow will set, as a compromise, an upper limit on the molecular weight.

Graph 1: Stress - Strain relationship for a hard and strong plastic.



If the crystallinity is high (~100%), the molecular lattice is so regular that once a crack is initiated it

propagates very quickly. This is the case with diamond. Such materials tend to be very hard as the main energy required to break them lies in the crack initiation, a direct measure of their hardness. But such materials also tend to be very brittle, i.e. have a low crack propagation energy - a direct measure of their toughness (see equation 1).

$$E_{\text{fracture}} = E_{\text{crack initiation}} + \int_0^D \frac{dE_{\text{crack propagation}}}{dl} \cdot dl$$

- equation 1

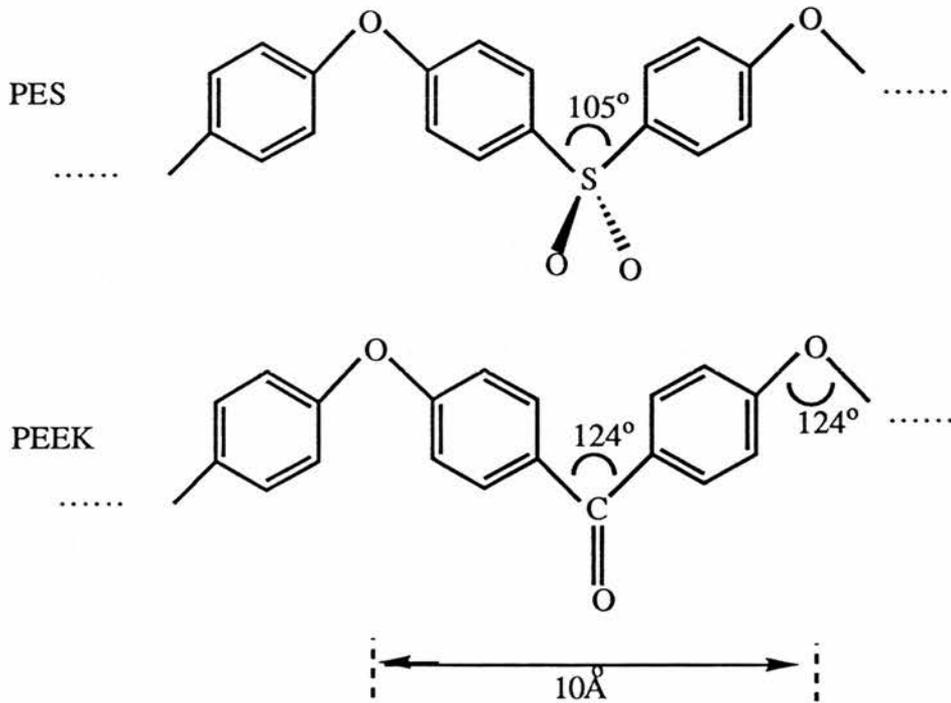


However, aromatic polymers such as PEEK rarely have a crystallinity exceeding 40%, so that there is enough amorphous material between the crystalline domains to inhibit crack propagation. But the added packing density resulting from the crystallinity enhances PEEK's flexural modulus (4.1 GPa), and hence hardness, compared to PES (3.0 GPa) where the crystallinity<sup>67</sup> is less than 1%. Hence the strength of PEEK probably is determined by its amorphous phase. However, when that yields or tears the crack is probably prevented from propagating by the chains which go into the crystals, and they tie the crack together.

b) Good solvent resistance is usually obtained if the material in question is highly crystalline and of a high

molecular weight. High crystallinity is a result of close packing of the molecules which inhibits the ingress of solvent molecules and hence stops the structure fragmenting<sup>2</sup>. Polymers which tend to be highly crystalline are mainly linear, planar and regular with few or no pendant groups. Although both PES and PEEK have no pendant groups, the PES sulphone group, which has a tetrahedral structure, orientates the oxygen atoms diagonally out of plane from the rest of the structure disrupting its packing (see figure 33). Also the differing bond angle for the C-S-C bond<sup>69</sup> ( $105^\circ$ ) when compared to the C-O-C and C-CO-C bonds ( $124^\circ$ ) results in further disruption to the crystalline packing for PES and hence only a low crystallinity (<1%) and moderate solvent resistance results for this polymer<sup>70</sup>.

Figure 33: Linkage Bond Angles for PES and PEEK.



c) Stability at high temperatures requires a polymer which has:

i) stable functional groups at these elevated temperatures, and

ii) a high purity, i.e. freedom from reactive foreign bodies.

Stability is required at those temperatures around which the thermoplastic is processable into the shape required, otherwise discolouration and chemical degradation may set in, leading to a loss of mechanical strength, solvent resistance, melt processability, etc. Long term stability is also required at any working temperature.

d) A high  $T_g$  coupled with a low melting point ( $T_m$ ) is desirable. Beyond  $T_g$  the polymer molecules start to rotate in their lattice and the material starts to soften, rapidly losing mechanical strength. However, if the polymer is crystalline this process is inhibited to a greater or lesser degree, depending on the extent of crystallinity, until the melting point is reached whereupon the crystalline units break up and the mixture becomes a uniform viscous liquid. Between  $T_g$  and  $T_m$  there may exist regions of crystallinity in the softening material known as spherulites. Therefore if the material is to be satisfactorily melt-processed,  $T_m$  must be exceeded, otherwise flaws and irregularities which act as crack initiators and propagators will occur in the final product (see figure 34).

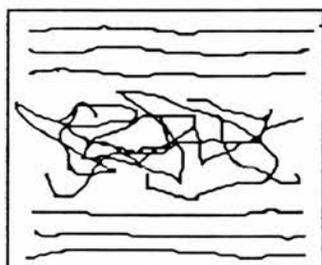
Hence a low  $T_m$  will result in a lower processing temperature. This imposes fewer restrictions on temperature

stability, and also has lower energy requirements. A low  $T_m$  may be achievable by reducing or eliminating the crystallinity of the polymer by incorporating chain disruptors, flexible (aliphatic) links or bulky pendant groups into the polymer thereby disrupting its packing<sup>71</sup>. The packing can also be disrupted by introducing a third monomer into the polymerisation process which will have the effect of destroying the long range order necessary for crystal formation.

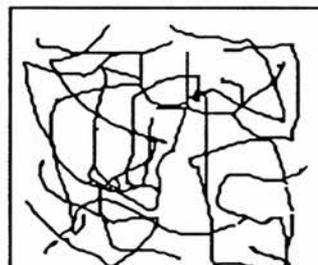
A further class of polymers are semi-crystalline as made, but upon moulding or reheating (and then quenching) revert to an amorphous state. Once in this state they may or may not revert to being crystalline upon annealing<sup>72</sup>.

A high  $T_g$  is also needed in order to increase the creep resistance at moderate temperatures. This can be achieved by incorporating bulky pendant groups, thereby hindering chain rotation.

Figure 34: Chain ordering for varying crystalline states.



semi-crystalline



amorphous

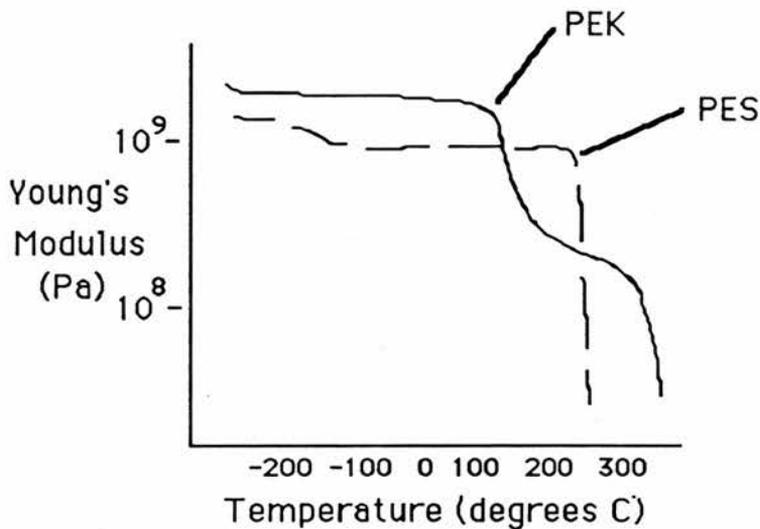
e) High melt flow is only achievable by reducing the viscosity of the molten polymer in some way. Unless there

is a reasonable melt flow the filling of the mould will present practical difficulties.

One way around this, provided that thermal stability is not a problem, is to raise the moulding temperature, since this usually decreases the viscosity of the molten polymer. However, this solution may be energy-expensive, so the usual way to reduce the melt viscosity is to limit the molecular weight of the polymer during the polymerisation process.

f) Having a high  $T_m$  and heat of fusion ( $\Delta H_F$ ) will result in good creep resistance and mechanical strength being retained even when  $T_g$  is exceeded. This is the case with semi-crystalline PEK (poly[aryl-ether-ketone],  $T_g=145^\circ\text{C}$ ,  $T_m>330^\circ\text{C}$ ) which has a reduced modulus when  $T_g < T < T_m$ , compared to amorphous PES ( $T_g=225^\circ\text{C}$ ), where the modulus virtually disappears when  $T > T_g$  (see graph 2)<sup>67</sup>.

Graph 2: Young's Modulus versus Temperature



### Summary of Desired Properties

In practical terms any polymer to be synthesised will represent a compromise on each of these properties with the object of obtaining the maximum effect from each desired property. Overall, however, these properties can be simplified to three factors: molecular weight, crystallinity and pendant groups.

As it will be mainly methyl groups that are the pendant groups in this study there is a great likelihood that polymer chains will be forced further apart creating disorder and thereby rendering the polymer less crystalline and less solvent resistant than might otherwise be expected. However the bulk of these methyl groups is likely to restrict torsional chain movement, thereby increasing the working temperature of the moulded polymer.

Firstly, however, high molecular weight material must be synthesised i.e. it must be demonstrated that the monomers synthesised in the previous chapter are polymerisable.

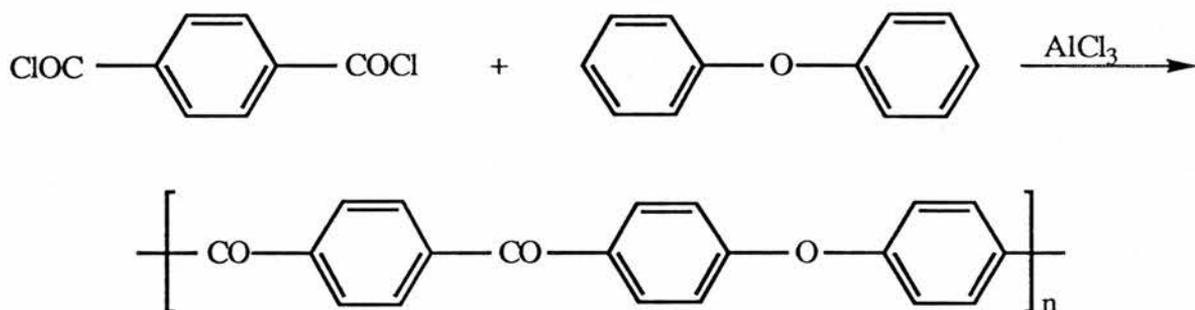
### 3.2 Poly[aryl-ether-ether-ketone] (PEEK) Type

#### Polymerisations

Although it is possible to synthesise polymers such as PEEK by electrophilic aromatic substitution, involving Friedel-Crafts catalysts (e.g. PEKK (poly[aryl-ether-ketone-ketone] synthesised with an aluminium chloride catalyst, see figure 35)<sup>73</sup>, until recently, with the use of

trifluoromethanesulphonic (triflic) acid catalysts/reaction media<sup>60</sup>, and acetal monomers<sup>74</sup> (where an amorphous polymer is first synthesised and then hydrolysed to a crystalline one) only low molecular weight oligomer resulted.

Figure 35: PEKK synthesised by electrophilic aromatic substitution.



The difficulties and expense of using triflic acid render Colquhoun et al.'s method<sup>60</sup> inferior at present to the more conventional nucleophilic aromatic substitution method<sup>67</sup>, and hence it is this latter method that is generally used in this study and will now be discussed in mechanistic terms.

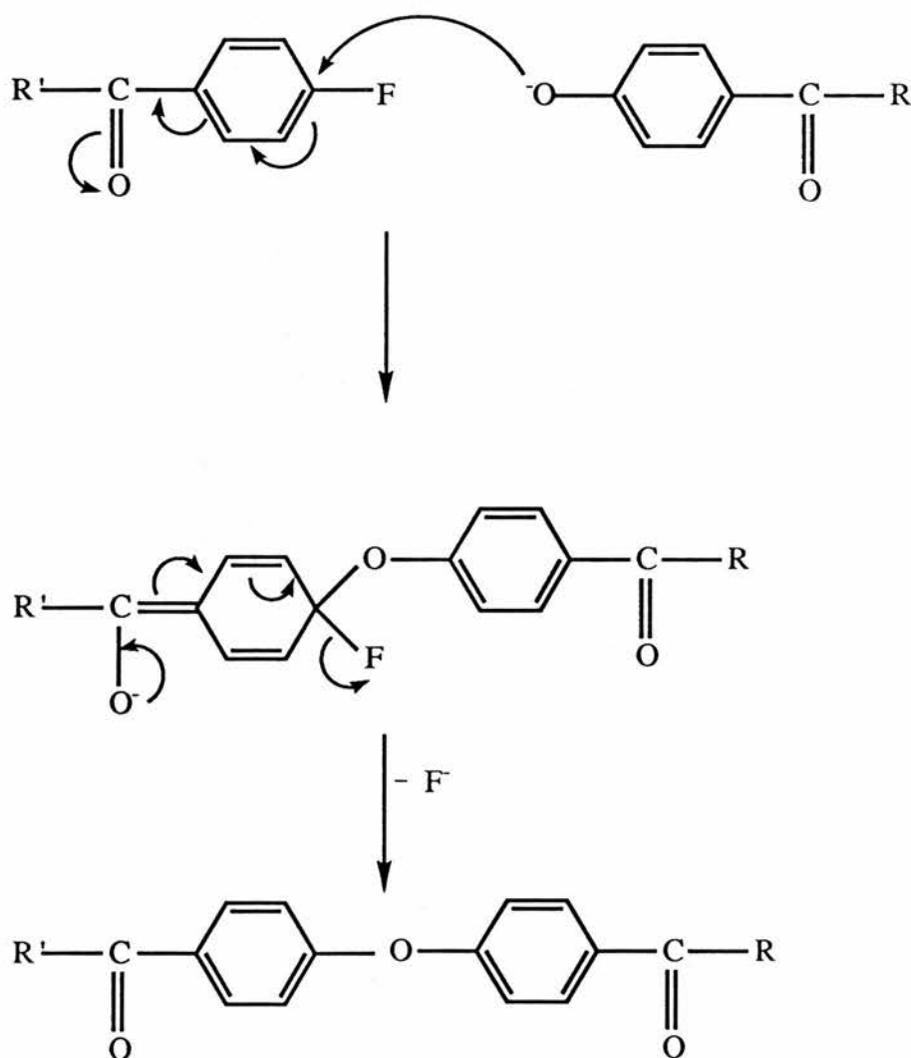
### 3.2.1 Mechanism

Condensation polymerisation of a bis-phenol with a bis-halide proceeds via nucleophilic aromatic substitution (see figure 36).

The attacking nucleophile may have resonance stability, enabling it to be formed in high concentration, if an electron withdrawing group (CO, SO<sub>2</sub>) lies *o*- or *p*- to the phenoxide. However, this also diminishes the

nucleophilicity of the bis-phenol rendering it less reactive. In the substitution process itself, stabilisation of the anionic intermediate (and transition state) is essential. Hence the bis-halide monomers require activating (i.e. electron accepting) substituents  $p$ - (or  $o$ -) to the halogen. Fluorine is by far the most easily displaced halogen in nucleophilic aromatic substitution. 4,4'-Dichlorobenzophenone can be used for the preparation of PEEK, but more severe conditions are required<sup>67</sup>.

Figure 36: Mechanism of polymerisation.



Hydroquinone (HQ) is the comonomer used in the synthesis of PEEK. For a poly(aryl-ether-sulphone) (PES) polymerisation the monomers usually are, however, 4,4'-dichlorodiphenyl sulphone and bis(4-hydroxyphenyl)sulphone (Bis-S).

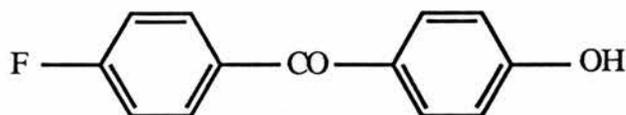
In general the two monomers are mixed in a 1:1 ratio, any significant deviation from which results in less than high molecular weights being obtained in accordance with equation 2 (for small values of r):

$$\text{repeat units/molecule} = \frac{100}{r}$$

- equation 2

where r = % excess of one monomer over the other.

Although 4-fluorophenyl 4-hydroxyphenyl ketone can be used in the synthesis of PEK (poly[aryl-ether-ketone]), it has been shown to be much less reactive<sup>67</sup> than the difluoro monomer.



4-fluorophenyl 4-hydroxyphenyl ketone

Synthesis of crystalline PEEK is generally carried out in a diaryl sulphone solvent such as diphenyl sulphone

(DPS), while the synthesis of amorphous PES can be made in an N-methyl-2-pyrrolidone (NMP)/toluene mixture<sup>75</sup>.

### 3.2.2 Temperature

When choosing the reaction temperature for an ordinary organic reaction, several factors (reaction activation, reactant and product stability, etc.) have to be taken into account. When the reaction is a polymerisation, however, several additional factors must be considered<sup>67</sup>:

(i) For a polymer of low solubility, such as crystalline PEEK, the temperature must be sufficiently high to prevent premature precipitation of the product, before the required molecular weight is reached.

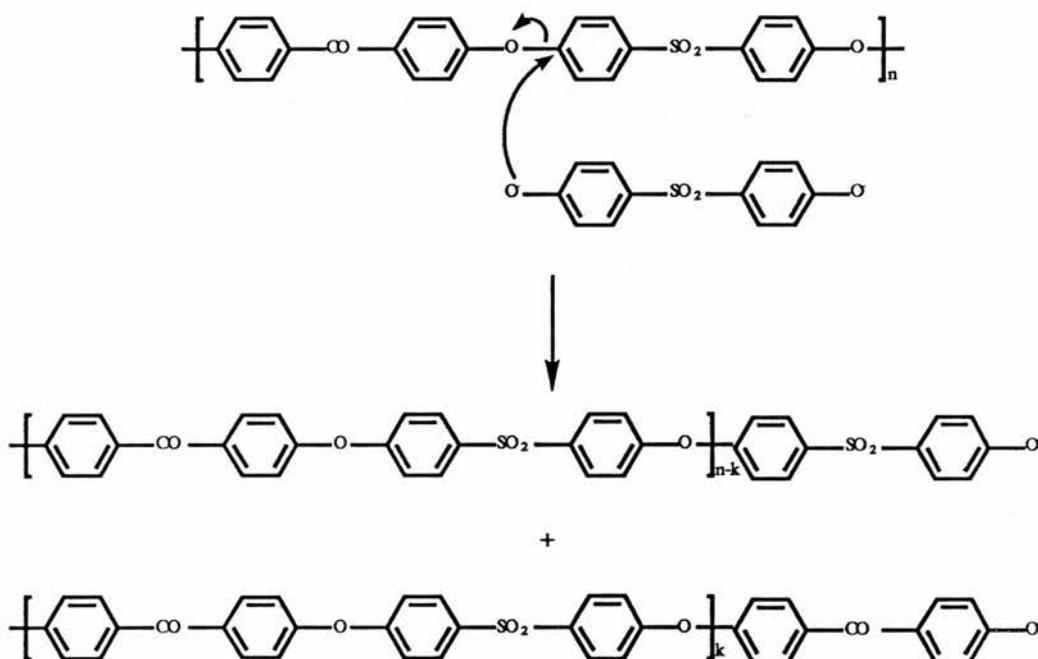
(ii) As the molecular weight increases, so does the viscosity of the solution. The temperature must be sufficiently high to maintain the mobility of the mixture as long as required.

(iii) If one or more of the monomers is volatile at the working temperature, reaction monomer inequivalence in accordance with equation 2 may occur.

(iv) If side-reactions occur at high temperatures, a polymer with poorer physical properties may result. In the case of PEEK and related polymers, competing nucleophilic substitutions, in which a phenoxide is the leaving group instead of fluorine, lead to chain cleavage resulting in a block copolymer structure (see figure 37). This transesterification may be minimised by using hydroquinone

as one of the monomers (less resonance stabilisation of the phenoxide ion) or a lower temperature<sup>76-78</sup>.

Figure 37: An example of transesterification in the synthesis of PESEK.



Overall in PEEK type polymerisations a compromise temperature, close to PEEK's melting point, of 330°C is used in these polymerisations.

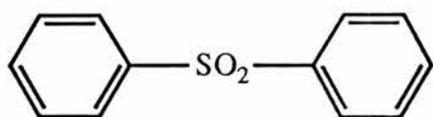
### 3.2.3 Solvents

As previously stated, premature crystallisation of PEEK limits its molecular weight. This was the problem which prevented high molecular weight PEEK being obtained for a considerable period<sup>79</sup>.

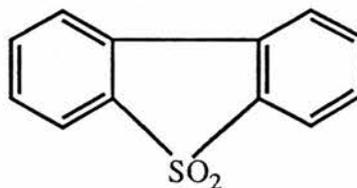
Use of high-boiling aprotic solvents limits this. Although a wide range of solvents has been tried, few compare with diphenyl sulphone (DPS, mp. 125°C, bp. 378°C)

for high temperature solubility (see figure 38). Also, DPS is readily available and is easily purified.

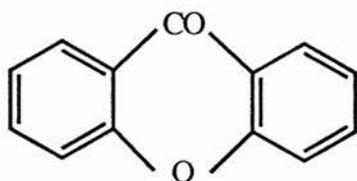
Figure 38: Polymerisation solvents



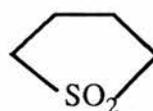
Diphenyl sulphone (DPS)



Dibenzothiophene-10,10-dioxide



Xanthone



Sulpholane

Other solvents which have shown promise in the Attwood study<sup>6 7</sup> apart from DPS were 4-(phenylsulphonyl)biphenyl and dibenzothiophene-10,10-dioxide from which PEEK molecular weights of about half that obtainable in DPS were achieved. The use of sulpholane gave PEEK of only modest molecular weight. Xanthone, used in an American study<sup>80</sup> showed promise also. However, although all these solvents are readily available, and similarity in structures should be noted (see figure 38), DPS remains the most satisfactory solvent for this type of polymerisation.

The reaction mixture concentration is critical. As it is a bimolecular mechanism, reaction rate will change according to equation 3.

$$\frac{-d[A]}{dt} \propto (\text{concentration})^2$$

- equation 3

However, with an ever-increasing viscosity owing to the average polymer molecular weight increasing, anything more than a one to one ratio (by mass) of polymer to solvent is undesirable.

PES does not have the solubility problem to such an extent, as it is essentially amorphous owing to the irregular shape of the sulphone group (see section 3.1).

Also, incorporation of another comonomer into a two comonomer system will disrupt this regularity (if the third comonomer is irregularly shaped) and thus prevent premature crystallisation.

#### 3.2.4 Molecular Weight Control

If too high a molecular weight is obtained, problems can occur with viscosity (melt flow) in any subsequent application such as mould filling. Molecular weight control in this series is achieved by using an excess of one monomer, preferably the dihalide, as a halide end group is more stable to higher temperatures than a phenoxide end group<sup>67</sup>. By using an excess the stoichiometry is thrown out of balance in accordance with equation 2.

If neither end group is stable (as in the polyimides<sup>81</sup>, see chapter 1), an end-capping reagent must be used, although dispersion of this into a solution of ever-increasing viscosity presents practical difficulties.

Monomer purity is essential for the reasons outlined in section 2.4.3.

This polycondensation is a reaction between an arylene halide and a bisphenol as its anion, hence a base is necessary. The choice of base used to deprotonate the phenol (usually sodium or potassium carbonate), can have a dramatic effect on the course of the polymerisation. Potassium carbonate is found to activate the reaction more strongly but is much more insoluble in the reaction medium.

### 3.2.5 Characterisation<sup>82</sup>

From X-ray diffraction (XRD) studies PEEK is semi-crystalline, the crystallinity content depending upon its thermal history<sup>83</sup>.

High molecular weights have been obtained, as determined by viscometry techniques, and PEEK is generally only soluble in concentrated acids, via protonation of its carbonyl oxygens<sup>84</sup>

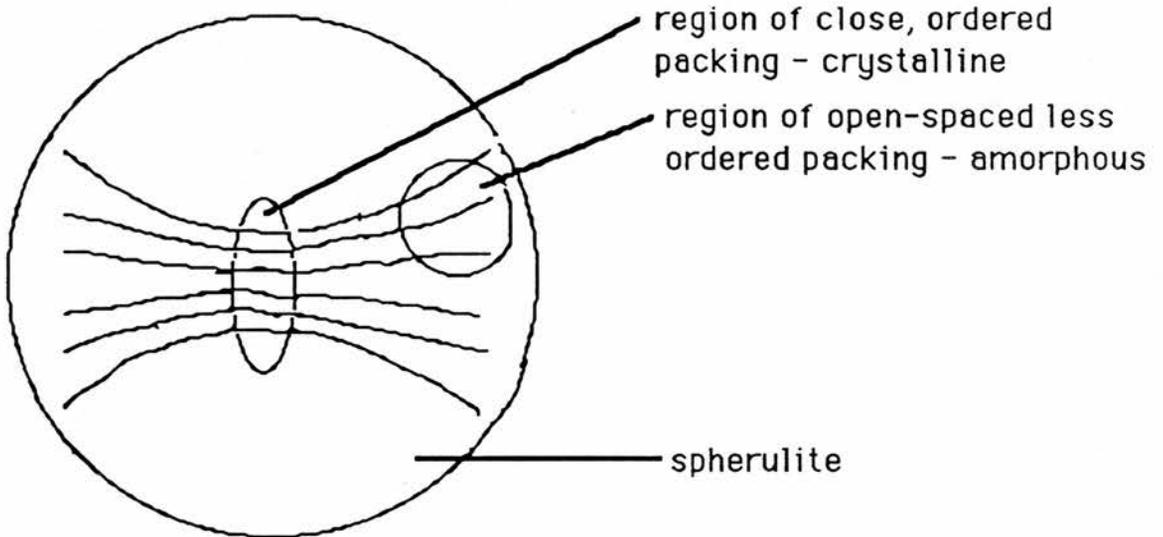
PES is found by XRD to be almost totally amorphous, and although it is also obtainable in high molecular weight it shows only moderate solvent resistance to a wide range of solvents<sup>85</sup>.

Both PES and PEEK show high temperature stability, the latter to nearly 600°C before it degrades in a non-oxidative environment<sup>7</sup>.

Analysis of PEEK by differential scanning calorimetry (DSC) indicates that its crystallinity content is dependent on the rate of cooling or annealing of the polymer around its melting point (>330°C). Double melting point

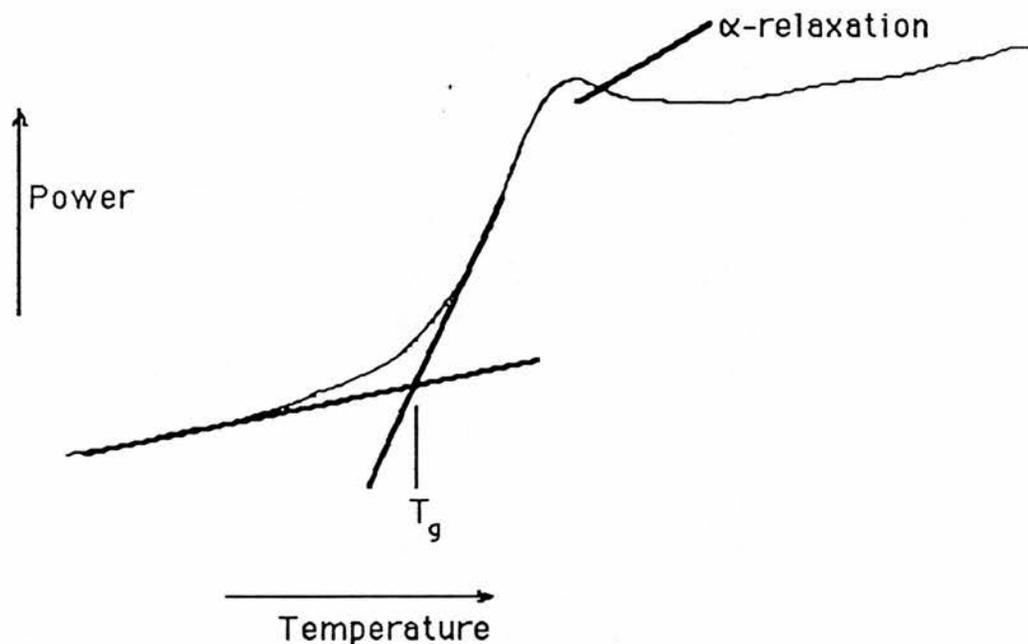
endotherms, sometimes widespread (100°C), usually result for this polymer<sup>86,87</sup>. The high temperature endotherm is due to primary crystallisation, resulting in the formation of spherulites which contain amorphous and crystalline regions. The lower temperature endotherm is due to the ordering of the remaining amorphous regions within the formed spherulite (see figure 39)<sup>88,89</sup>.

Figure 39: Spherulite formation within a crystallising polymer.



Observation of  $T_g$  values by DSC makes a fascinating study for these aromatic polymers. Care has to be taken with analysis of DSC thermograms in that relaxation processes occur around  $T_g$ . The  $\alpha$ -relaxation above  $T_g$  is a result of large-scale conformational rearrangement of the polymer chain backbone, which occurs as a result of the hindered rotation now possible (see figure 40).

Figure 40: Observation of a  $T_g$  point of inflection by DSC.



A low molecular weight polymer has a proportionally greater contribution from chain-end segments in molecular motion, which increases the free volume, and therefore lowers the  $T_g$  as in equations 4 and 5.

$$T_g = T_{g\infty} - (K/M_N) \quad \text{- equation 4}$$

where  $T_{g\infty}$  is  $T_g$  for  $M_N = \infty$

$M_N$  is the number-average molecular weight, and

$$K = 2V_c\rho N_A/\alpha \quad \text{- equation 5}$$

where  $V_c$  is the free volume contributed by a chain end

$\rho$  is the density

$N_A$  is Avogadro's number

$\alpha$  is the thermal expansion coefficient.

In general terms unless the RV (reduced viscosity, see section 3.8.11) for PEEK type polymers (1% in c.H<sub>2</sub>SO<sub>4</sub>) is greater than 0.6,  $T_g$  may be artificially low<sup>69,72</sup>.

The effect of pendant groups on the torsional rotation has been noted by Hergenrother, et al.<sup>61</sup> (see table 14) where large increases in  $T_g$  values have occurred through use of the bulky pendant fluorene group. Certainly replacement of the carbonyl group by the tetrahedral sulphonyl group results in a dramatic increase in  $T_g$  (for PEEK and PES, the difference is 80°C).

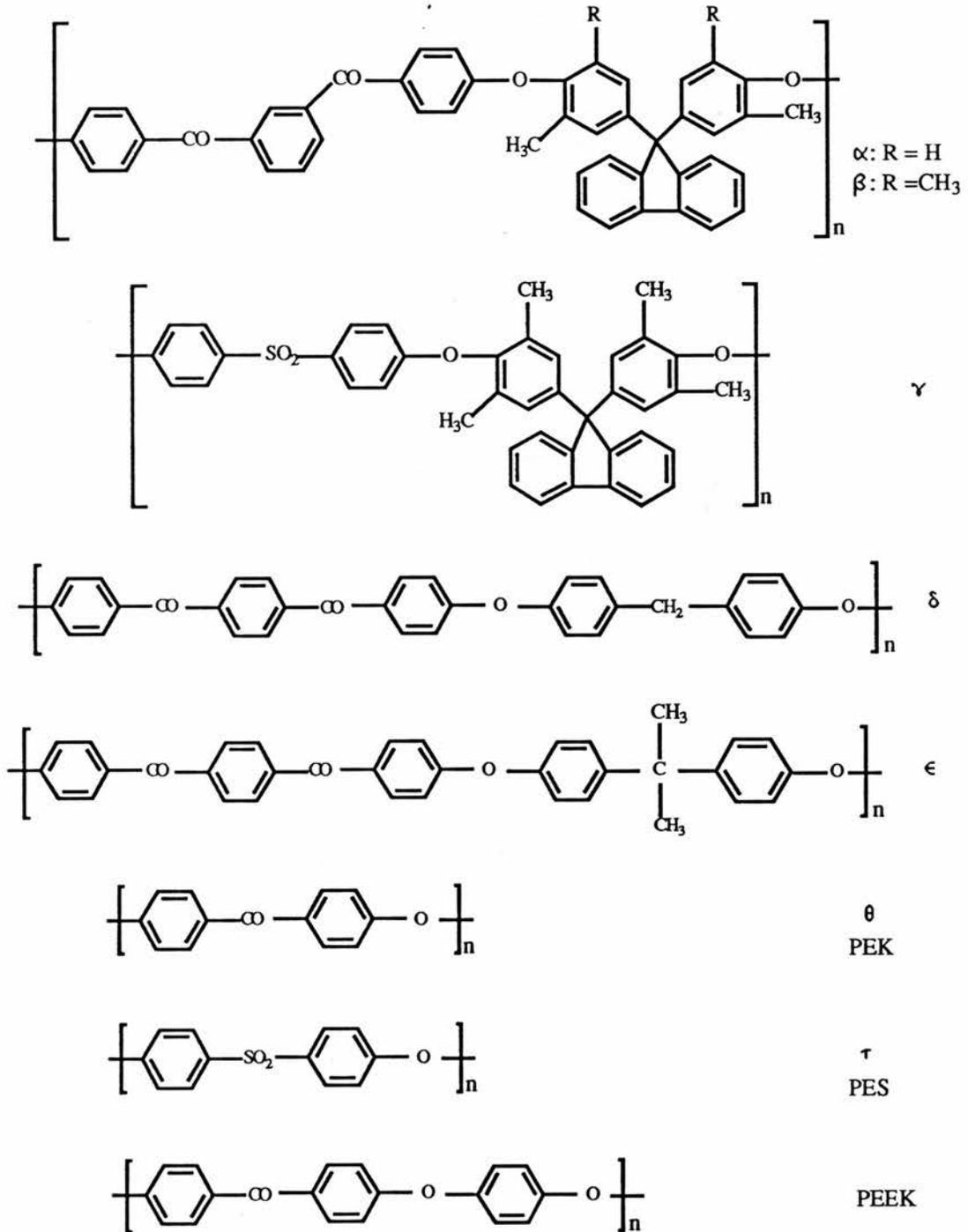
Table 14:  $T_g$  values of some polyarylethers (see figure 41)

Dihalide	Diol	$\eta_{inh}$	$T_g$ (°C)	$\Delta T_g$ (°C)	Structure
1,3-CBB	9,9-MHPF	0.55	217	1	$\alpha$
1,3-FBB	9,9-MHPF	1.20	218		
1,3-CBB	9,9-DMHPF	0.32	229	28	$\beta$
1,3-FBB	9,9-DMHPF	1.24	257		
4-CPS	9,9-DMHPF	0.37	294	16	$\gamma$
4-FPS	9,9-DMHPF	0.64	310		
1,4-CBB	4-HPM	0.16	120	46	$\delta$
1,4-CBB	BPA	0.68	166		$\epsilon$
DFBP	DHBP		145	80	$\theta$
DCS	DFS		225		$\tau$

$$\eta_{inh} = \ln(\eta_r/c), \quad RV = \eta_r - 1 \quad (\text{see section 3.8.11}).$$

Polymers with chlorine as opposed to fluorine end groups tend to have lower  $T_g$  values although care must be taken with this observation as differences in molecular weights will distort this result.

Figure 41: Hergenrother, et al. structures.<sup>61</sup>



### 3.3 Results and Discussion

In all 54 polymers were prepared. The monomers used, the reaction times and temperatures, and some of the characteristics of the polymers are summarised in table 18 and their structures in figure 46. Unless indicated otherwise, the solvent used in the polymerisations was diphenyl sulphone (DPS), and the catalyst was anhydrous sodium carbonate used in 2% excess.

#### 3.3.1 Initial Investigation

Polymerisations 1-5 were initially carried out to test the effectiveness of the monomers Bis-F [bis(4-fluorobenzoyl)durene] and Bis-Cl [bis(4-chlorobenzoyl)durene] in the polymerisation procedure, and to see which of the comonomers (HQ, Bis-S, Bis-A [2,2-bis(4-hydroxyphenyl)propane] and DHBP) gave the most satisfactory products (see figure 42). A strictly 1:1 ratio of comonomers was used.

As expected Bis-F was more reactive than Bis-Cl, as indicated by the higher RV (reduced viscosity, see section 3.8.11) obtained under similar conditions for polymerisation 2 (RV = 0.84) as compared with 1 (RV = 0.40). The Bis-Cl/Bis-A combination (polymerisation 4) was so unreactive that only low molecular weight oligomer formed which could not be separated from the DPS owing to its very low melting point. As the DHBP comonomer yielded the product of highest RV (polymerisation 5, RV = 1.32), and best moulding characteristics (flexibility = 2), this diol was primarily used in subsequent reactions. It soon

became apparent, however, in this preliminary investigation that some form of decomposition was occurring as observed by discolouration, which in the extreme case of the comonomer Bis-S (polymerisation 3) led to a totally degraded, insoluble, blackened product, even when the experiment was repeated (polymerisation 6).

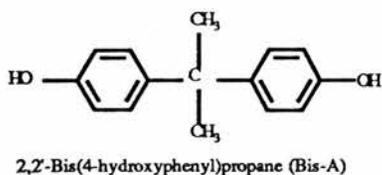
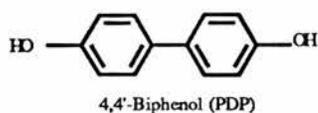
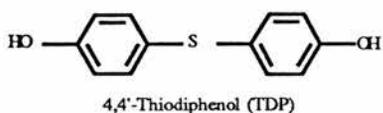
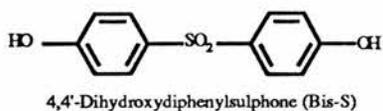
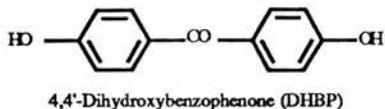
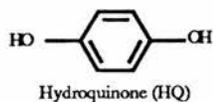
### 3.3.2 Time/Temperature Optimisation

Attempts to limit the decomposition by choice of a lower temperature gave problems owing to premature crystallisation (polymer 7, 265°C, 2 hours, RV = 0.33). Once crystallisation has occurred, further polymerisation is inhibited so that even prolonged heating times lead to only low-moderate molecular weights being achieved (polymer 12, 265°C, 32 hours, RV = 0.62).

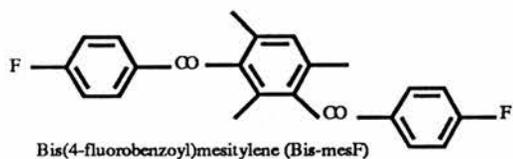
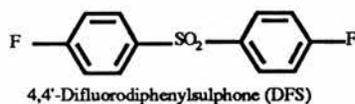
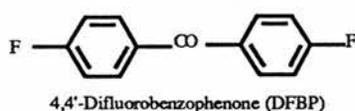
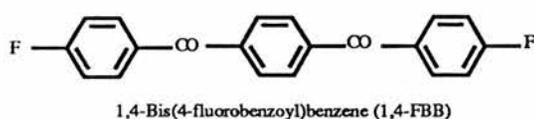
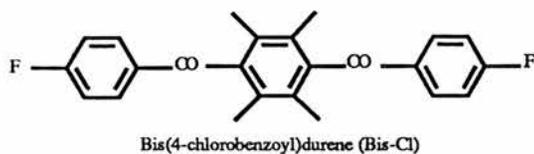
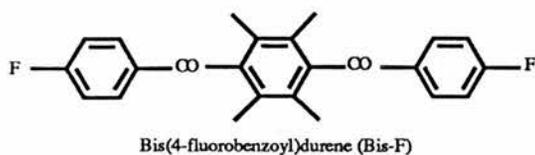
Attempts to optimise conditions (temperature/time) then followed (polymerisations 8-12 and 14-16) finally resulting in a procedure where the polymerisation temperature is initially set at 265°C, the lowest point at which polymerisation is observable. The temperature is then progressively raised, whenever the viscosity substantially increases, to a maximum of 300°C, the point beyond which decomposition, observed by discolouration, becomes apparent. High RV material (polymerisations 15 and 16 where RV is (2.6) and (3.1) respectively) was obtained by this method. A high level of inconsistency occurred during this series, probably owing to difficulties in controlling the nitrogen gas flow, and subsequent release and removal of volatile reaction side-products (e.g. water, free phenols

Figure 42: Structures of monomers and solvents

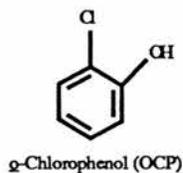
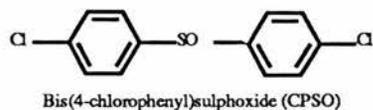
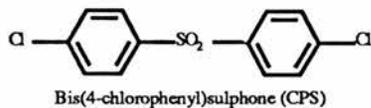
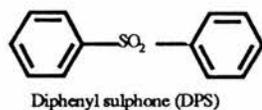
Diol Monomers



Dihalide Monomers



Polymerisation solvents



etc.). Certainly temperature control to within 5°C was no problem.

A further attempt to use the Bis-Cl monomer, this time with the more promising DHBP monomer, resulted in only low RV material (polymerisation 13, RV = 0.24) and substantial discolouration when greater temperatures and times were employed.

### 3.3.3 Polymerisation Solvents

An attempt was made at this point to use alternative polymerisation solvents. Although this had already been tried for PEEK, it was hoped that the situation might be different for polymers with pendant methyl groups, particularly as the Bis-F/DHBP polymers synthesised so far showed that although they were crystalline as made, they were amorphous when reprecipitated (see section 3.8.6). Sulpholane, however, yielded only low RV polymer (polymerisation 17, 270°C, 5 minutes, RV = 0.30) in the short time before premature crystallisation occurred.

o-Chlorophenol (OCP), although an excellent polymer solvent, boils at a temperature too low to activate the reaction (160°C), and despite an extensive period of time results in only extremely low RV oligomer (polymerisation 18, 160°C, 97 hours, RV = 0.02). Although the high boiling point chlorinated solvent, bis(4-chlorophenyl) sulphoxide (CPSO) was used, it proved unstable with time at the temperatures employed (polymerisation 23, 315°C, 5.5 hours, decomposed). And the structurally similar solvent bis(4-chlorophenyl)sulphone (CPS, see figure 42) proved

sufficiently reactive to participate in the reaction to yield further oligomer (polymerisation 20, 315°C, 2 hours, RV = 0.09) in accordance with equation 2.

#### 3.3.4 Diphenol Variation

At this point, with the temperature/time method refined, other phenol comonomers were investigated with Bis-F.

Bis-A, despite an extensive period of time, still only yielded oligomer, which was of such low molecular weight that further analysis was not worthwhile (polymerisation 19, 315°C, 6 hours, RV = 0.09).

HQ showed promise firstly in a 1:1 ratio with Bis-F (polymerisation 21, 315°C, 2 hours, RV = (1.0)), and then incorporated as a third monomer in an HQ : DHPB : Bis-F ratio of 1:1:2, thereby preventing premature crystallisation (polymerisation 22, 315°C, 6 hours, RV = 0.55, polymer type A, Bis-F/HQ) by disruption of the polymer's long range order (see section 3.7.2, NMR, indicating that full randomisation exists in polymer 22), although the RV shows no improvement on the two comonomer systems. Longer times spent at the polymerisation temperature only resulted in decomposed material (polymerisation 27, 315°C, 20 hours, decomposed).

A 9% excess of Bis-F was used in its polymerisation with Bis-S and this yielded material of high RV (polymerisation 24, 315°C, 2 hours, RV = (3.2), polymer type B)! at last overcoming the problem of rapid decomposition with this monomer (Bis-S) at the

polymerisation temperature. This was probably due to the polymer now being fluorine ended (more stable) although this was not realised at the time, as the excess was primarily made to counter volatilisation effects (see section 3.3.5). When the reaction was again repeated using lower graduated temperature increases (polymerisation 28, 280°C for 2 hours then 290°C for 4 hours, RV = 1.14) although a lower RV was obtained, no insoluble gel occurred.

4,4'-Thiodiphenol (TDP) with Bis-F however, only yielded degraded, largely insoluble, blackened material (polymerisation 25, 315°C, polymer type F) despite the use of lower temperatures (polymerisation 29, 260°C) when a strictly 1:1 ratio of monomers was used. And PDP (4,4'-biphenol) with Bis-F crystallised prematurely yielding only product of low RV (polymerisation 31, 315°C, 0.02 hours, RV = 0.42, polymer type G).

### 3.3.5 Monomer Volatility Analysis

A quantitative NMR analysis (see table 15) was made on the volatile products for polymerisations 20-22 and 24 (these crystallised out in the condenser of the polymerisation apparatus). Approximately 1-2 grams of material were subliming off in each case so that if 10% of it was Bis-F (as in polymerisation 20) a 2% molar imbalance could occur.

An interesting picture arises in that apart from evaporation of solvent (which is of little consequence) the only volatile components detected here are Bis-F and HQ

which appear to vary in no predictable way. Therefore, in polymerisations involving Bis-F with DHP and Bis-S, Bis-F volatility can be compensated for by using an excess of Bis-F. In polymerisations involving Bis-F with HQ, however, unpredictable volatility behaviour of both monomers probably explains why no really high molecular weight polymers involving these two components have been synthesised in this thesis (polymerisations 21 and 47 involving HQ have RV values of (1.0) and 1.08 respectively, and also polymerisation 22 involving the three component system, HQ, DHP, and Bis-F, has an RV of only 0.55, while polymerisations 49 and 50 involving DHP and Bis-S have RV values of 2.69 and 2.31 respectively).

Table 15: Analysis of polymerisation volatiles.

Polymer	Halide Monomer	Diphenol Monomer	Polymerisation Solvent	Analysis
20	Bis-F	DHP	CPS	80% CPS, 10% Bis-F, 10% unknown
21	Bis-F	HQ	DPS	44% HQ, 56% DPS
22	Bis-F	0.5 DHP and 0.5 HQ	DPS	100% DPS
24	Bis-F	Bis-S	DPS	97% DPS, 2.5% Bis-F

After this problem was recognised, HQ was not really used in this study, except to investigate the possibility of transesterification. As mentioned before (see section 3.2.2) this occurs at elevated temperatures. However (see section 3.7.3) no evidence for this could be found from NMR spectra of polymers 8 and 21 (double peak formation, or

peak broadening, are typical for such transesterifications) and hence this possibility can be discounted from this study.

### 3.3.6 Crystallinity

Analysis of the crystallinity of the polymers produced thus far, by XRD, DSC and solubility tests, showed that those with structure types D (Bis-F/DHBP) or G (Bis-F/PDP) (see figure 46) are crystalline as made but revert to an amorphous state when reprecipitated or cooled from a melt. Even annealing over considerable periods results in only very slow and limited crystallisation. As the small crystallinity peaks ( $\Delta H_F < 1 \text{ J g}^{-1}$ ) observed in DSC thermograms can be considered to be insufficient to indicate any real degree of crystallisation has taken place, polymer types A (Bis-F/HQ), B (Bis-F/Bis-S) and E (Bis-F/0.5 HQ, 0.5 DHBP) can be considered to be essentially amorphous. No polymers of sufficiently high RV were made of types C (Bis-F/Bis-A) and F (Bis-F/TDP).

### 3.3.7 Carbonate Variation

Polymers 32 (RV = 1.27, 260-300°C, 6 hours) and 33 [RV = (2.9), 300°C, 1 hour] represent the best developments of the two most promising monomer combinations: Bis-F/DHBP (polymer type D) and Bis-F/Bis-S (polymer type B) respectively.

Polymer 34 (RV = 1.10, 300°C, 1.5 hours, Bis-F/Bis-S) was made under similar conditions to polymer 33, except that potassium carbonate was used instead of sodium

carbonate (still in 2% excess). Although a lower RV was obtained no insoluble material was found (as had occurred in the case of polymer 33 when the measurement was made), and the mouldings from polymer 34 appeared to have a better quality (flexibility = 1, colour = 2, cf. flexibility = 3, colour = 3 for polymer 33), and hence potassium carbonate was also used for polymerisation 44. However this latter polymer did contain insoluble material although a higher RV was obtained (RV = (4.6), 300°C, 1.5 hours, Bis-F/Bis-S). Therefore no real change from the choice of carbonate was indicated in polymer quality, the source of this variation appearing to lie elsewhere, although eventually (polymerisations 47-53) a mixture of sodium carbonate and potassium carbonate (sieved to a maximum particle size of 250µm) in the ratio of 50:1 was used (still in 2% excess).

### 3.3.8 Non-methylated Analogues

Comparison of Bis-F with the behaviour of its non-durene analogue 1,4-FBB (1,4-bis(4-fluorobenzoyl)benzene yielded some interesting results. Polymers 36 and 38 (1,4-FBB/DHBP, polymer type H) were much more crystalline, retaining this characteristic even after reprecipitating, or quenching from the melt. This proved a problem in their synthesis as they both precipitated prematurely yielding only low-moderate molecular weight material (RV values are only 0.25 and 0.46 respectively, despite the use of higher temperatures or prolonged times (315°C, 5 hours) in the latter case of polymer 38). Polymer 42 (1,4-FBB/HQ, polymer type J) behaved similarly (RV = 0.56). Polymer 41 (1,4-

FBB/Bis-S, polymer type I) showed some crystalline properties but only in that after reprecipitation it had significant solvent resistance to chlorinated solvents (chloroform, OCP) and was not fully dissolved in c.H<sub>2</sub>SO<sub>4</sub>. However its DSC thermogram indicated that it was amorphous and certainly there were no premature precipitation problems such as were observed in the preparation of polymers 36, 38 and 42, so that polymer 41 had a high molecular weight (RV = (3.0)). The solvent resistance is possibly a result of using a 1:1 ratio of 1,4-FBB : Bis-S, leading to some insoluble, decomposed material - a situation observed in the extreme state with polymerisations 3 and 6, which yielded black decomposed material insoluble even in c.H<sub>2</sub>SO<sub>4</sub>.

No stability problems for these non-durene polymer analogues (types H, I and J [1,4-FBB with DHBP, Bis-S and HQ respectively]) were obvious during the polymerisations. When later dissolved in solvents these polymers (apart from type I) did not leave behind insoluble cross-linked gels as did many of the early polymerisations involving Bis-F where temperature was not limited. Furthermore, polymer types H, I and J (1,4-FBB with DHBP, Bis-S and HQ respectively) showed substantially greater temperature stability (see table 16) than the durene and mesitylene analogues (polymer types A, B, D (Bis-F with HQ, Bis-S and DHBP respectively) and N (Bis-mesF/Bis-S), by TGA (Thermal Gravimetric Analysis)).

Table 16: Thermal Gravimetric Analysis results ( $\Delta T = 4^\circ\text{C}/\text{min}$ ).

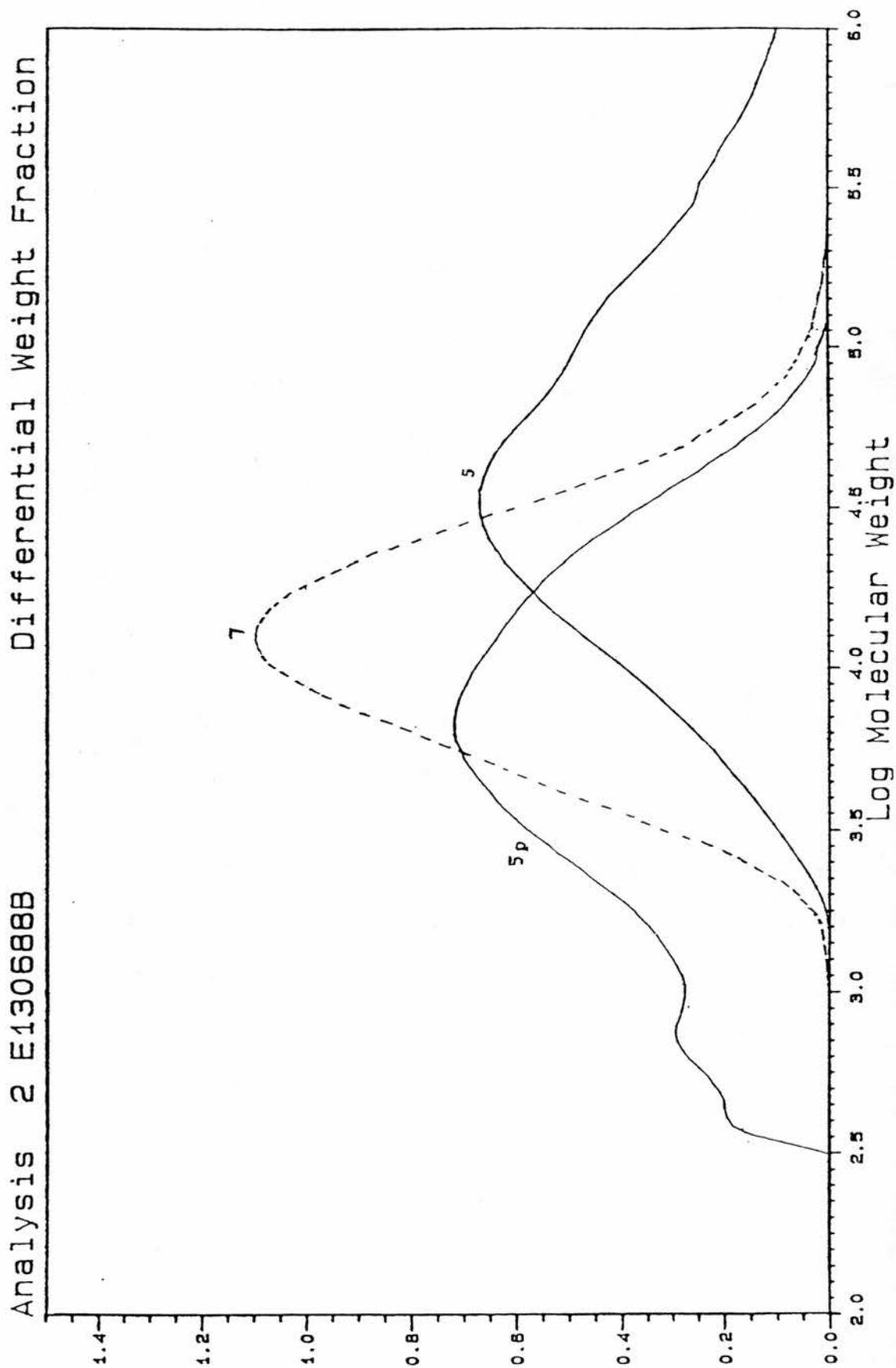
Polymer	Halide Monomer	Phenol Monomer	Temperatures at which weight losses exceed given percentages of starting material ( $^\circ\text{C}$ )		
			1%	10%	50%
1	Bis-Cl	HQ	326	425	578
2	Bis-F	HQ	255	299	412
7	Bis-F	DHBP	369	409	480
15	Bis-F	DHBP	350	415	525
21	Bis-F	HQ	406	434	499
32	Bis-F	DHBP	360	408	495
33	Bis-F	Bis-S	395	419	516
34	Bis-F	Bis-S	370	408	494
35	Bis-F	DHBP	395	417	500
36	1,4-FBB	DHBP	520	542	610
37	Bis-F	Bis-S	387(466) <sup>a</sup>	402	505
38	1,4-FBB	DHBP	536	548	617
41	1,4-FBB	Bis-S	470	504	541
42	1,4-FBB	HQ	528	551	620
54	Bis-mesF	Bis-S	390(490) <sup>a</sup>	410	510

<sup>a</sup> - Point of inflexion of the TGA curve owing to the Bis-S unit decomposition becoming dominant.

### 3.3.9 Thermal Stability

Analysis by GPC (gel permeation chromatography) of polymer 5 before and after reprecipitation (figure 43) indicated a substantial proportion of low molecular weight material and the profile was significantly distorted from a Gaussian curve, when compared to polymer 7 where the degradation was almost non-existent owing to the lower temperatures used in its synthesis ( $265^\circ\text{C}$ , cf.  $315 \pm 20^\circ\text{C}$  for polymer 5).

Figure 43: Gel Permeation Chromatography (GPC).



Studies by HSM (hot stage microscopy) on a polymer of type D (polymer 48, Bis-F/DHBP) confirmed the TGA findings (table 17), i.e. decomposition became quite observable (discolouration) at temperatures little higher than those used for the polymerisation.

Table 17: HSM of polymer 48.

Temperature (°C)	Observation
200	translucent, light brown
310	no change after 5 minutes
340	some discolouration, medium brown after 4 minutes
360	medium/dark brown
370	going black
380	slightly shrivelled, black
460	no change

One obvious possibility is that some sort of thermal decomposition involving the pendant methyl groups only present on the durene and mesitylene analogues is occurring, resulting in cross-linking to form insoluble gels (even in c.H<sub>2</sub>SO<sub>4</sub>), possibly by the mechanism<sup>90-93</sup> in figure 44.

The possibility of photocrosslinking<sup>94-98</sup> promoted by background ultraviolet (UV) light was considered but quickly rejected when it was found that despite prolonged exposure (of a polymer solution) to a UV lamp no gelling occurred.

The possibility of phenolic end groups contributing has not been discounted and would certainly appear dominant in the decomposition of polymers of type B (Bis-F/Bis-S) when equimolar proportions of both comonomers

Figure 44: Possible polymer cross-linking mechanism.

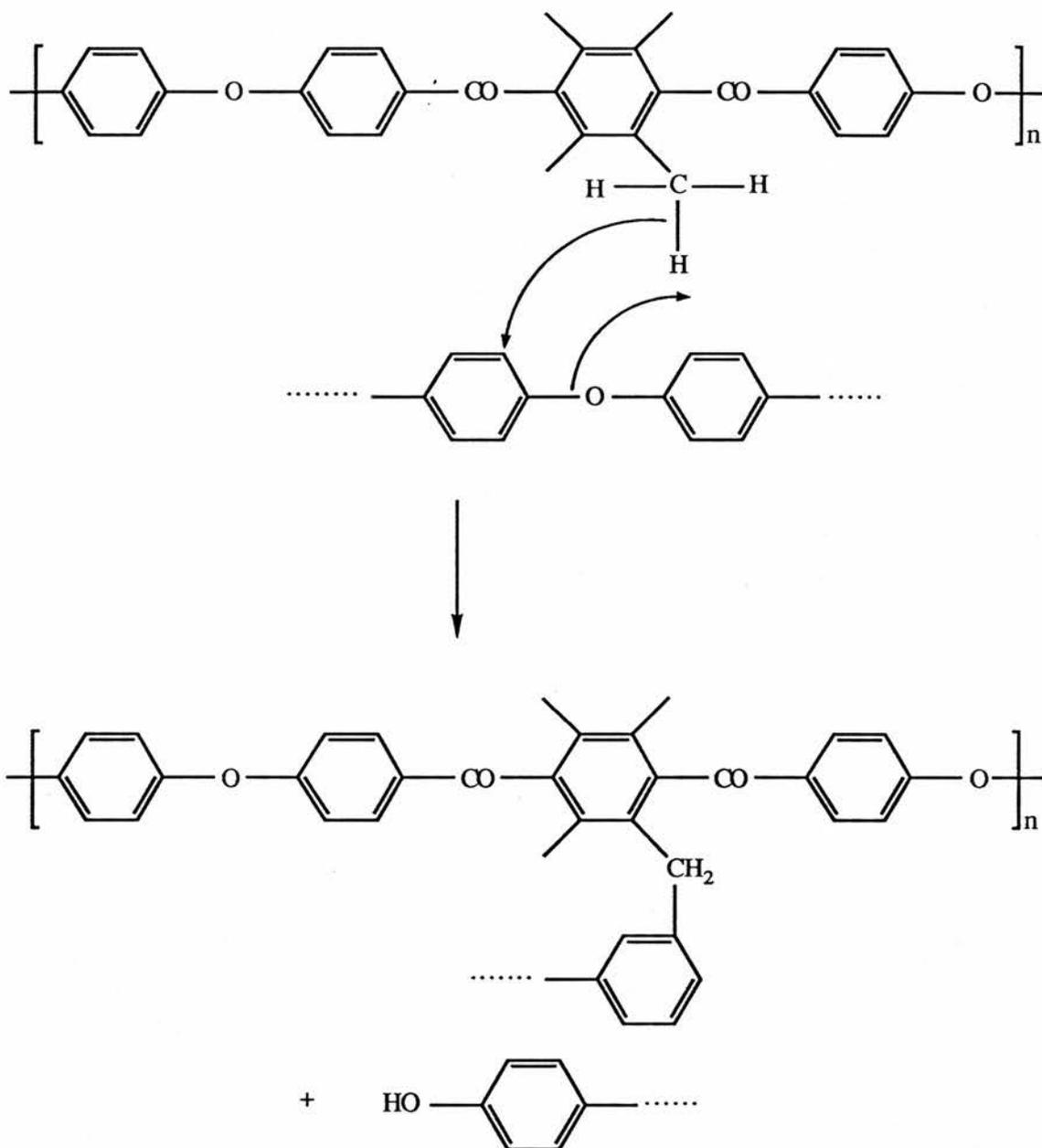
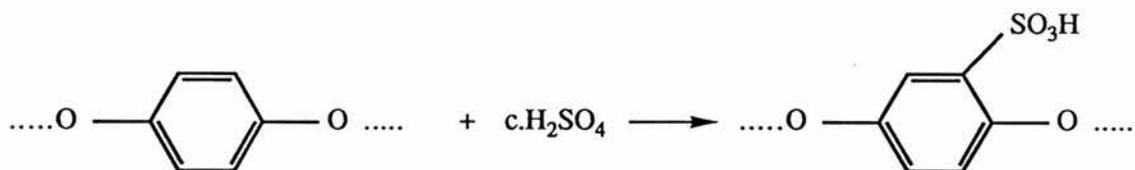


Figure 45: Sulphonation of polymers



are used (polymers 3 and 6) resulting in a large proportion of phenol-ended polymers. However, this lower temperature decomposition is easily eliminated by the use of an excess of the halide monomer (polymer 24). Varying the monomer ratio back to 1:1 (Bis-F : Bis-S) led to reasonable molecular weight polymer without noticeable degradation although the reaction took much longer at 4 hours (290°C, polymer 37, RV = 1.16). Attempts to increase the temperature (polymer 39, 290°C for 1 hour, 303°C for 4 hours) yielded only degraded, insoluble material as before (polymerisations 3 and 6). So the conditions thus used for polymers 32 (1:1 ratio of Bis-F : DHBP, 260-300°C, 6 hours) and 34 (9% excess of Bis-F, K<sub>2</sub>CO<sub>3</sub>, 300°C, 1.5 hours) were repeated on a large scale (polymers 43 (RV = 1.33) and 44 [RV = (4.6)]) to produce sufficient material for mechanical testing (~100 grams). As just mentioned, although the Bis-F/DHBP combination had a very consistent RV value for both polymers 32 and 33, the RV value for the Bis-F/Bis-S combination varied substantially as did the insoluble gel (c.H<sub>2</sub>SO<sub>4</sub>) fraction (see section 3.8.11).

### 3.3.10 Copolymers

Further experiments were undertaken (polymers 45 and 46) whereby other fluorinated monomers (4,4'-difluorobenzophenone [DFBP] and bis(4-fluorophenyl)sulphone [DFS]) were copolymerised with Bis-F to see if the properties of polymer types D (Bis-F/DHBP) and B (Bis-F/Bis-S) could be retained if Bis-F was used in smaller proportions. Polymer types K (0.5 Bis-F, 0.5 DFBP/DHBP) and

L (0.5 Bis-F, 0.5 DFS/DHBP) which resulted are certainly similar in crystallinity to polymer types D (Bis-F/DHBP) and B (Bis-F/Bis-S) respectively. The lowering in  $T_g$  values makes a fascinating study which will be discussed later (see section 3.4.3.2).

### 3.3.11 Other Comonomers and Fine Tuning

Polymer 47 (RV = 1.08, 270-350°C for 0.5 hours, 350°C for 0.75 hours) shows an improvement on polymer 21 in that some crystallinity has been obtained in the Bis-F/HQ combination as evidenced by DSC measurements. However, thermal degradation occurring around the DSC-observed melting point ( $T_m = 386^\circ\text{C}$ ), as evidenced by HSM observations, may have falsified this result. Also the RV values of both these polymers (RV ~ 1) may be double what is expected for a given molecular weight as the possibility of sulphonation of the aryl groups, which do not have neighbouring deactivating groups, may occur<sup>99,100</sup> (see figure 45). Furthermore, although polymer 47 yields a lightly coloured plate when compression moulded, this plate is slightly brittle which suggests that the molecular weight is a lot lower than is indicated by the RV value.

Further Bis-F purification, reducing its melting point range from 1-2°C to 0.2°C and removing the slight discolouration (by repeated crystallisation), along with its use in 1% excess and a lower polymer-to-solvent concentration (of 30% cf. 50% before) in the polymerisation mixture, resulted in increased molecular weight and less gel (now negligible) of polymer types B (Bis-F/Bis-S) and D

(Bis-F/DHBP) (polymers 48-50 and 52). Polymers 49, 50 and 52 represent scaled-up reactions (100 g). Polymer 49 (RV = 2.69, 260-310°C, 1.5 hours, Bis-F/DHBP) was of too high an RV to be moulded into a large plate for mechanical testing; the problem was overcome by prematurely terminating the polymerisation via temperature lowering (polymer 52, 280°C, 1.5 hours, RV = 1.89), although even here the viscosity appears to be higher than desired. While polymer 48 (RV = 2.79, 260-310°C, 2 hours) also had a high RV value, it was successfully compression moulded into a thin plate (2-3 grams). However, for making the larger plates required for mechanical testing (100 grams), much more time at elevated temperatures is needed in the mould, leading to a greater likelihood of thermal degradation. Polymer 50 (RV = 2.31, 280-310°C, 1.75 hours) was successfully plate moulded despite its high RV value, and it, along with polymer 52 were mechanically tested (see section 3.4.1).

From measurements of RV values compared to flexibility results (from compression mouldings), an ideal RV would appear to be in the range 1.0 - 1.3 (if the polymers which contain substantial proportions of insoluble (in c.H<sub>2</sub>SO<sub>4</sub>) material are ignored (bracketed RV values), as they appear to degrade the mouldings somewhat) although values as low as 0.64 (polymer 14, Bis-F/DHBP, type D) can be tolerated.

In polymerisation 51 an attempt to overcome the premature crystallisation observed with the Bis-F/PDP combination (polymer type G (Bis-F/PDP), polymerisation 31) by addition of a third monomer (Bis-S) was successful only in that crystallisation did not occur in the reaction

vessel. However, only moderate molecular weight (RV = 0.56, polymer type M, Bis-F/0.5 PDP, 0.5 Bis-S) material resulted.

An attempt to obtain reasonable molecular weight material from the chloro-monomer Bis-Cl was successful (polymerisation 53, 275°C for 0.8 hours, 300°C for 3 hours, RV = 0.84) although decomposition (discolouration) was still apparent, and only a poor, brittle moulding resulted (flexibility = 3).

Finally, low-moderate molecular weight polymer was synthesised from the mesitylene monomer Bis-mesF (Bis(4-fluorobenzoyl)mesitylene, polymerisation 54, RV = 0.53, 275°C for 1.5 hours, 290°C for 5.5 hours, polymer type N, Bis-mesF/Bis-S), which was found to have little solvent resistance to most common organic solvents and was also observed to be moderately coloured (degraded).

Table 18: Polymerisation Results.

Polymer	Halide Monomers	Phenoxide Monomers	Temp (°C) <sup>a</sup>	Time <sup>b</sup> (hours)	RV <sup>c</sup>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>F</sub> (J g <sup>-1</sup> )	Flex. <sup>d</sup>	Colour <sup>e</sup>
1	Bis-Cl	HQ	315	2	0.40	203	268	7.6	4	4
2	Bis-F	HQ	315	2	0.84	231	283	2.2	4	4
3 <sup>f</sup>	Bis-F	Bis-S	315	2	-				4	4
4 <sup>g</sup>	Bis-Cl	Bis-A	315	2	-					
5	Bis-F	DHBP	315	2	1.32	197	-	-	2	3
6 <sup>f</sup>	Bis-F	Bis-S	315	2	-				4	4
7	Bis-F	DHBP	265	2	0.33	209	347	43	4	3
8	Bis-F	DHBP	315	2	0.60	228	313	46	2	2
9	Bis-F	DHBP	290	6.5	0.82	231	331	46	1	2
10	Bis-F	DHBP	340	2	(1.1)	233	-	-	3	3
11	Bis-F	DHBP	315	8.5	1.01	240	305	77	4	3
12	Bis-F	DHBP	265	32	(0.62)	228	355	51	3	3
13	Bis-Cl	DHBP	315	2	0.24	183	-	-	3	3
14	Bis-F	DHBP	290	5.5	0.64	230	-	-	1	1
15	Bis-F	DHBP	300	5.5	(2.6)	240	313	42	2	3
16	Bis-F	DHBP	265-300	4.5	(3.1)	232	302	22	2	3
17 <sup>h</sup>	Bis-F	DHBP	270	0.1	0.30	199	328	40	4	2
18 <sup>i</sup>	Bis-F	DHBP	160	97	0.02 <sup>j</sup>					
19	Bis-F	Bis-A	315	6	(0.06) <sup>j</sup>					
20 <sup>k</sup>	Bis-F	DHBP	315	2	0.09 <sup>j</sup>					
21	Bis-F	HQ	315	2	(1.0)	234	299	0.5	2	4
22	Bis-F	0.5 DHBP 0.5 HQ	315	6	0.55	226	265	1.5	3	2
23 <sup>l,f</sup>	Bis-F	DHBP	315	5.5						
24	Bis-F	Bis-S	315	2	(3.2)	248	318	0.2	2	2
25	Bis-F	TDP	315	2	-	187	301	0.1	4	4
26 <sup>m</sup>	Bis-F	DHBP	315	20	0.10 <sup>j</sup>					
27 <sup>f</sup>	Bis-F	0.5 DHBP 0.5 HQ	315	20						
28	Bis-F	Bis-S	280 290	2.5 4	1.14	252	-	-	2	2
29	Bis-F	TDP	260	10	(0.04)	174	233	0.1	4	4
30	Bis-F	HQ	270 280 290	1.5 2 2.5	0.33	209	-	-		
31	Bis-F	PDP	315	0.02	0.42	218	324	0.5	4	4
32	Bis-F	DHBP	260-300	6	1.27	227	298	19	1	1
33	Bis-F	Bis-S	300	1	(2.9)	255	-	-	3	3
34	Bis-F	Bis-S	300	1.5	1.10	250	295	0.1	1	2
35	Bis-F	DHBP	274 285 330	2 1 1	2.09	228	301	20	1	1
36	1,4-FBB	DHBP	290 325	0.5 1	0.25	243	371	70	4	3

Polymer	Halide Monomers	Phenoxide Monomers	Temp (°C) <sup>a</sup>	Time <sup>b</sup> (hours)	RV <sup>c</sup>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>F</sub> (J g <sup>-1</sup> )	Flex. <sup>d</sup>	Colour <sup>e</sup>
37	Bis-F	Bis-S	290	4	1.16	237	-	-	3	3
38	1,4-FBB	DHBP	315	5	0.46	-	376	79	4	2
39 <sup>f</sup>	Bis-F	Bis-S	290	1	(0.01)					
			303	4						
40	Bis-F	Bis-S	290	1	(1.7)	242	-	-	1	2
			305	4						
41	1,4-FBB	Bis-S	290	1	(3.0)	180	-	-	1	3
			302	1						
42	1,4-FBB	HQ	308	0.5	0.56	283	350	50	4	2
			322	0.75						
43	Bis-F	DHBP	265	1.5	1.33	212	251	15	1	2
			280	1						
			300	2						
44	Bis-F	Bis-S	300	1.5	(4.6)	235	-	-	1	2
45	0.5 Bis-F	DHBP	280	2	1.32	178	247	30	1	2
	0.5 DFBP		300	1						
			330	1						
46	0.5 Bis-F	DHBP	300	2	(1.8)	197	-	-	1	2
	0.5 DFS									
47	Bis-F	HQ	270-	0.5	1.08	240	386	35	2	1
			350							
			350	0.75						
48	Bis-F	DHBP	260-	2	2.79	213	253	16	1	1
			310							
49	Bis-F	DHBP	260-	1.5	2.69	212	269	22	1	1
			310							
50	Bis-F	Bis-S	280-	1.75	2.31	237	-	-	1	1
			310							
51	Bis-F	0.5 PDP	280	1	0.56	222	-	-	4	4
		0.5 Bis-S	300	2						
52	Bis-F	DHBP	280	1.5	1.89	214	253	19	1	1
			300	0.2						
53	Bis-Cl	DHBP	275	0.8	0.84	185	-	-	3	3
			300	3						
54	Bis-mesF	Bis-S	275	1.5	0.53	200	-	-	3	3
			290	5.5						

a - Temperature of synthesis, b - Time of synthesis.

c - Reduced viscosity (RV) measured in c.H<sub>2</sub>SO<sub>4</sub> (98%), 1% polymer by weight, T = 25.00 ± 0.05 °C. ( ) indicates polymer not fully dissolved.

d - Flexibility of best thin compression mould cf. crease test. Scale 1-4 where 1 = bend 180° without folding, 2 = bend 90° without breaking, 3 = breaks on bending, 4 = dust.

e - Colour of compression mould. Scale 1-4 where 1 = light brown, 2 = medium brown, 3 = dark brown, 4 = black.

f - Black. Insoluble and crumbly (decomposed). g - Too soft to mill (low molecular weight oligomer), h - Polymerisation solvent is sulpholane, i - Polymerisation solvent is OCP,

j - RV too low to make further analysis worthwhile, k - Polymerisation solvent is CPS. l - Polymerisation solvent is CPSO, m - Polymerisation solvent is CPS.

Figure 46: Structures of polymers

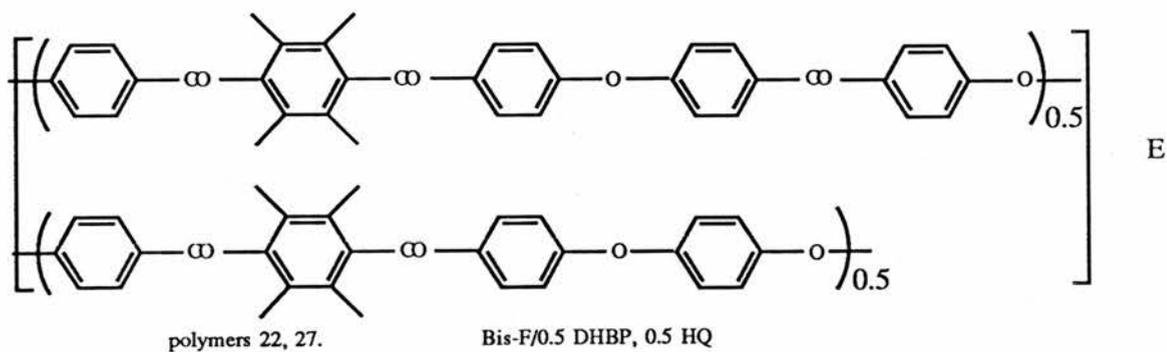
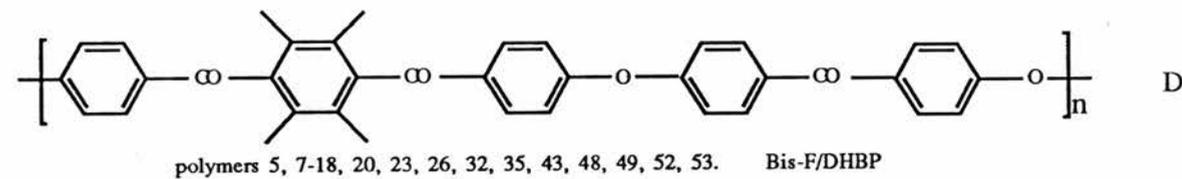
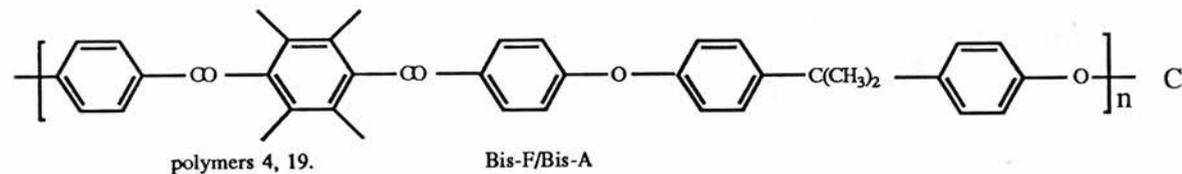
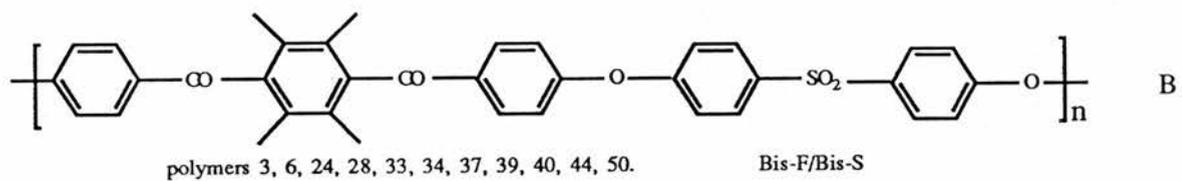
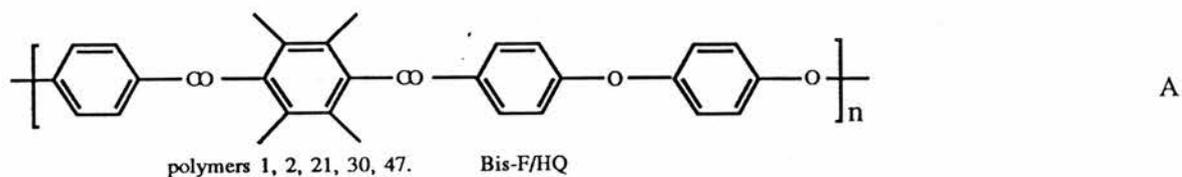


Figure 46 continued: Structures of polymers

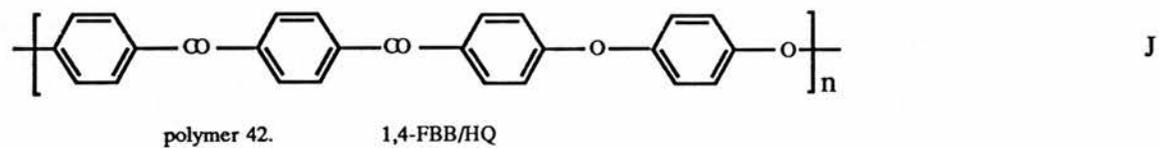
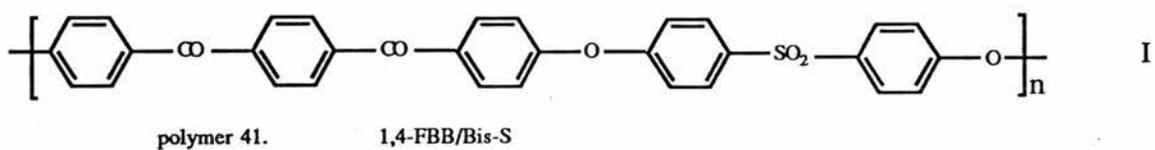
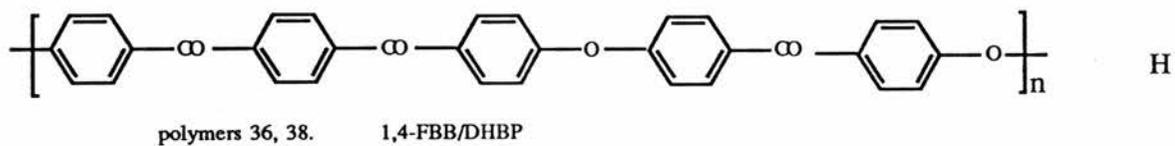
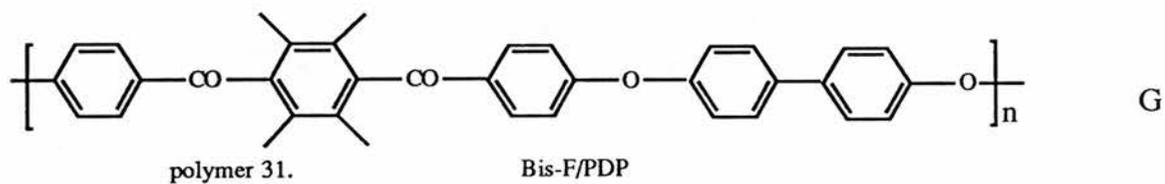
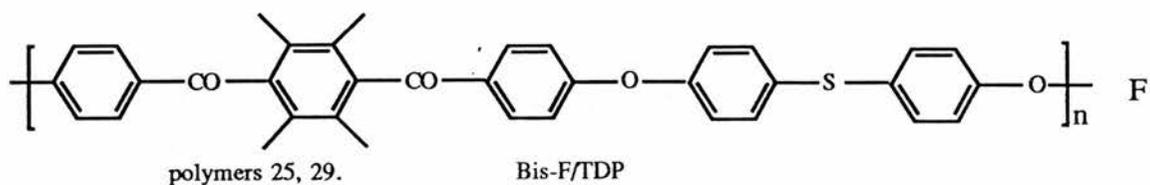
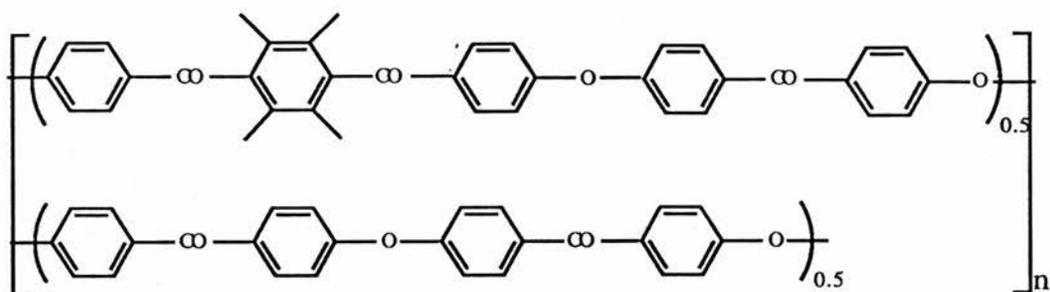
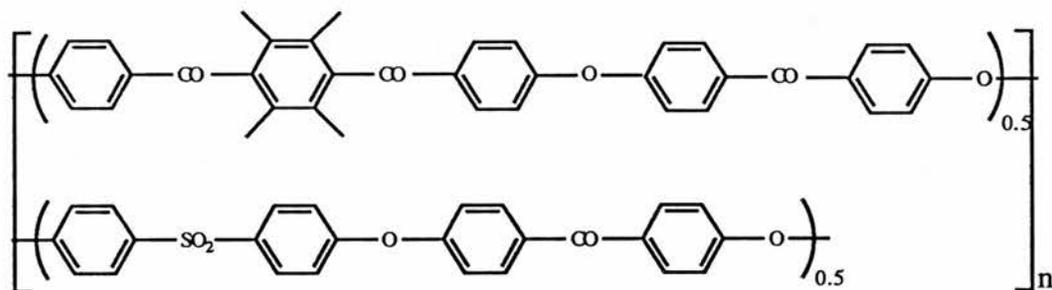


Figure 46 continued: Structures of polymers



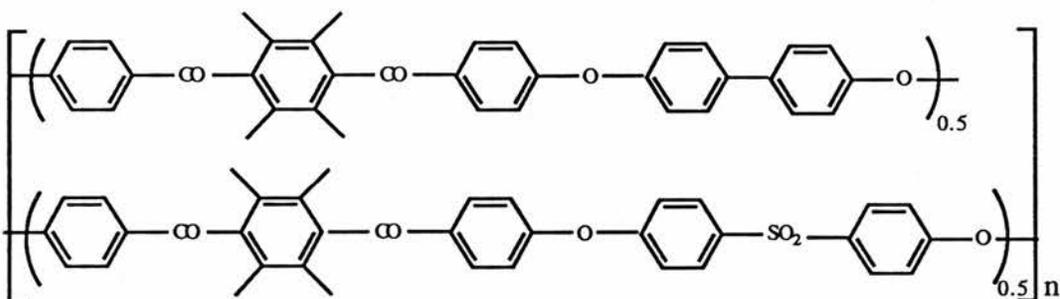
polymer 45. 0.5 Bis-F, 0.5 DFBP/DHBP

K



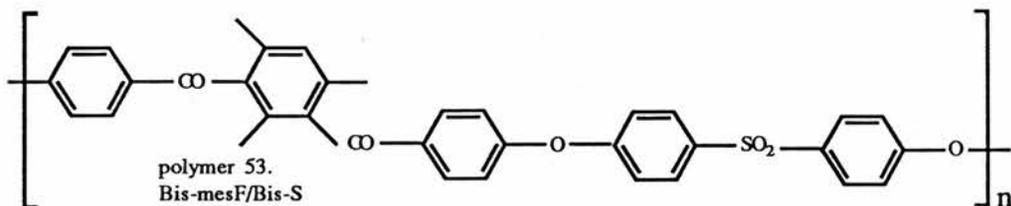
polymer 46. 0.5 Bis-F, 0.5 DFS/DHBP

L



polymer 51. Bis-F/0.5 PDP, 0.5 Bis-S

M



polymer 53.  
Bis-mesF/Bis-S

N

### 3.4 Characterisation

#### 3.4.1 Mechanical Testing<sup>101,102</sup>

Thin film compression mouldings were made of most polymers synthesised, and then subjected to a crease test (see table 18, under 'Flex.'). Care had to be taken to obtain consistent results as the way by which the mouldings were made had a considerable effect on their properties.

Materials that were cooled slowly under pressure tended to give smoother mouldings, as volatiles that had formed within the molten polymer had a chance to condense. However, crystalline materials also had a chance to recrystallise.

Materials that were quench cooled from the melt by cold water tended to contain bubbles and were therefore weakened, as the volatiles were able to expand after the pressure was released but prior to cooling. However, the durene-based polymers nearly always formed an amorphous moulding.

The main aim at this point was to obtain strong, tough, flexible and lightly coloured mouldings. Only mouldings which had a flexibility and colour rating of 1 meet these requirements (see table 18 footnotes).

Durene-based polymers, however, had stability problems for reasons previously mentioned (see section 3.3.9). Therefore moulding had to take place at as low a temperature as possible, for a minimum amount of time. However, the lowest practical limit was set by the molten polymers' flow properties which must be sufficient to fill the mould in a uniform way.

Therefore moulding temperatures (MT) for these materials varied depending on the molecular weight (viscosity) and, for crystalline polymers, the melting point ( $T_m$ ).

From Table 19 it can be seen that, for polymers 9, 22, 32 and 48, moulding temperature (MT) has to exceed the melting point ( $T_m$ ) to achieve the best moulds. Using a lower moulding temperature (MT) for polymer 22 results in an inadequate polymer flow, even although the material is essentially amorphous ( $\Delta H_f$  only  $1.5 \text{ J g}^{-1}$ ).

Table 19: Optimum moulding conditions.

Polymer	Type	RV <sup>t</sup>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	$\Delta H_f$ (J/g)	MT (°C)	Colour <sup>t</sup>	Flex. <sup>t</sup>
9	D	0.82	231	331	46	350	2	1
22	E	0.55	226	265	1.5	280	2	3
32	D	1.27	227	298	19	310	1	1
43	D	1.33	212	251	15	320	1	1
44	B	(4.6)	235			330	1	1
48	D	2.79	213	268	8.3	340	1	1
50	B	2.31	237			390	1	1
52	D	1.89	214	253	19	370	1	1

t - see table 18 for definitions.

Polymers 44 and 50 again demonstrate the point regarding polymer viscosity where a MT well above  $T_g$  is required owing to the high RV.

As only polymers involving the monomers Bis-F/Bis-S, and Bis-F/DHBP were found to give mouldings of satisfactory quality, only these polymer types (B and D) were used in the mechanical testing. Hence polymers 43, 44, 50 and 52 were synthesised in larger quantities (100-200g), and

moulded into plates (150 x 150 x 3 mm) which were subjected to mechanical testing, yielding the results in Table 20.

Table 20: Mechanical Test Results on Polymer Types B (Bis-F/Bis-S) and D (Bis-F/DHBP).

Polymer	Type	RV	Mod.	Mod.	Yield Strength (MPa)	Fracture Mechanics		Density (g cm <sup>-3</sup> )
			0° (GPa)	90° (GPa)		K <sub>IC</sub> (MN/m <sup>3/2</sup> )	G <sub>IC</sub> (kJ/m <sup>2</sup> )	
43	D	1.33	2.78	2.71	115.8(.3)	2.54(.26)	2.48(.50)	1.24
44	B	(4.6)	2.62	2.81	125.9(.1)	1.89(.32)	1.34(.11)	1.24
50	B	2.31	2.51	2.10	115.0(.8)	2.12(.14)	1.62(.16)	1.20
52	D	1.89	2.43	2.51	109.7(.1)	2.45(.11)	2.32(.37)	1.20
PEEK			4.2	4.2	138.6	4.13(.17)	6.31(.62)	
PES	τ		3.0	3.0	105.3	1.88(.13)	1.85(.22)	1.37

Mod. - Flexural modulus

From table 20 it can be seen that polymer type B (Bis-F/Bis-S) has a slightly superior yield strength while polymer type D (Bis-F/DHBP) has a significantly superior fracture resistance. The fracture resistance result is not surprising; when comparing PEEK and PES the same trend is observed, in that the polymer with superior fracture resistance contains the ketone, as opposed to the sulphone, groups.

### 3.4.2 Solvent Resistance

Of all the polymer types (see figure 46), A, B, E, L, M and N showed only moderate solvent resistance to most organic solvents; type D demonstrates good solvent resistance after synthesis but upon moulding or reprecipitation (its semi-crystalline morphology changes to an amorphous one) becomes only moderately solvent resistant

as well; types G, H, I, J and K demonstrate good solvent resistance except to c.H<sub>2</sub>SO<sub>4</sub>, while polymer types C and F were too poor in condition to be tested.

### 3.4.3 Differential Scanning Calorimetry (DSC)

#### 3.4.3.1 Melting Points (T<sub>m</sub>)

The polymers as analysed by their DSC melting endotherms fall into three main morphology groups (see table 21):

- (i) permanently semi-crystalline even after quenching (psc).

Table 21: DSC Melting Endotherm Results

Type	Monomers	Polymer Example	T <sub>m</sub> (°C)	ΔH <sub>F</sub> (J g <sup>-1</sup> )	Rerun DSC Morphology		Overall Morphology
					T <sub>m</sub> (°C)	ΔH <sub>F</sub> (J g <sup>-1</sup> )	
A	Bis-F/HQ	47	386	35	a	-	scam
B	Bis-F/Bis-S	50	a	-	a	-	a
C	Bis-F/Bis-A	19	-	-	-	-	-
D	Bis-F/DHBP	49	269	22	a	-	scam
E	Bis-F/0.5 HQ, 0.5 DHBP	22	265	1.5	a	-	a
F	Bis-F/TDP	29	233	0.1	a	-	a
G	Bis-F/PDP	31	324	0.5	a	-	a
H	1,4-FBB/DHBP	38	376	79	335	47	psc
I	1,4-FBB/Bis-S	41	a	-	a	-	a
J	1,4-FBB/HQ	42	350	50	317	22	psc
K	0.5 Bis-F, 0.5 DFBP/DHBP	45	247	30	a	-	scam
L	0.5 Bis-F, 0.5 DFS/DHBP	46	a	-	a	-	a
M	Bis-F/0.5 PDP, 0.5 Bis-S	51	a	-	a	-	a
N	Bis-mesF/ Bis-S	54	a	-	a	-	a

(ii) semi-crystalline as made but crystallinity is lost upon melting and not recovered upon annealing (scam).

(iii) amorphous (a).

It can be seen that all the durene-based polymers lose any initial crystallinity they had after melt processing. As mentioned before, even after prolonged annealing, only very slow crystallisation occurs for those durene-based polymers that were "semi-crystalline as made" (scam).

#### 3.4.3.2 Glass Transition Temperatures ( $T_g$ )

By analysing the  $T_g$  values for each polymer type, it is possible to interpret the effect of the pendant methyl groups of the durene units, coupled with the intrinsic structural properties of the comonomers. Polymers being such poor heat conductors, care must of course be taken in the interpretation of such results, as the heat flow depends upon the sample state. Also, since some of the polymers are of low molecular weight, care must be taken that these examples do not artificially lower the  $T_g$  average for a given polymer type (see equation 4). The results are averaged from tables 22-24 and summarised in table 25.

Polymer type G (Bis-F/PDP, polymer 31, RV = 0.42) was artificially adjusted upwards (+22°C) owing to its low molecular weight. As the correction had to be so much for this polymer it will no longer take part in the following discussion.

Table 22:  $T_g$  values for Polymer Type A (Bis-F/HQ); average  $T_g = 235^\circ\text{C}$  ( $\sigma_n=4^\circ\text{C}$ ).

Polymer	RV	$T_g$ ( $^\circ\text{C}$ )
1	0.40	203 <sup>a,b</sup>
2	0.84	231
21	(1.0)	234
30	0.33	209 <sup>a</sup>
47	1.08	240

Table 23:  $T_g$  values for Polymer Type B (Bis-F/Bis-S); average  $T_g = 245^\circ\text{C}$  ( $\sigma_n=7^\circ\text{C}$ ).

Polymer	RV	$T_g$ ( $^\circ\text{C}$ )
24	(3.2)	248
28	1.14	252
33	(2.9)	255
34	1.10	250
37	1.16	237
40	(1.7)	242
44	(4.6)	235
50	2.31	237

As was noticed in section 3.2.5, polymers with chlorine end-groups tended to have lower values of  $T_g$  than polymers with fluorine end-groups (see table 14). For example, the  $T_g$  for polymer type D depended upon whether Bis-Cl ( $T_g = 185^\circ\text{C}$ ) or Bis-F ( $T_g = 225^\circ\text{C}$ ,  $\sigma_n = 9^\circ\text{C}$ ) was used in the synthesis. Also the crystallinity of the "as made" polymer varied with the former always being amorphous. The reason for the large variation in  $T_g$  is unknown, since both reactions should yield the same structure. Certainly both examples are of sufficient molecular weight not to affect the result significantly (see equation 4). There is the possibility that the less polar chlorine end group may create a smaller "drag" on the chain than its fluorine

counterpart. Also, as Bis-Cl has a lower reactivity than Bis-F, the degree of branching may be somewhat different, but at a level too low to be easily observed by NMR spectroscopy.

Table 24:  $T_g$  values for Polymer Type D (Bis-F/DHBP);  
average  $T_g = 224^\circ\text{C}$  ( $\sigma_n=9^\circ\text{C}$ )

Polymer	RV	$T_g$ ( $^\circ\text{C}$ )
5	1.32	197
7	0.33	209 <sup>a</sup>
8	0.60	228
9	0.82	231
10	(1.1)	233
11	1.01	240
12	(0.62)	228
13	0.24	183 <sup>a,b</sup>
14	0.64	230
15	(2.6)	240
16	(3.1)	232
17	0.30	199 <sup>a</sup>
32	1.27	227
35	2.09	228
43	1.33	212
48	2.79	213
49	2.69	212
52	1.89	214
53	0.84	185 <sup>b</sup>

For tables 22-24:

$T_g$  - Glass transition temperature

a - RV too low; result discarded.

b - Chloride end-group; result not included in overall average.

When it comes to bulky side groups such as those demonstrated by Hergenrother, et al.<sup>61</sup> (see figure 41), the further addition of a pendant methyl group (structure  $\alpha$  going to structure  $\beta$ ) increases the  $T_g$  by only 12-39 $^\circ\text{C}$  depending upon the halogen end group.

Table 25: Glass Transition Temperatures ( $T_g$ ).

Polymer Type	Monomers	$T_g$ (°C)	$\sigma_n$ (°C)
A	Bis-F and HQ .	235	4
A'	Bis-Cl and HQ	203	-
B	Bis-F and Bis-S	245	7
C	Bis-F and Bis-A	-	-
D	Bis-F and DHBP	224	11
D'	Bis-Cl and DHBP	185	-
E	50% Bis-F, 25% DHBP and 25% HQ	226	-
F	Bis-F and TDP	181	-
G	Bis-F and PDP	218	-
H	1,4-FBB and DHBP	243?	-
I	1,4-FBB and Bis-S	180	-
J	1,4-FBB and HQ	283	-
K	25% Bis-F, 25% DFBP and 50% DHBP	178	-
L	25% Bis-F, 25% DFS and 50% DHBP	197	-
M	50% Bis-F, 25% PDP and 25% Bis-S	222	-
N	Bis-mesF and Bis-S	200	-

However, upon observation of the non-methylated structures synthesised in this thesis (polymer types H, I and J) it can be seen that the  $T_g$  values for H and J appear to be artificially high. This is because these polymers are crystalline which results in their structures being stiffened<sup>72</sup>. Close packing in the crystalline regions inhibits the chain rotation that would normally occur in the amorphous regions. As these latter regions are also proportionally smaller,  $T_g$  processes become much more difficult to identify unambiguously. The other polymers which are "semi-crystalline as made" (scam) are not affected in this way as their crystallinity has been destroyed by the first DSC run. Hence the following discussion will also exclude polymer types H and J.

Therefore this leaves only two comparisons remaining as to the effect of durene's pendant methyl groups. The first is between polymers B and I ( $T_g = 245^\circ\text{C}$  and  $180^\circ\text{C}$  respectively) where  $\Delta T_g$  is a large  $65^\circ\text{C}$ .

This compares with the Hergenrother, et al. structures  $\delta$  and  $\epsilon$  ( $T_g = 120^\circ\text{C}$  and  $166^\circ\text{C}$  respectively) where  $\Delta T_g$  is  $46^\circ\text{C}$ , although the pendant methyl groups here are between, rather than on, the rings which probably limits their effect in a similar way to comparisons of structures  $\alpha$  and  $\beta$ .

This can be also seen in a gradual way with a second comparison by observation of structures  $\theta$ , K and D ( $T_g = 145^\circ\text{C}$ ,  $178^\circ\text{C}$  and  $224^\circ\text{C}$  respectively) where there is 0%, then 25% and finally 50% replacement of DHBP by Bis-F, resulting in an upward curving plot for monomer weight fraction against  $T_g$  (see graph 3).

The following equation can be fitted<sup>72</sup>

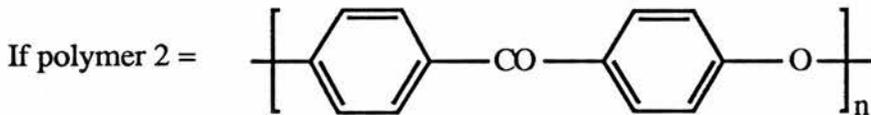
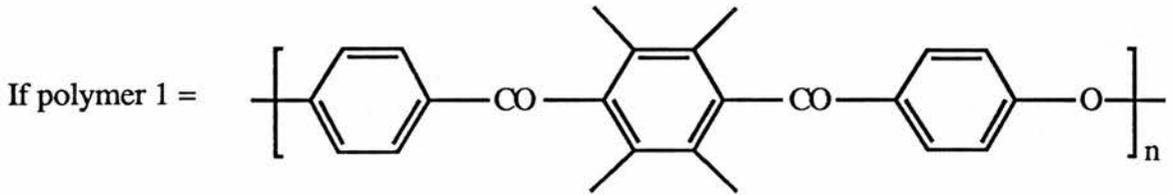
$$T_g = \frac{Kw_1T_{g1} + w_2T_{g2}}{Kw_1 + w_2}$$

where  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the two homopolymers,  $w_1$  and  $w_2$  are their weight fractions and

$$K = \frac{(\alpha_r - \alpha_g)_2}{(\alpha_r - \alpha_g)_1}$$

where  $\alpha_r$  and  $\alpha_g$  are the thermal expansion coefficients of the homopolymers in the rubber (above  $T_g$ ) and glassy states (below  $T_g$ ) respectively.

Solving algebraically, for the three data points in graph 3, the following results were obtained:



then

$$T_{g1} = 375.4^{\circ}\text{C}$$

$$T_{g2} = 145^{\circ}\text{C}$$

$$K = 0.290$$

i.e. a polymer synthesised from Bis-F, with its theoretical diol analogue bis(4-hydroxybenzoyl)durene, is predicted by this analysis to have a  $T_g = 375.4^{\circ}\text{C}$ . More data would really be needed before the above figures could be confirmed.

When the DHBP part (polymer D) is subsequently replaced partially (50% polymer E) and then fully (polymer A) by HQ, however,  $T_g$  is seen to remain fairly steady at  $224^{\circ}\text{C}$  ( $\sigma_n=11^{\circ}\text{C}$ ),  $226^{\circ}\text{C}$  and  $235^{\circ}\text{C}$  ( $\sigma_n=4^{\circ}\text{C}$ ) respectively. This would appear to indicate that even though the proportion of

durene units has increased from one per 5 aromatic rings to one per 4 rings, this results in only a small, almost experimentally insignificant, increase in  $T_g$  of  $11^\circ\text{C}$ .

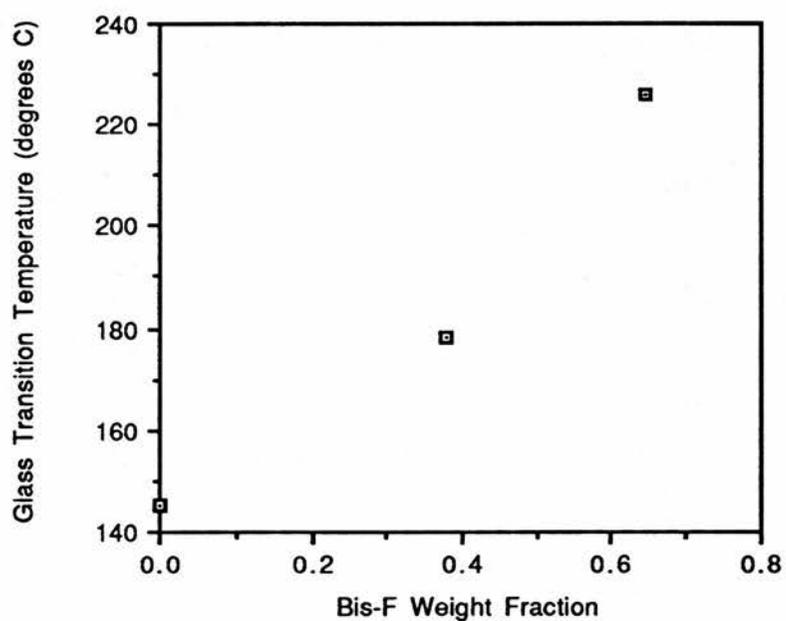
It would appear that the methyl groups associated with the durene unit have the predominant effect on  $T_g$ ; variation of the comonomer, resulting in polymer types A, B, D, E, G and M ( $T_g = 235^\circ\text{C}$  [ $\sigma_n=4^\circ\text{C}$ ],  $245^\circ\text{C}$  [ $\sigma_n=7^\circ\text{C}$ ],  $226^\circ\text{C}$  [ $\sigma_n=9^\circ\text{C}$ ],  $226^\circ\text{C}$ ,  $240^\circ\text{C}$  [ $\sigma_n=5^\circ\text{C}$ ] and  $222^\circ\text{C}$  respectively), produces a minimal effect, with a  $T_g$  range of only  $23^\circ\text{C}$ . It is not until the ratio of Bis-F is reduced that real  $T_g$  movement, in a downwards direction, is observed with polymer types K and L ( $T_g = 178^\circ\text{C}$  and  $197^\circ\text{C}$  respectively).

Polymer N, which is the analogue of B where Bis-F has been replaced by Bis-mesF, shows a sharp reduction in  $T_g$  ( $245^\circ\text{C}$  to  $200^\circ\text{C}$ ) although this may be influenced by the low molecular weight of the one example of N (polymer 54, RV = 0.53).

If polymer type M (a single experiment of low RV) is ignored, it can be seen that the structures involving  $\text{SO}_2$  units (polymers B and L) have greater  $T_g$  values than their CO counterparts (polymers D and K) by  $23^\circ\text{C}$  and  $19^\circ\text{C}$  respectively. This difference has of course been suppressed by the contribution of the pendant methyl groups which can be clearly seen from the non-durene structures  $\theta$  and  $\tau$  (PEK and PES) where  $\Delta T_g = 80^\circ\text{C}$ .

Therefore there appears to exist a "saturation level" beyond which the incorporation of further pendant methyl groups or tetrahedral sulphone groups into the polymer backbone leads to only a minimal increase in  $T_g$ .

**Graph 3: Weight fraction vs Tg for Bis-F incorporated into a PEK polymer.**



### 3.5 Discussion

The 'best-case' (highest RV) polymers for each type are listed in table 26.

Table 26: Best-case polymer examples for each type.

Type	Sample Number	Halide Monomer	Phenol Monomer	RV	T <sub>g</sub> <sup>z</sup> (°C)	T <sub>m</sub> (°C)	ΔH <sub>f</sub> (J g <sup>-1</sup> )	Morp. <sup>b</sup>	Flex. <sup>c</sup>	Col. <sup>d</sup>
A	47	Bis-F	HQ	1.08	235	386	35	sc	2	1
B	50	Bis-F	Bis-S	2.31	245	-	-	a	1	1
C	19	Bis-F	Bis-A	0.06	-	-	-	-	-	-
D	49	Bis-F	DHBP	2.69	226	269	22	scam	1	1
E	22	Bis-F	0.5 DHBP 0.5 HQ	0.55	226	265	1.5	a	3	2
F	29	Bis-F	TDP	(0.04)	181	233	0.1	scam	4	4
G	31	Bis-F	PDP	0.42	218	324	0.5	sc	4	4
H	38	1,4-FBB	DHBP	0.46	243	376	79	sc	4	2
I	41	1,4-FBB	Bis-S	(3.0)	180	-	-	scam	1	3
J	42	1,4-FBB	HQ	0.56	283	350	50	sc	4	2
K	45	0.5 Bis-F 0.5 DFBP	DHBP	1.32	178	247	30	a	1	2
L	46	0.5 Bis-F 0.5 DFS	DHBP	(1.8)	197	-	-	a	1	2
M	51	Bis-F	0.5 PDP 0.5 Bis-S	0.56	222	-	-	a	4	4
N	53	Bis- mesF	Bis-S	0.53	200	-	-	a	3	3
θ	PEK	DFBP	DHBP		145	340	~70	sc	1	1
τ	PES	DCS	Bis-S		225	-	-	a	1	1

<sup>z</sup> - mean values derived from table 21

<sup>b</sup> - Morphology, see section 2.4.2.1

<sup>c,d</sup> - see table 18

Also, as only durene-based polymer types B and D had moulding flexibility ratings of 1, they were further plate moulded and mechanically tested. The results of these tests are displayed in table 20. Although durene-based polymer types K and L had level 1 flexibility ratings they are considered to be only partly durene-based (compared to B and D), and hence mechanical tests were not made on them.

This means that, out of all the new polymers synthesised in this thesis (A-G and K-N), only polymers B, D, K and L were able to be synthesised to high enough molecular weight ( $RV \geq 0.6$ ) to yield materials, which when moulded demonstrated minimum flexibility ratings (flexibility = 1, see table 18) required.

Assessment of these four materials by the criteria laid down at the beginning of this chapter (see section 3.1) is as follows:-

(a) Good mechanical strength:-

From table 20 it can be clearly seen that polymers 43, 44, 50 and 52 possess mechanical properties which approximate much more closely those of amorphous PES than of crystalline PEEK which is a much stronger polymer. This is not a surprising result when it is considered that polymers B and D are amorphous upon cooling from the melt. Also it can be seen that the durene-based polymers are approximately 10% less dense than PES which improves their strength : weight ratio somewhat beyond that of PES.

However other factors must now be considered.

(b) Good solvent resistance:-

Table 27: Solubility and Morphology

Polymer Type	Soluble in:- t	Morphology
B (Bis-F/Bis-S)	c.H <sub>2</sub> SO <sub>4</sub> , CHCl <sub>3</sub> , NMP, DMF	a
D (Bis-F/DHBP)	c.H <sub>2</sub> SO <sub>4</sub> , CHCl <sub>3</sub>	scam
K (0.5 Bis-F, 0.5 DFBP/DHBP)	c.H <sub>2</sub> SO <sub>4</sub>	scam
L (0.5 Bis-F, 0.5 DFS/DHBP)	c.H <sub>2</sub> SO <sub>4</sub> , CHCl <sub>3</sub> , NMP, DMF	a
θ (PEK)	c.H <sub>2</sub> SO <sub>4</sub>	sc
τ (PES)	c.H <sub>2</sub> SO <sub>4</sub> , CHCl <sub>3</sub> , NMP, DMF	a
PEEK	c.H <sub>2</sub> SO <sub>4</sub>	sc

t - NMP = N-methyl-2-pyrrolidone

- DMF = Dimethylformamide

- CHCl<sub>3</sub> = Chloroform

This must be considered only for polymers which have been moulded. Although polymers A and D are crystalline as made, they change to an amorphous state upon melting and cooling, which substantially lowers their resistance to many organic solvents. The odd case is polymer K, which although it is in the same morphology class (scam) retains a remarkable degree of solvent resistance even when reprecipitated. However, a total removal of the pendant methyl groups as in polymers H, J, θ and PEEK will result in easily formed semi-crystalline polymers from the melt with very good solvent resistance to all common solvents except concentrated acids.

Polymer G does demonstrate, as mentioned before, some solvent resistance. This is an odd case as it shows virtually no crystallinity in its DSC scan although this may be due to thermal decomposition before it reaches its melting point ( $T_d < T_m$ ). Solvent resistance in this case may arise partially from its difficult-to-solvate biphenyl group, and it comes as no surprise that some of this resistance remains even after reprecipitation from concentrated sulphuric acid, therefore sulphonation of this polymer in  $c.H_2SO_4$  is unlikely to have occurred. As mentioned before solvent resistance does cause problems during synthesis as polymer G (Bis-F/PDP) is so insoluble in DPS that it falls out of solution before high molecular weight is obtained ( $RV = 0.42$ ).

Polymers B, E, F, L, M and N are all amorphous with only minimal solvent resistance.

(c) Stability at high temperatures:-

Here the 'Achilles heel' of the durene-based polymers truly manifests itself (see table 28).

The commercial polymers  $\theta$  (PEK) and  $\tau$  (PES) require moulding temperatures (MT) of  $400^\circ C$  for sufficient melt flow to occur, while if the durene-based polymers are held above  $340^\circ C$  for any period of time, thermal cross-linking followed by decomposition rapidly occurs (5-10 minutes). As polymers are generally pre-heated to their MT for a period of time in an extruder before moulding, this would tend to

indicate that the durene-based polymers are unsuitable for this application unless the time spent at these elevated temperatures is limited to, say, less than 2 minutes - a situation unlikely to be commercially feasible.

Table 28: High Temperature Stability.

Polymer Type	Temperature of Decomposition	Moulding Temperature (MT)
B (Bis-F/Bis-S)	340°C + (5 - 10 minutes)	< 340°C
D (Bis-F/DHBP)	340°C + (5 - 10 minutes)	< 340°C
K (0.5 Bis-F, 0.5 DFBP/DHBP)	340°C + (5 - 10 minutes)	< 340°C
L (0.5 Bis-F, 0.5 DFS/DHBP)	340°C + (5 - 10 minutes)	< 340°C
θ (PEK)	600°C +	< 400°C
τ (PES)	500°C +	< 400°C

(d) High T<sub>g</sub>, low T<sub>m</sub>:-

Table 29: T<sub>g</sub> and T<sub>m</sub> values.

Polymer Type	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>F</sub> (J g <sup>-1</sup> )
B (Bis-F/Bis-S)	245	-	-
D (Bis-F/DHBP)	226	269	22
K (0.5 Bis-F, 0.5 DFBP/DHBP)	178	247	30
L (0.5 Bis-F, 0.5 DFS/DHBP)	197	-	-
θ (PEK)	145	~340	~70
τ (PES)	225	-	-

This is where the durene-based polymers demonstrate their remarkable character. The high  $T_g$  values for B (Bis-F/Bis-S) and D (Bis-F/DHBP), compared to those of their  $\tau$  (PES) and  $\theta$  (PEK) counterparts, extend the high-modulus working range of these materials a further 20°C and 81°C respectively. Even the polymer hybrids K (0.5 Bis-F, 0.5 DFBP/DHBP) and L (0.5 Bis-F, 0.5 DFS/DHBP) show significant increases in  $T_g$  over  $\theta$  (PEK) at 33°C and 52°C respectively.

However the use of Bis-S already provides an alternative means of increasing the working range ( $\tau$ ,  $T_g = 225^\circ\text{C}$ , PES); therefore the real increase only occurs for B (20°C, Bis-F/Bis-S) and this must be balanced against the lack of temperature stability just discussed. As the crystallinity of the durene-based materials is lost upon moulding, there is no real difference in crystallinity from the type  $\tau$  (PES) material; hence comparisons with the  $T_g$  of polymer  $\theta$  (PEK) may not be valid.

From table 25 it can also be observed that polymers A, E, G and M have  $T_g$  values in the range 222-240°C, which are quite high compared to  $\theta$  (145°C, PEK). However, unless an improvement in molecular weight can be made, they will not meet the mechanical strength requirements.

Polymers B, D, K and L all exhibit low values for  $T_m$  and  $\Delta H_f$  (or none at all) which render them more easily melt processable at lower temperatures. However, as they are all amorphous when processed, again the comparison must be with

the amorphous material  $\tau$  (PES). Materials which are semi-crystalline as made, but amorphous after being moulded (scam), are likely to be inferior in terms of energy required for processing when compared to materials which remain amorphous throughout. Having crystalline properties is only an advantage if they can be retained upon moulding and then used to make the material harder, so that the material retains a moderately high tensile modulus once  $T_g$  is surpassed, as well as being more impact resistant.

(e) High melt flow:-

This is a function of the viscosity of the melted polymers. As polymers B, D, K and L all had low values of  $T_m$  and  $\Delta H_F$ , or none at all, the only factor that had to be considered was molecular weight.

It has already been demonstrated (see table 19) how reductions in RV led to reductions in MT. At present, low temperature stability sets a ceiling on the MT. If RV is reduced too far, however, loss of mechanical strength will result.

Hence it may be possible, by limiting the molecular weight to a certain degree, that a sufficiently high melt flow may be achieved at a low enough temperature such that decomposition of the polymer being moulded does not take place.

The durene-based polymers synthesised thus far do not meet these criteria and therefore suffer limitations with regard to the properties indicated for a "good" polymer.

(f) High  $T_m$  and  $\Delta H_f$ :-

$\theta$  (PEK) retains a significant part of its mechanical strength after its  $T_g$  (145°C) is exceeded but before its  $T_m$  (~340°C) is reached.

However, of the durene-based polymers synthesised in this study, none showed any tendency to recrystallise from the melt except the scam types and even then the crystallisation was extremely slow. Hence all the durene-based polymers, after moulding, must lose virtually all their mechanical strength once the temperature again exceeds their respective  $T_g$  values.

If the proportion of Bis-F in polymer K (0.5 Bis-F, 0.5 DFBP/DHBP) could be reduced, making it more like PEK, an increase in its crystallinity might occur. However  $T_g$  would be further reduced in doing so, thereby lowering its high temperature use range.

### 3.6 Summary

The durene-based polymers B and D synthesised in this thesis fall into the amorphous bracket (semi-crystalline as made), and as high molecular weights may be achieved they demonstrate good mechanical strength. However despite high  $T_g$  values, leading to good high-temperature creep

resistance, they are unstable at the temperatures required for moulding. Also they have poor solvent resistance.

If it were not for the high-temperature instability problem, polymers B and D would be as good as PES, and even lighter.

This last factor could be moderated by reducing the polymers' molecular weights such that mechanical strength is maintained but so that moulding may take place at a lower temperature.

However the costs likely to be incurred with the difficult-to-make Bis-F (see chapter 2) coupled with only the marginal increase in  $T_g$  (+20°C) over PES render the durene-based polymers synthesised in this chapter to be currently uneconomical as engineering materials. If a more efficient route could be found for the synthesis of Bis-F, or perhaps a similar, easier-to-make, methylated analogue could be used, some of these practical difficulties could be overcome.

This however, does not rule out their possible application through further chemical modification to specialist purposes as will be discussed in chapter 4.

### 3.7 Nuclear Magnetic Resonance (NMR) Analysis of Polymers

#### 3.7.1 $^{13}\text{C}$ -NMR Analysis

The polymers studied in this thesis, which were soluble in common deuterated solvents, were analysed by  $^{13}\text{C}$ -NMR, comparison being made to the spectra of their constituent monomers (see section 2.5). Correction factors were applied to chemical shifts : The fluorinated and hydroxylated monomers were corrected as if their end-functional groups (fluorine or hydroxyl) were replaced by phenyl ether<sup>64</sup>. The numbering system as in figure 47 was used (note: differs from system used in section 2.5). which led to the corrections in table 30.

Table 30: Chemical shift corrections.

Carbon	Chemical Shift F / OH <sup>a</sup>	Chemical Shift OC <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Correction <sup>c</sup>
1	+32.6 (+31.2) <sup>d</sup>	+29.2	-3.4 (-2.0)
2	-12.7 (-12.9) <sup>d</sup>	-9.4	+3.3 (+3.5)
3	+2.7 (+3.3) <sup>d</sup>	+1.6	-1.1 (-1.7)
4	-3.5 (-3.8) <sup>d</sup>	-5.1	-1.6 (-1.3)
9	+26.9	+29.2	+2.3 (+4.5) <sup>e</sup>
10	-12.7	-9.4	+3.3 (+3.5) <sup>e</sup>
11	+1.4	+1.6	+0.2
12	-7.3	-5.1	+2.2

For table 30 -

a - chemical shifts from Bis-H (see section 2.5) for the fluorine component (carbons 1-4), and from benzene<sup>64</sup> for the hydroxyl component (carbons 8-12).

b - chemical shifts for phenyl ether (OC<sub>6</sub>H<sub>5</sub>) from benzene<sup>64</sup>.

c - i.e. b minus a.

d - figures for 1,4-FBB.

e - figures for hydroquinone (HQ).

These figures were applied to the constituent monomers chemical shifts (see table 31 and 32) to arrive at calculated values which were then directly compared to the observed values for the copolymers (see table 33).

Table 31: Difluoro monomers chemical shifts.

	1	2	3	4	5	6	7	8
Bis-F	166.33	116.15	132.34	133.61	199.52	140.43	130.58	16.54
1,4-FBB	164.90	115.95	132.86	133.30	194.07	140.23	129.55	

Table 32: Diol monomers chemical shifts.

	9	10	11	12	13
DHBP	161.92	115.77	133.01	130.67	194.34
Bis-S	161.51	115.87	129.22	132.12	
HQ	149.73	115.68			
PDP	156.52	116.06	127.37	131.69	

These values, with few exceptions, show a level of consistency indicating that the proposed structures for the synthesised copolymers are not at variance with the observed  $^{13}\text{C}$ -NMR spectra.

The experimentally determined values for the comonomers in table 33 were used to predict, where applicable, the chemical shifts of the more complex three-monomer systems, the results of which are summarised in table 34. The spectrum of Bis-F/PDP was predicted by the method used in table 33, as polymers of this type (G) were found to be too insoluble in chloroform to obtain a reasonable  $^{13}\text{C}$ -NMR spectrum.

What can be noticed from table 34 is the extreme closeness of those values predicted from NMR spectra of polymers A, B, and D to the observed values for polymers E and M, i.e. the Bis-F unit is sufficiently long to prevent its own  $^{13}\text{C}$ -NMR signals being split by differing adjacent monomer units. For example, an HQ - Bis-F - DHBP sequence shows up in the  $^{13}\text{C}$ -NMR spectrum as two different entities; HQ - Bis-F and Bis-F - DHBP.

This can not be said for polymer L (50% DHBP, 25% Bis-F, 25% Bis-S) where the intervening DHBP monomer has not less than 4 signals for each of its aromatic ring carbons which led to a spectrum not easily analysed.

**Table 33:** <sup>13</sup>C-NMR copolymer (two monomer system) spectra chemical shifts.

Polymer	1	2	3	4	5	6	7	8	9	10	11	12	13
A	calc.	162.9	119.5	131.2	132.0	140.4	130.6	16.5	154.2	119.3			
	obs.	162.70	122.00	131.87	132.10	140.49	130.44	16.61	151.82	117.22			
B	calc.	163.8	119.5	131.0	132.0	140.4	130.6	16.5	163.8	119.2	129.4	134.3	
	obs.	160.06	119.49	132.15	133.26	140.36	130.53	16.63	160.29	119.19	130.09	136.89	
D	calc.	163.8	119.5	131.0	132.0	140.4	130.6	16.5	164.2	119.1	133.2	132.9	194.3
	obs.	159.27	119.07	132.11	133.47	140.78	130.48	16.61	161.11	118.68	132.38	132.68	194.00
I	calc.	162.9	119.5	131.2	132.0	140.2	129.6	-	163.8	119.2	129.4	134.3	
	obs.	159.55	119.29	132.69	133.03	140.43	129.61	-					

calc. - calculated value, obs. - observed value.

Table 34: <sup>13</sup>C-NMR copolymer (three monomer system) spectra chemical shifts.

Polymer Type	Constituent Polymers	1	2	3	4	5	6	7	8	9	10	11	12	13	
E	D	calc.	159.27	119.07	132.11	133.47	199.78	140.38	130.48	16.61	161.11	118.68	132.38	132.68	194.00
	Bis-F/DHBP	obs.	159.30	119.08	132.11	133.51	199.82	140.42	130.49	16.62	116.12	118.68	132.39	132.72	194.03
	A	calc.	162.70	122.00	131.87	132.10	199.82	140.49	130.44	16.61	151.82	117.22			
M	Bis-F/HQ	obs.	162.71	122.00	132.11	132.39	199.82	140.55	130.44	16.62	151.80	117.21			
	B	calc.	160.06	119.49	132.15	133.26	199.64	140.36	130.53	16.63	160.29	119.19	130.09	136.89	
	Bis-F/Bis-Sobs.	obs.	160.08	119.51	132.11	133.26	199.52	140.29	130.53	16.62	160.29	119.19	130.09	136.87	
	G	calc.	163.8	119.5	131.0	132.0	199.5	140.4	130.6	16.5	158.8	119.4	127.5	133.9	
	Bis-F/PDP	obs.	160.64	120.44	131.36	133.04	199.31	140.67	130.91	16.62	154.66	120.74	128.64	130.45	

Figure 47:  $^{13}\text{C}$ -NMR chemical shift assignments.

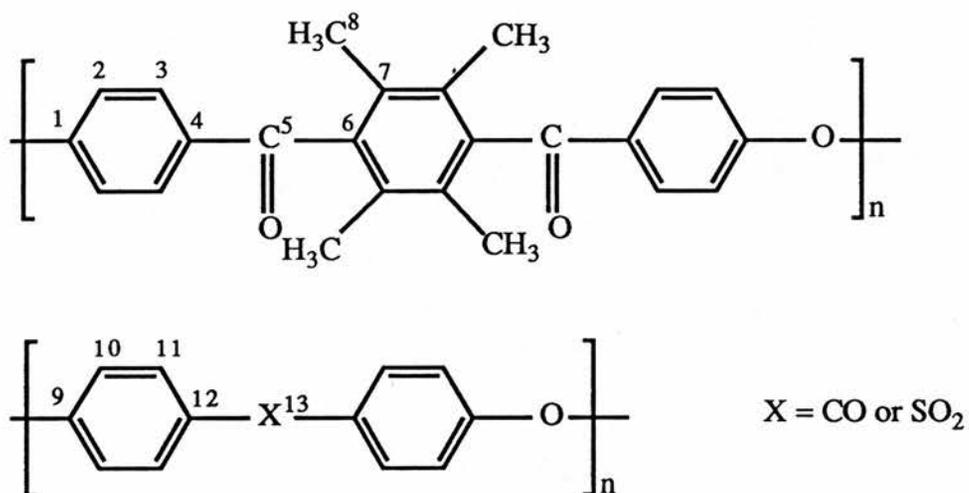
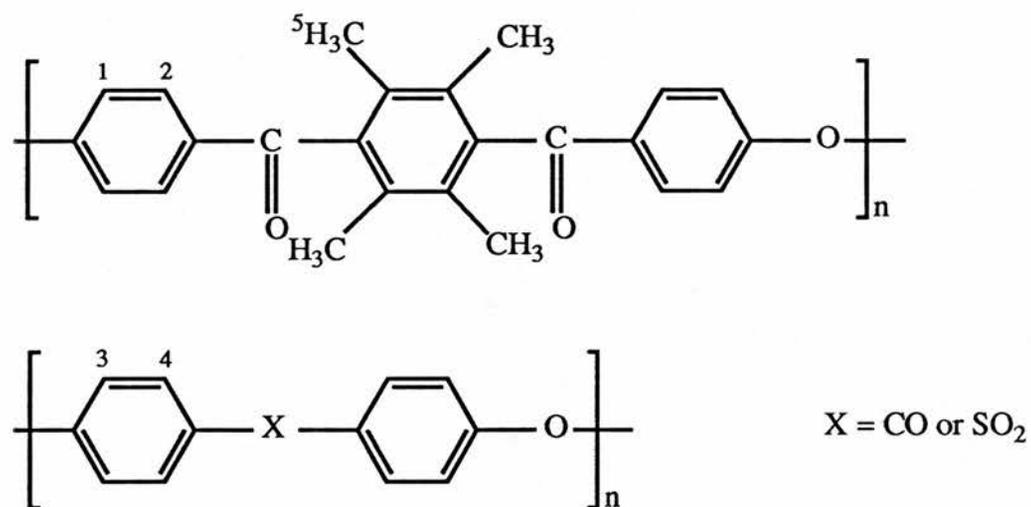


Figure 48:  $^1\text{H}$ -NMR chemical shift assignments.



### 3.7.2 $^1\text{H-NMR}$ Analysis

In a similar way to the  $^{13}\text{C-NMR}$  spectra, the  $^1\text{H-NMR}$  spectra were analysed in comparison to their constituent monomer chemical shifts suitably corrected.

The numbering system in figure 48 was used which led to the corrections in table 35 (figures are rounded up to the nearest 0.05ppm).

Table 35: Chemical shift corrections

Hydrogen	Chemical Shift F/OH <sup>a</sup>	Chemical Shift OC <sub>6</sub> H <sub>5</sub> <sup>b</sup>	Correction <sup>c</sup>
1	-0.30	-0.50	-0.20
2	0.00	0.00	0.00
3	-0.50	-0.50	0.00 (+0.20) <sup>d</sup>
4	-0.20	0.00	+0.20

a - chemical shifts from Bis-H (see section 2.5) for the fluorine component (carbons 1-4), and from benzene<sup>64</sup> for the hydroxyl component (carbons 8-12).

b - chemical shifts for phenyl ether (OC<sub>6</sub>H<sub>5</sub>) from benzene<sup>64</sup>.

c - i.e. a minus b.

d - figures for hydroquinone (HQ).

These figures were applied to the constituent monomers chemical shifts (see table 36) to arrive at calculated

values which were then directly compared to the observed values for the copolymers (see table 37).

Table 36: Monomers chemical shifts.

Monomer	1	2	3	4	5
Bis-F	7.15 q	7.90 q			2.04 s
1,4-FBB	7.55 q	8.03 q			8.01
DHBP			6.99 d	7.74 d	
Bis-S			6.94 d	7.75 d	
HQ			6.62 s		

q - doublet of doublets

d - doublet

s - singlet

All  $J_{HH}$  couplings were  $8.5 \pm 0.5$  Hz. All peaks in table 37 were doublets unless indicated otherwise. As can be seen there was some difficulty in assignment of the doublet peaks given their close proximities and the apparent inaccuracies of the method of prediction.

Overall these spectra are in accordance with the structures proposed, and when peak integrals are measured the ratios calculated are nearly as predicted in all cases.

Table 37:  $^1\text{H-NMR}$  copolymer (two monomer system) spectra  
chemical shifts.

Polymer		1	2	3	4	5
A	calc.	6.95	7.90	6.82 s		2.04 s
Bis-F/HQ	obs.	7.01	7.86	7.15 s		2.03 s
B	calc.	6.95	7.90	6.94	7.95	2.04 s
Bis-F/Bis-S	obs.	7.08	7.88	7.15	7.94	2.03 s
		7.15	7.94	7.08	7.88	
D	calc.	6.95	7.90	6.99	7.94	2.04 s
Bis-F/DHBP	obs.	7.15	7.93	7.20	7.93	2.08 s
		7.20		7.15		
I	calc.	7.35	7.90	6.94	7.95	8.01 s
1,4-FBB/Bis-S	obs.	7.13	7.90	7.13	7.97	7.88 s
		7.16	7.97	7.16	7.90	

calc. - calculated value, obs. - observed value

As the chemical shift values were not overall determined unambiguously for the copolymers they were not applied to the more complicated three-monomer systems. However, as  $o\text{-H}$ ,  $m\text{-H}$  and methyl assignments were clearly made, the integrals of these systems were analysed algebraically to confirm that the ratios of monomers incorporated into the resultant polymer were in accordance with those predicted from the experimental mixture.

For example, polymer E (50% Bis-F, 25% DHBP, 25% HQ) had three broad absorbance regions in its <sup>1</sup>H-NMR spectrum (the chloroform peak being negligible, see table 38 where a + b = 1).

Table 38: <sup>1</sup>H-NMR spectrum analysis for polymer E.

Region (ppm)	Integral	Attributed to Hydrogen...	Number of Hydrogens
1.6 - 2.4	107	5 (Bis-F CH <sub>3</sub> )	12
6.7 - 7.5	71	1 (Bis-F, <u>o</u> - to ether)	4
		3 (DHBP, <u>o</u> - to ether)	4a
		3' (HQ, <u>o</u> - to ether)	4b
7.5 - 8.1	53	2 (Bis-F, <u>m</u> - to ether)	4
		4 (DHBP, <u>m</u> - to ether)	4a

$$\text{Hence } (53 + 71) / 107 = (8 + 8a + 8b) / 12$$

$$\text{Therefore } a = 0.48, \quad b = 0.52.$$

$$\text{Or alternatively } 71 / 53 = (4 + 4a + 4b) / (4+4a)$$

$$\text{Therefore } a = 0.49, \quad b = 0.51.$$

$$(\text{Predicted } a = b = 0.5)$$

As these values are in close accordance it can be said that true equivalence of DHBP and HQ in the resultant polymer has occurred.

This was also found to be so for polymers M and L.

### 3.7.3 Transesterification

Transesterification arises during the polymerisation process if the attacking nucleophile (phenoxide) displaces another phenoxide ion, rather than fluoride from the reservoir of monomer or from a chain end, and thus causes rupture of the chain (see figure 37, section 3.2.2). It has been observed by NMR studies on PEEK/PES<sup>103</sup>; it is liable to occur where the phenoxide leaving group is stabilised (e.g. by a *p*-situated C=O or SO<sub>2</sub> group), and the problem is exacerbated at higher temperatures.

Although only a shift in the order of 0.1ppm is expected in the <sup>13</sup>C-NMR peaks for carbons close to the ether linkages, there is no indication that linewidths have increased or changed at all (see table 39) and certainly no double peaks are observed in figure 59 (see appendix) (polymer 8, type D, Bis-F/DHBP) when compared to figure 60 (polymer 21, type A, Bis-F/HQ) where the possibility of transesterification is negligible in the latter case, owing to HQ being a poorly stabilised leaving group when ionised. Upon observation of the difference linewidths in table 39, peak 7 (difference +18ppb) is the comparison reference around which it can be seen that one peak (peak 1, 26ppb) is above, while 3 peaks (peaks 9, 2, 10 at -10, 9 and 10ppb) are below this value which appears to be a totally

random result indicating no transesterification has occurred at all, for the Bis-F/DHBP monomer/polymer system.

Table 39: Spectra intensities and linewidths at half maximum from figures 59 (polymer 8) and 60 (polymer 21).

Peak Number	Chemical Shifts (ppm)		Intensity		Linewidth (ppb)		Difference Linewidth
	59	60	59	60	59	60	
Figure:-	59	60	59	60	59	60	60-59=...
1	159.27	162.70	5.2	4.1	60	86	+26
9	161.11	151.82	3.7	4.8	78	68	-10
7	130.48	130.44	13.1	11.1	48	66	+18
2	119.07	122.00	18.0	13.2	60	69	+9
10	118.68	117.22	15.5	13.6	73	83	+10

### 3.8 Experimental

#### 3.8.1 Heating Equipment

The requirements for the heating equipment are such that a temperature in excess of 330°C can be maintained to  $\pm 5^\circ\text{C}$ , and the applied heat spread evenly over the reaction vessel (usually a round bottom flask of capacity varying from 100ml to 1000ml) without localised 'hot spots' occurring.

A heating mantle was initially used to synthesise polymers 1-6 (see table 18), this was however unsatisfactory as the temperature could only be controlled to  $\pm 20^\circ\text{C}$  and hot spots occurred which degraded the polymer as observed by a darkening in colour.

A silicone oil (£25/kg) bath was subsequently used, even though after a short time the oil undergoes self-polymerisation, a reaction promoted by contamination through accidental spillage from the polymerisation. The high energy requirements were provided by a Redring 1500W table cooker.

Polymers 39-46 and 49-53 were synthesised using a Techne, 0-600°C, 2860W fluidised sand bath. The only problem with this equipment is a slight messiness with the sand, as the equipment uses compressed air, but this is easily controlled/ignored.

Polymers 47 and 48 were synthesised using a solder bath. While this presented positive buoyancy problems, conduction of heat was excellent, although care had to be taken to remove the flask before the bath resolidifies (180°C).

The use of graphite as a heat conduction medium was investigated but found to be unsatisfactory owing to large temperature anisotropies ( $\pm 30^{\circ}\text{C}$ ) in this medium.

Bath temperature control was provided by a PYE Ether 'Mini' 0-450 $^{\circ}\text{C}$  temperature controller to  $\pm 1^{\circ}\text{C}$ .

The overhead stirrer facility was provided by a Griffin and George Ltd., Type KQPS/28, 60W, 250-1200RPM (variable) overhead stirrer. When the torque for this proved insufficient for the 1000ml flask large scale polymerisations it was replaced by a Parvalux, Type SD24, 5 lbs.ins, 200RPM (fixed) overhead stirrer, or a high pressure (70 psi) air rotator.

### 3.8.2 Condenser Use

A condenser (air) was used for a while in order to maintain monomer equivalence in the polymerisation, but was soon discarded owing to the possibility of trapping unwanted volatile side products (water). Eventually a simple 'through-flow' (see figure 50) system was used and monomer inequivalence was corrected for by using an excess of the more volatile monomer (usually the dihalide) in the initial reaction mixture.

### 3.8.3 Monomers

#### Bis(4-hydroxyphenyl)sulphone (Bis-S)

ICI Wilton plant grade 4,4'-dihydroxydiphenylsulphone (Bis-S, 2 kg) was dissolved in hot methanol (2l) and distilled water (750ml). The resulting dark brown-orange solution was treated with decolourising charcoal and

filtered hot through celite. Boiling distilled water (8l) was added to the filtrate, which was then allowed to cool overnight to 35°C and subsequently cooled to 20°C by the addition of dry ice. White crystals were filtered and twice washed with water/methanol (4:1; 2 x 1l) before being oven dried overnight (110°C). GLC of the resulting purified Bis-S showed that less than 0.02% of the 2,4'- isomer and less than 0.1% of the 2,4,4'- analogue were present. The product had a melting point of 247°C (lit.<sup>104</sup> mp. 244-246°C (97% pure)) (yield 178g, 89%).

#### 4,4'-Dihydroxybenzophenone (DHBP)

ICI Wilton plant grade 4,4'-dihydroxybenzophenone (DHBP, 1kg) was dissolved in hot methanol (2l). To the resulting light brown solution decolourising charcoal and celite were added and this mixture was then filtered hot. Hot distilled water (2l) was added and the solution allowed to cool while stirring. The white crystals were filtered off and washed with water/methanol (1:1, 500ml), before being oven dried (100°C) overnight. Yield 172g (86%), m.p. 215°C (lit.<sup>104</sup> mp. 213-215°C (97% pure)).

#### Diphenyl Sulphone (DPS)

ICI Wilton plant grade diphenyl sulphone (DPS, 400g) was dissolved in hot propan-2-ol (IPA, 1.6l) under reflux, to yield a colourless solution which was then allowed to cool, with stirring, overnight. The resulting white crystals were filtered and washed twice with IPA (2 x 200ml) before being oven dried overnight (60°C). Yield 392g (98%), m.p. 128°C (lit.<sup>104</sup> mp. 123-125°C (97%pure)).

#### Other monomers from ICI Wilton

Hydroquinone (HQ), 4,4'-Biphenol (PDP), 4,4'-difluorodiphenylsulphone (DFS), 4,4'-difluorobenzophenone (DFBP) and 2,2-Bis(4-hydroxyphenyl)propane (Bis-A) were generously supplied in purified form by the staff of ICI Wilton.

#### Other monomers and solvents

4,4'-Thiodiphenol (TDP), 4,4'-Dichlorodiphenylsulphone (CPS), 4,4'-Dichlorodiphenylsulphoxide (CPSO), and 2-Chlorophenol (OCP) were obtained from Aldrich (99%+ purity) and used without further purification.

#### Monomers synthesised in this thesis

Bis(4-fluorobenzoyl)durene (Bis-F), Bis(4-chlorobenzoyl)durene (Bis-Cl), Bis(4-fluorobenzoyl)mesitylene (Bis-mesF) and 1,4-Bis(4-fluorobenzoyl)benzene (1,4-FBB) were obtained as described in Chapter II.

#### 3.8.4 Polymerisation

The following two cases are designed to show improvements in the techniques used for polymerisations during the progress of the work described in this thesis.

##### 3.8.4.1 Polymerisation of Polymer 1

A mixture of Bis-Cl (41.1g, 0.1 mol), HQ (11.0g, 0.1 mol) and DPS (45g) was mixed thoroughly in a 5-necked 250ml round bottomed flanged flask and heated (by isomantle), to 160°C while stirring (with a 60W low torque mechanical stirrer, see figure 49). After 30 minutes sodium carbonate (10.6g, 0.102 mol) was slowly added over 5 minutes to the brownish solution and the temperature raised to and held at

Figure 49: Experimental Apparatus initially used

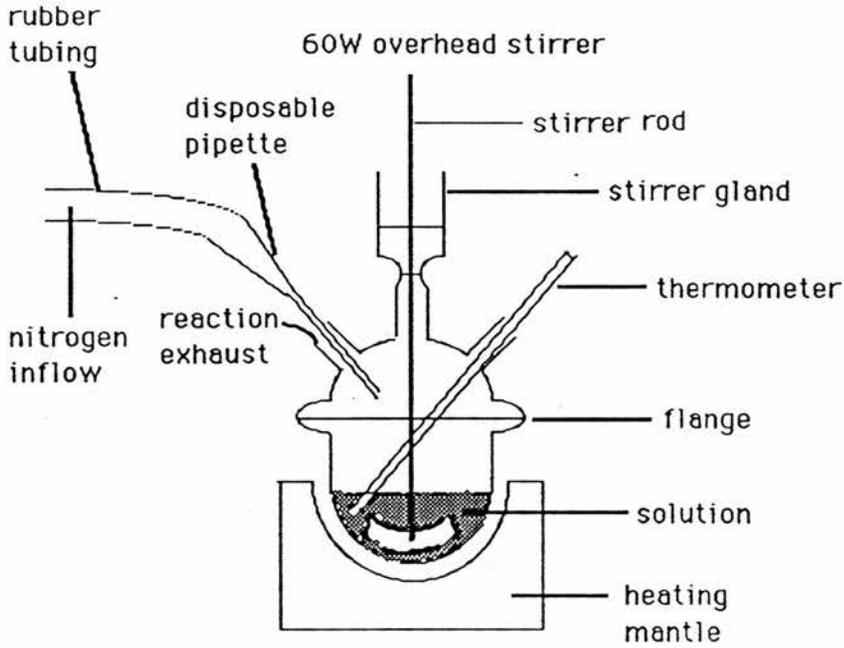
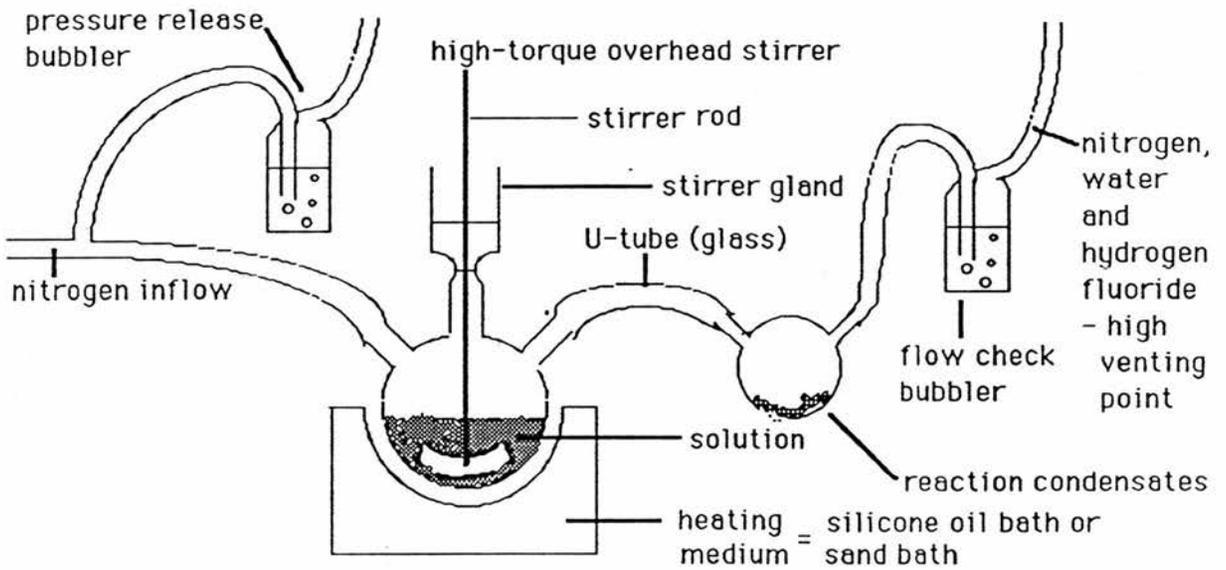


Figure 50: Experimental apparatus finally used



185°C for 1 hour. White crystals of DPS formed on the side of the flask above the solution. The temperature was raised to 215°C for 30 minutes, to ensure that adequate dispersion of the carbonate had taken place, before being increased to 315°C. Despite care and constant monitoring the temperature exceeded 330°C for a short period. Considerable liquid condensation (water ?) took place initially on the cold parts of the flask while the white crystals previously formed melt-flowed back into solution. After 2 hours the hot, dark brown, lightly viscous liquid was slowly poured into water where it immediately solidified.

The crude solid material was filtered off, ground into a powder and then leached as described later (see section 3.8.5), to yield 31.9g (71%) of darkly coloured polymer 1 (type A), whose physical properties are described in table 18.

#### 3.8.4.2 Polymerisation of Polymer 52

A mixture of Bis-F (120g, 0.317 mol), DHBP (67.26g, 0.314mol) and DPS (280g) was mixed thoroughly in a 3-necked 1000ml round bottomed flask and heated (by sand bath) with a high torque mechanical stirrer, to 200°C (see figure 50). After 30 minutes sieved (250µm) sodium carbonate (33.29g, 0.314 mol) and sieved (250µm) potassium carbonate (0.87g, 0.006 mol) were slowly added over 5 minutes to the colourless solution, and the temperature raised to and held at 230°C for 1 hour other stops being unnecessary as the sodium carbonate disperses easily. The white crystals that formed above the solution were periodically melted by a hot

air gun. The temperature was raised first to 280°C for 1.5 hours and then momentarily to 300°C (0.2 hours) when the solution started to thicken (after one hour) as observed by flow around the stirrer. Water vapour, a byproduct from the reaction, was rapidly dispersed into the neighbouring flask by keeping the nitrogen flow moderate and the U-tube hot. After 15 minutes, before the solution became too viscous, the reaction mixture was poured into water where it immediately solidified.

The solid polymer was filtered off, ground into a powder and then leached as described elsewhere, to yield 165.9g (96%) of lightly coloured polymer 52 (type D), whose physical properties are described in table 18.

#### 3.8.5 Polymer Workup

When the polymerisation has been completed the polymer must in some way be separated from the solvent. To facilitate this, as the polymer is a solid at room temperature, its surface to volume ratio must be maximised.

This is best achieved, if the viscosity of the solution is low, by discharging it as a thin stream into water. If the viscosity is too high for this the molten polymer can be coated on the inside of the flask, via rotation, until it solidifies forming a thin hollow ball ('lollipopping') which can be easily broken into small pieces. If the viscosity is extremely high the polymer sets as one lump and must be subsequently broken down using a stainless steel hammer and mallet, within a multi-layer plastic bag system to contain all the fragments. Use of a

hydraulic cutting press with a better containment system was found to be too slow and cumbersome as a replacement for the hammer.

#### 3.8.5.1 Grinding

The polymer pieces were reduced to a maximum length of 10mm, annealed at 120°C for 2 hours and then slow cooled to room temperature (promotes DPS crystallisation). A 1:1 mixture of polymer : dry ice (crushed) was ground to a powder in a Glen Creston, Type 14-680, 360W, Micro Hammer Cutter Mill.

Initially a zirconium block rock grinder was used, however polymer softening, from the frictional heat created, led to single lump formation resulting in inadequate separation of the grinding stones (and their subsequent damage).

#### 3.8.5.2 Leaching

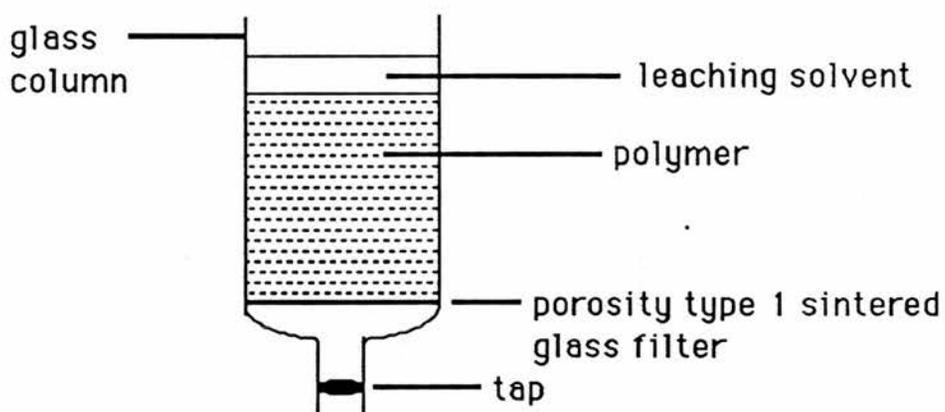
The method of leaching depended on the crystallinity of the polymer. The solvents used have to dissolve out the DPS, unreacted carbonate, unreacted monomers and preferably oligomers (polymer molecules with molecular mass < 1000-2000), but leave the polymer undissolved in powder form.

Acetone was very efficient at removing DPS and other organics but tended to soften amorphous polymers which then formed into lumps. If acetone, tested on a small portion of the polymer powder did not soften it the following method was used:-

(i) The extractor (see figure 51) was filled with acetone followed by the polymer powder thus avoiding air pockets. For every 100g of polymer, 2000ml of acetone was added taking care to maintain a layer of solvent over the polymer. Removal of DPS was checked by adding the extracted acetone into a five fold excess of water and observing for a white precipitate.

(ii) After the solid is sucked dry, distilled water (2l for every 100g polymer) at 80°C is allowed to percolate through to remove the carbonate, and other salts (NaF etc.)

Figure 51: Crystalline polymer leaching system



If acetone softens the polymer then the alternative longer method was used:-

The powder was extracted in a Soxhlet extractor over 24 hour periods with:-

- (i) an 8:2 mixture of methanol and water;
- (ii) a 9:1 mixture of water and acetic acid; and
- (iii) an 8:2 mixture of methanol and acetone.

The efficiency of the leaching process was confirmed by the  $^{13}\text{C}$ -NMR spectra of the cleaned polymers.

#### 3.8.6 Reprecipitation

In general the polymer was dissolved in a solvent (c.H<sub>2</sub>SO<sub>4</sub>, OCP, NMP etc.) and then filtered dropwise through a porosity 1 type sintered glass filter into a stirred solution which consists primarily of a solvent in which the polymer is insoluble (i.e. water for c.H<sub>2</sub>SO<sub>4</sub>, methanol for the other solvents). This mixture was filtered and the pellets of polymer macerated in a Sunbeam 200W kitchen blender, with more of the latter solvent. The solution/suspension was then left to stir for 30 minutes in a beaker before being filtered and washed. This stirring/filtering was repeated twice and the resulting polymer powder oven dried (100°C).

#### 3.8.7 Salt Treatment

This was performed on polymers thought to be sulphonated<sup>99</sup> by reprecipitation from c.H<sub>2</sub>SO<sub>4</sub>.

In general, 10g of powdered polymer was made into a slurry with 200ml of water. 10g of Na<sub>2</sub>SO<sub>4</sub> was added and the mixture stirred for 30 minutes. The mixture was filtered and the procedure repeated. The resulting polymer was oven dried and tested by elemental analysis for sodium uptake.

#### 3.8.8 Compression Mouldings

These were performed using either a Tangye or a Moore Hydraulic Press with integrated temperature control ( $\pm 1^\circ\text{C}$ )

and air/water cooling. Either press was capable of exerting 20 tonnes pressure on a 200 x 200mm surface.

In general, aluminium sheet moulds (0.43mm thick) using 2.3g polymer on a 70 x 70mm area were made, the general procedure being:-

(i) Three aluminium squares were cut (see figure 52, 2 of no.1 and 1 of no.2) and preheated in the press for 2 minutes.

(ii) 2.3g of polymer were loaded into the space when sheet no.2 was sandwiched between the two sheets of no.1.

(iii) This sandwich was placed in the press where the pressure was subsequently loaded and released in 5 tonne steps (i.e. 0, 5, 0, 10, 0, 15, 0, 20 tonnes) with 10 seconds spent at each intermediate step.

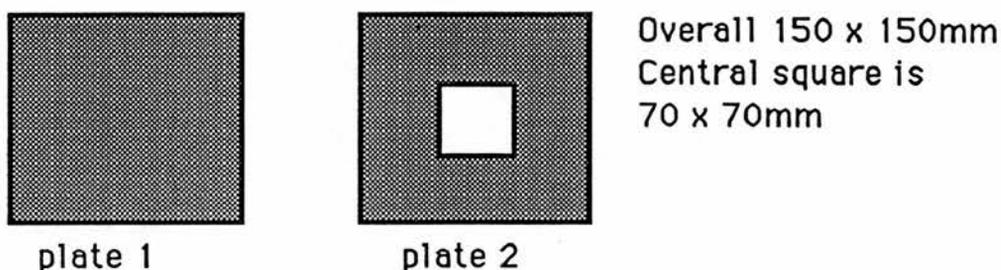
(iv) Cooling of the mould was carried out in one of two ways i.e. either;-

(a) cooling in the mould (more common) where the pressure is maintained (20 tonnes) while the press is quickly (3-5 minutes) air/water (above 280°C) then water (below 280°C) cooled until the press temperature is 50°C below the  $T_g$  of the polymer being pressed, or

(b) quench cooling, where the mould is removed and placed immediately in cold water.

For larger plates (150 x 150 x 3mm) generally steel cutouts with copper bases are used. 110g of polymer is generally necessary with slightly longer hold times to compensate for the greater thickness of the mould and poor thermal conductivity of polymers in general.

Figure 52: Plates used for compression moulds.



### 3.8.9 Photocrosslinking<sup>75</sup>

This experiment was performed in the following way:-

(i) Polymer 7 (0.1g) was dissolved in chloroform (10ml).

(ii) A UV spectrum was run using a Pye-Unicam SP8-100 ultraviolet spectrophotometer and a broad band of absorption was observed to occur below 330nm.

(iii) The solution was placed in a Pyrex test tube (20ml) and exposed from 50mm to a Hanover 125W UV lamp for 3 hours.

Upon filtering no insoluble precipitate was found.

### 3.8.10 Instruments

Differential scanning calorimetry (DSC) scans were performed at 20K min<sup>-1</sup> on a Perkin Elmer Delta series DSC7 with a TAC 7/3 Instrumental Controller, and a 3700 Data Station.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained from a Bruker AM300 NMR spectrometer, although some <sup>1</sup>H spectra were obtained from the older

Bruker WP80 NMR spectrometer. Solutions for this analysis were made in deuterated chloroform except for some of the diol monomers where the solvent was deuterated dimethylsulphoxide (DMSO). All chemical shifts are referenced to trimethylsilyl (TMS, 0ppm).

Gel Permeation Chromatography (GPC) was performed by the staff of ICI Wilton using a dedicated Waters HPLC and a 0.25% polymer solution in *o*-chlorophenol.

Thermal Gravimetric Analyses (TGA) thermograms were recorded using a Stanton Model TR-1 Automatic Thermo-Recording Balance at  $4\text{K min}^{-1}$ .

Hot Stage Microscopy (HSM) was performed using an Olympus BHS-P microscope fitted with a Stanton Redcroft TH-600 hot-stage.

### 3.8.11 Experimental Characterisation

Polymer solubility was analysed by test tube using ca. 0.1g polymer in 5ml solvent. Samples were vigorously shaken for two hours before observation.

X-Ray crystallisation analysis was performed by ICI Wilton using Wide Angle and Small Angle X-Ray Scattering (WAXS and SAXS) techniques.

Reduced viscosity (RV) measurements were generally made using 1% by weight polymer dissolved in c.H<sub>2</sub>SO<sub>4</sub> and analysed at  $25.00 \pm 0.05^\circ\text{C}$  by time measurements using a Technico BS/U size D viscometer in a thermostatted water bath. RV was calculated from equation 6

$$RV = \left( \frac{\text{Time for solution}}{\text{Time for solvent}} \right) \times \frac{1}{c} = \left( \frac{\eta}{\eta_0} - 1 \right) \times \frac{1}{c} = \eta_r - 1$$

- equation 6

for dilute solutions ( $c = 1 \text{ g dl}^{-1}$ ).

The solutions were filtered (porosity type 1 filter). In those cases where not all the polymer dissolved, RV's are quoted in brackets.

Mechanical testing experiments performed, on machined sections of the 150 x 150 x 3mm plates by staff at ICI Wilton, encompassed three tests known as the Thermoplastics Screen Analysis<sup>102</sup> (TSA):-

- (i) disc modulus at  $2\text{mm min}^{-1}$  and  $23^\circ\text{C}$ ;
- (ii) yield strength in compression at  $0.5\text{mm min}^{-1}$  and  $23^\circ\text{C}$ ; and
- (iii) fracture mechanics, on a sharply notched sample at  $1\text{m s}^{-1}$  and  $-65^\circ\text{C}$ .

Equipment used for TSA comes from the Instron series.

## Chapter IV : Possible Applications of Methylated Polymers

### 4.1 Introduction

At the conclusion of Chapter III it was shown that under carefully controlled conditions high molecular weight polymers involving the monomer bis(4-fluorobenzoyl)durene (Bis-F) could be synthesised, and subsequently moulded into strong, tough, flexible materials. However, owing to the expense and difficulty of synthesising Bis-F, these new polymers are not currently affordable as engineering materials, but might be economic in some type of specialised application involving a high added-value. This high added-value could consist of two forms:-

- (i) capital/labour intensive; and/or
- (ii) intellectually intensive (patent).

Whichever form the high added-value takes, this component must dwarf the costs involved in producing the polymer up to the stage described at the end of Chapter III.

### 4.2 Special Features of Type B and D Polymers

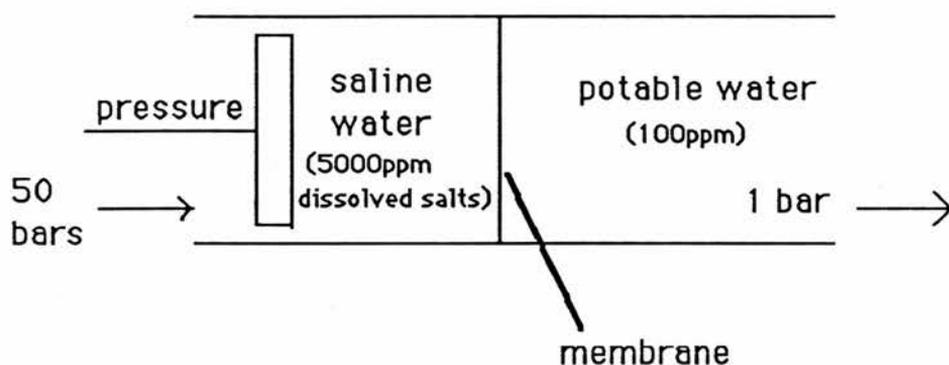
The most obvious difference between type B and D polymers and PEEK are the four methyl groups on every fifth ring. Any possible application should involve these methyl groups, or their effect on the polymer chain conformation, in some way.

As materials are already available with pendant methyl groups, the desired application should ideally require the pendant groups to be adjacent to each other.

#### 4.2.1 Reverse Osmosis

Desalination of seawater by reverse osmosis (see figure 53) requires the use of a hydrophilic membrane material, which until recently has been cellulose acetate<sup>100,105</sup>. Certain ionic polymers based on the sulphonation of PES have been developed recently as membrane materials;<sup>99</sup> they have greater chemical stability and resistance to biological degradation, and yet are still strong enough to withstand the high pressures (50 bars) applied to such thin films (0.02-1.0 $\mu$ m).

Figure 53: Desalination of water by reverse osmosis.



However, the difficulty in controlling the degree of sulphonation causes problems with regard to overswelling with subsequent loss of strength.

The carboxylic acid ion group could also perform the same function. Hence by specifically oxidising the pendant

functional groups in B and D type polymers, a hydrophilic material, which could be cast into a membrane, may be synthesised.

The oxidation could take place in various ways, for example, by the use of potassium dichromate and sulphuric acid.<sup>106</sup> The use of 30% nitric acid<sup>51</sup> has been shown to give satisfactory oxidation of the methyl groups on dibenzoyldurene.

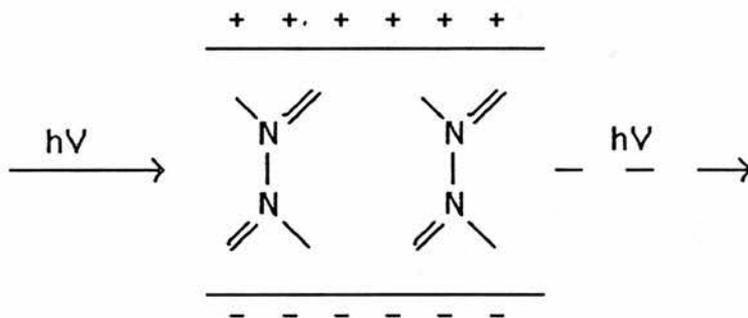
#### 4.2.2 Optic Cables

With the recent development of optoelectronic switches and other non-linear devices<sup>107</sup> (the light equivalent of an electrical transistor), the need has arisen for the incorporation of a functional dye in high concentration into such devices. This dye must be fixed in place by a matrix material such that the dye molecules can be aligned perpendicular to the cable axis (see figure 54). Hence the matrix material must be curable, most conveniently by exposure to UV light, while an electric field is applied to align the dye. After the matrix is set it must be optically transparent so as not to inhibit the transmission of light down the cable.

Mohanty et al.<sup>75</sup> have shown that some methylated polymers are photocrosslinkable provided they have benzophenone units in the main chain (see figure 55).

Hence the possibility of the use of D type polymers exists. However, attempts thus far, both here (see section 3.8.8) and from irradiation of cast films at ICI Wilton, have failed to produce photocrosslinking.

Figure 54: An optoelectronic dye transistor.



#### 4.2.3 Cross-linking Agents

Introduction of chemical cross-linking agents active towards the methyl groups could vastly improve the solvent resistance and stiffness of the resulting polymer, which then becomes a thermoset rather than a thermoplastic.

For example, imine cross-links, formed from the incorporation of 1,4-phenylenediamine into PEEK, raised the glass transition temperature from 143°C to somewhere in excess of 280°C with no loss of thermal stability (see figure 56).<sup>7</sup>

#### 4.2.4 Catalysis

Through the subsequent modification of the pendant methyl groups into ligand functionalities, the catalysis of certain reactions, requiring or aided by ring formation between the adjacent modified pendant methyl groups, may be achieved.

For example, the copper (II) catalysed hydrolysis of diamino-acid esters, is achieved by the formation of labile

Figure 55: Photocrosslinking

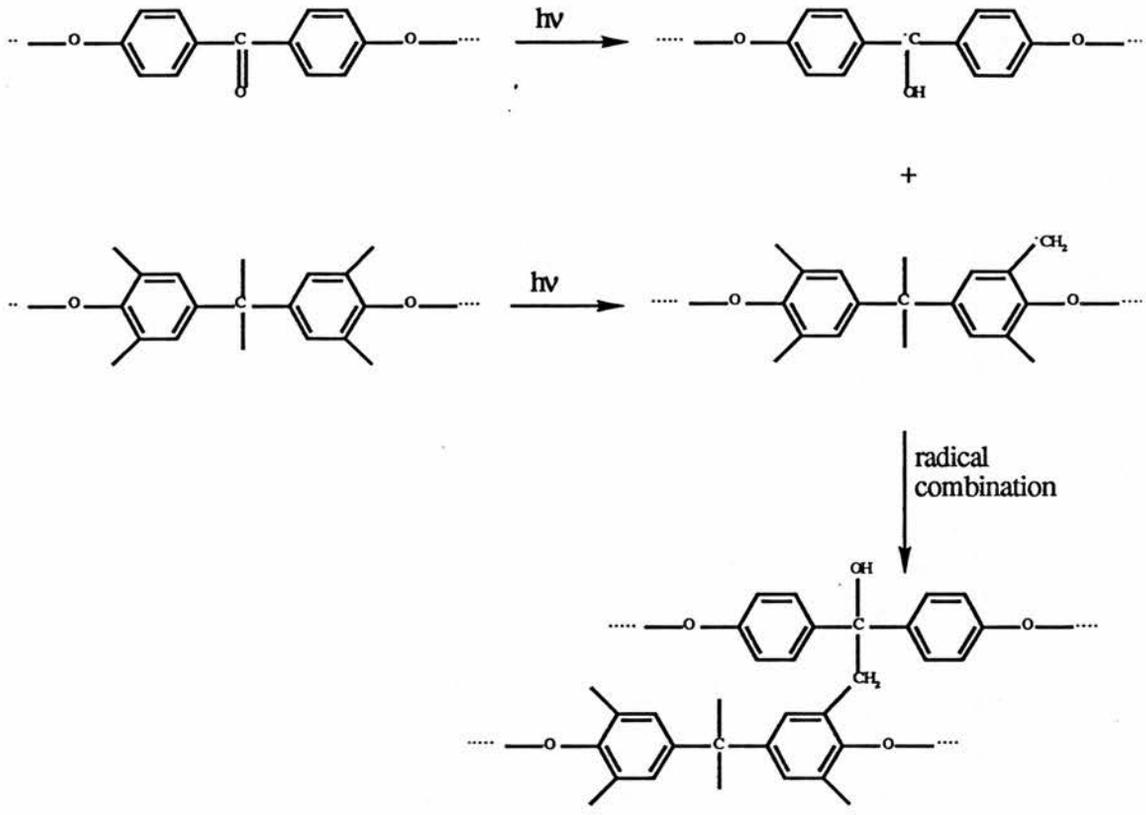
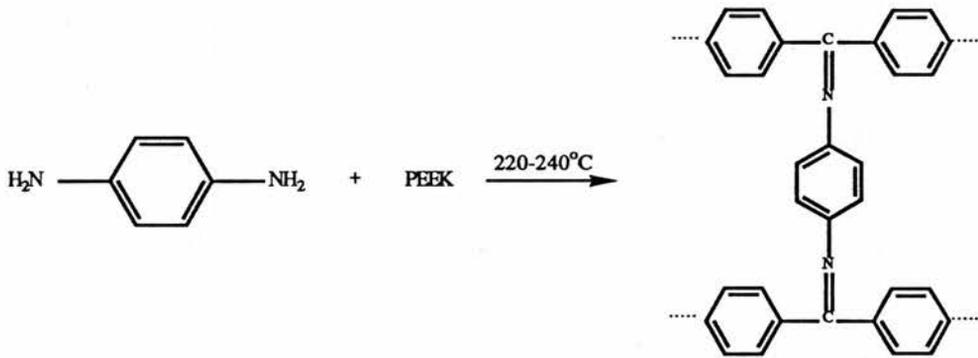


Figure 56: Cross-linking PEEK



rings between the metal ion and carboxyl groups (see figure 57).<sup>108</sup>

With a polymer acting as a catalyst it can be fixed to the walls of a column and therefore not need to be separated from the solution in which the catalysis takes place.

#### 4.2.5 Fire Retardancy

Durene, if incorporated into a phosphine oxide, can then be used (10%) with polypropylene as a fire retardant (see figure 58).<sup>109</sup> Durene can be used for two reasons:-

(i) it is easily difunctionalised in a linear way (see Chapter II); and

(ii) being an aromatic molecule it has a high carbon : hydrogen ratio thereby adding to the fire retardancy of the molecule via charring.<sup>5</sup>

Adaptation of Bis-F into a similar type of molecule as that illustrated in figure 58 could result in significant fire retardancy being imparted to the resulting aromatic polymer.

#### 4.2.6 Incorporation of Methylated Monomers into PEK

As mentioned in the summary of Chapter III (see section 3.6), by reducing the proportion of Bis-F in polymer L, a polymer with a higher glass transition temperature ( $T_g$ ), yet still retaining the crystallinity (and hence solvent resistance) of PEK, could result. However, although the costs would be much lower (small proportion of Bis-F in final product), the temperature

Figure 57: Catalysis aided by 5-membered ring formation

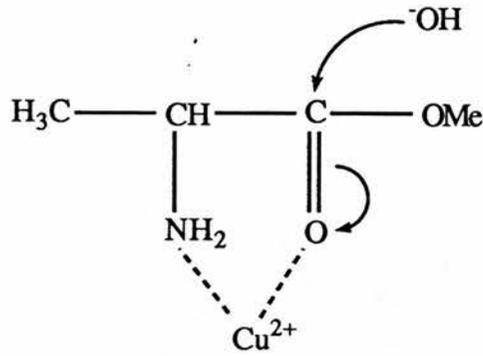
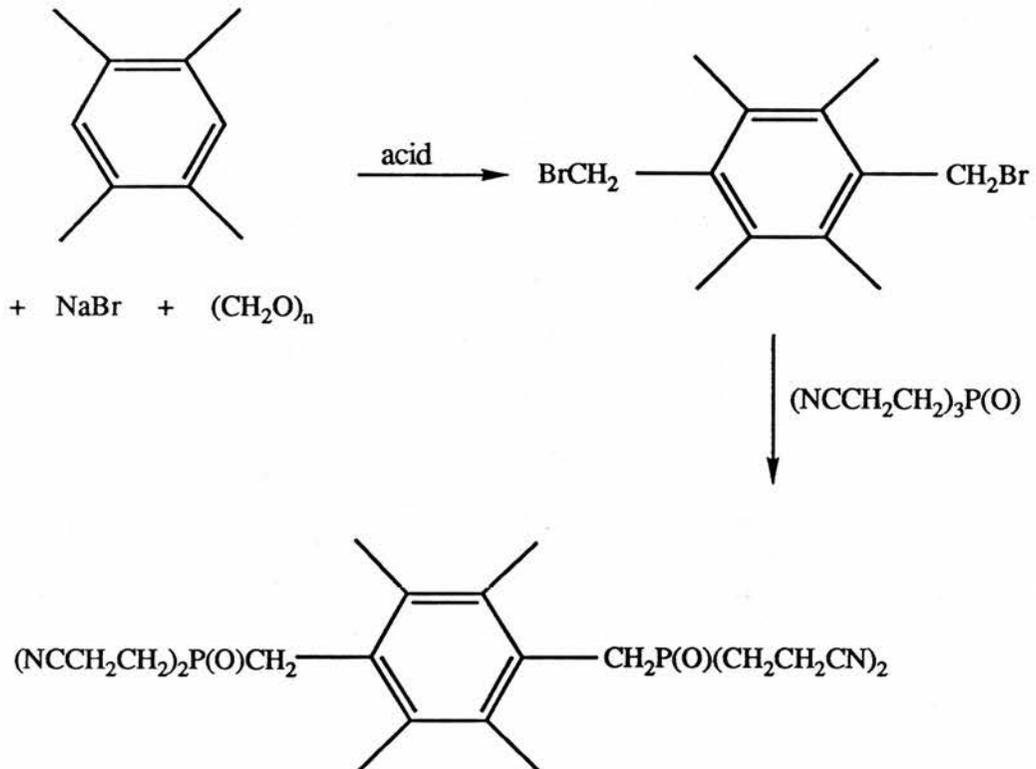


Figure 58: Durene as a fire retardant



stability problem still exists, hence requiring some form of chemical modification of the pendant methyl groups.

#### 4.3 Results and Discussion

The attempted oxidation of polymer 34 (type B, Bis-F/Bis-S) by a sodium dichromate/sulphuric acid/water solution resulted in no observed change visually or by  $^{13}\text{C}$ -NMR.

Applying more vigorous conditions, by using sodium dichromate in  $\text{c.H}_2\text{SO}_4$ , resulted in complete dissolution of the polymer with subsequent degradation.

This situation illustrates the problem of chemical modification of polymers. Owing to difficulties in dissolution only a small part of the polymer (i.e. the surface of the exposed material) can be attacked. When a stronger solvent was used ( $\text{c.H}_2\text{SO}_4$ ) the resulting conditions are vigorous enough to effectively digest the polymer.

Oxidising conditions often precludes the use of organic solvents hence a compromise was now sought whereby the methyl groups will oxidise but the polymer backbone will remain intact.

The oxidation of Bis-F, by a sodium dichromate/sulphuric acid/water solution as before, resulted, on average, in 1.78 methyl groups per molecule being oxidised to carboxylic acid groups, this being determined by acid-base titration. The midpoint buffer region indicated an average  $\text{pK}_a = 5.79 \pm 0.01$  ( $T = 25^\circ\text{C}$ ).

From the Balme patent<sup>51</sup> it has been indicated that oxidation with 30% nitric acid for 2 hours at 170°C would achieve the desired result. However, oxidation of polymer 45 (0.5 Bis-F, 0.5 DFBP/DHBP, type K, RV = 1.32) by this method resulted in a drop in RV to 0.21. <sup>13</sup>C-NMR yielded multiple peaks indicating that some limited degradation had occurred; however lack of insoluble gel formation suggested that cross-linking was not the likely cause. Attempts to compression-mould the yellow material resulted only in a black brittle material.

Hence, although it appears likely that the pendant methyl groups have been oxidised, polymer molecular weight has been degraded to such an extent as to render the polymer non-utilisable.

#### 4.4 Conclusions

Although the applications attempted thus far have not been successful, it can be clearly seen that there is considerable scope for the possible application of methylated aromatic polymers.

In the future, as the demands for new materials increase and change in new directions, methylated polymers could well be in demand, particularly as it has been demonstrated in this thesis that they can be synthesised, albeit with some moderate difficulty, to high molecular weights, yielding materials with all the strength and solvent resistance (although somewhat inferior thermal stability) of their commercial non-methylated analogue Victrex PES.

#### 4.5 Experimental

##### Attempted oxidation of polymer 34 (Bis-F/Bis-S, type B) by dichromate solution

Polymer 34 (15.48g), sodium dichromate dihydrate (10.72g, 36.0mmol) and distilled water (25ml) were stirred together in a 250ml 3 necked round bottomed flask. c.H<sub>2</sub>SO<sub>4</sub> (14.5ml) was added over 30 minutes to the yellow lumpy mixture which reddened and then darkened. Water (100ml) was added and the mixture refluxed for two hours before filtering. The remaining lumps were digested on a water bath by a 5% sulphuric acid solution (200ml), filtered, and treated with 5% sodium hydroxide solution at 50°C for 2 hours. The filtered solution yielded no precipitate when treated with a 15% sulphuric acid solution. The solid remaining was washed with water to yield 14.01g of unreacted polymer 34 as identified by <sup>13</sup>C-NMR.

##### Oxidation of polymer 34 (Bis-F/Bis-S, type B) by dichromate/sulphuric acid

A solution of polymer 34 (13.00g) in c.H<sub>2</sub>SO<sub>4</sub> (80ml) was added dropwise over 30 minutes to a solution of sodium dichromate dihydrate (8.96g, 30.1mmol) in c.H<sub>2</sub>SO<sub>4</sub> (30ml) in a 100ml round bottomed flask. The solution was heated to 100°C for 1 hour before discharging into 1000ml of iced water. A black sediment was filtered which when analysed by <sup>13</sup>C-NMR had only multiple small peaks (probably degraded material).

Oxidation of bis(4-fluorobenzoyl)durene (Bis-F) by dichromate solution

The first method was used the reactants being Bis-F (10g, 26.0mmol), sodium dichromate dihydrate (10.72g, 36.0mmol) and distilled water (25ml). After refluxing the mixture became green (oxidation). Later, after treatment with 5% sodium hydroxide, the filtered solution, upon addition to a 15% sulphuric acid solution, yielded a white precipitate (1.67g, 14.7% if two methyls are oxidised to two carboxylic acid groups per molecule) with a melting point of 273°C. Elemental microanalysis was consistent with the product being Bis-F with approximately two methyl groups being oxidised to carboxylic acid groups.  $^{13}\text{C}$ -NMR indicated a mixture of mainly two compounds of approximately even proportions; 1,4-bis(4-fluorobenzoyl)-3,6-dimethylbenzene-dicarboxylic acid (I) and 1,4-bis(4-fluorobenzoyl)-3,5-dimethylbenzene-dicarboxylic acid (II). Average  $\text{pK}_a = 5.79 \pm 0.01$  ( $T = 25.0^\circ\text{C}$ ), 1.78 carboxylic acid groups per molecule. (Found: C, 64.1; H, 3.5.  $\text{C}_{24}\text{H}_{16}\text{F}_2\text{O}_6$  (2 COOH) requires C, 65.8; H, 3.7%,  $\text{C}_{24}\text{H}_{14}\text{F}_2\text{O}_8$  (3 COOH) requires C, 61.6; H, 3.0%).  $m/z$  438 ( $\text{M}^+$ ).  $\delta_{\text{C}}$  44 peaks. 10 correspond to I while 16 correspond to II.

Oxidation of polymer 45 (type K, 0.5 Bis-F, 0.5 DFBP/DHBP) by 30% nitric acid

Polymer 45 (type K, 10g,  $\text{RV} = 1.32$ ) and 30% by weight strength nitric acid (52g) were introduced into a stainless steel autoclave. The autoclave was heated and kept at  $170^\circ\text{C}$  for 2 hours. The mixture was cooled and washed with distilled water. 9.97g (yield 89.7% if all the pendant

methyl groups were oxidised to carboxylic acid groups) of a light yellow solid (RV = 0.208) was obtained.  $\delta_C$  50+ peaks obtained. Upon compression moulding (350°C) a black brittle plate was formed.

# Appendix

Figure 59:  $^{13}\text{C}$ -NMR spectrum of polymer 8.

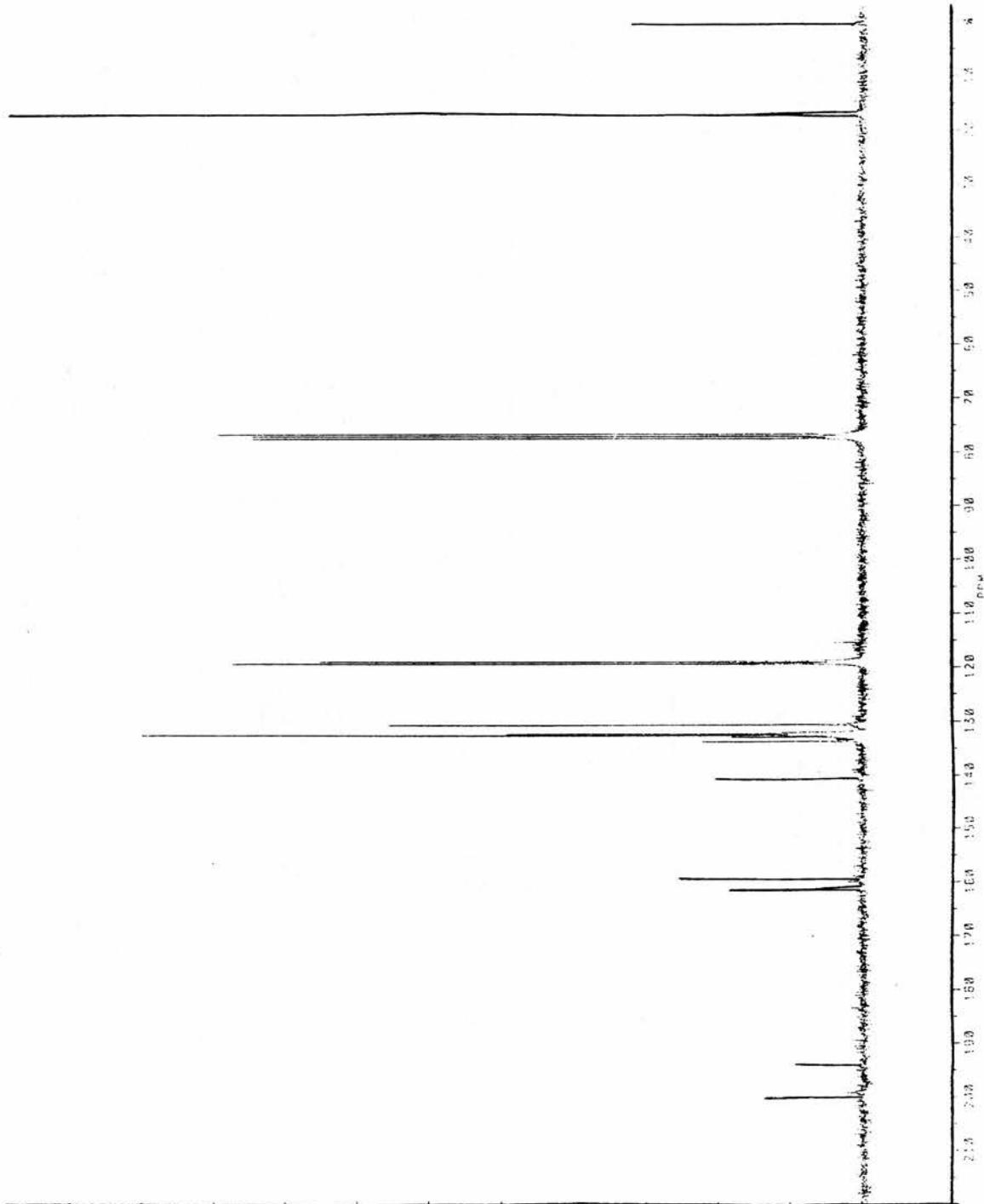


Figure 59 continued:  $^{13}\text{C}$ -NMR spectrum of polymer 8.

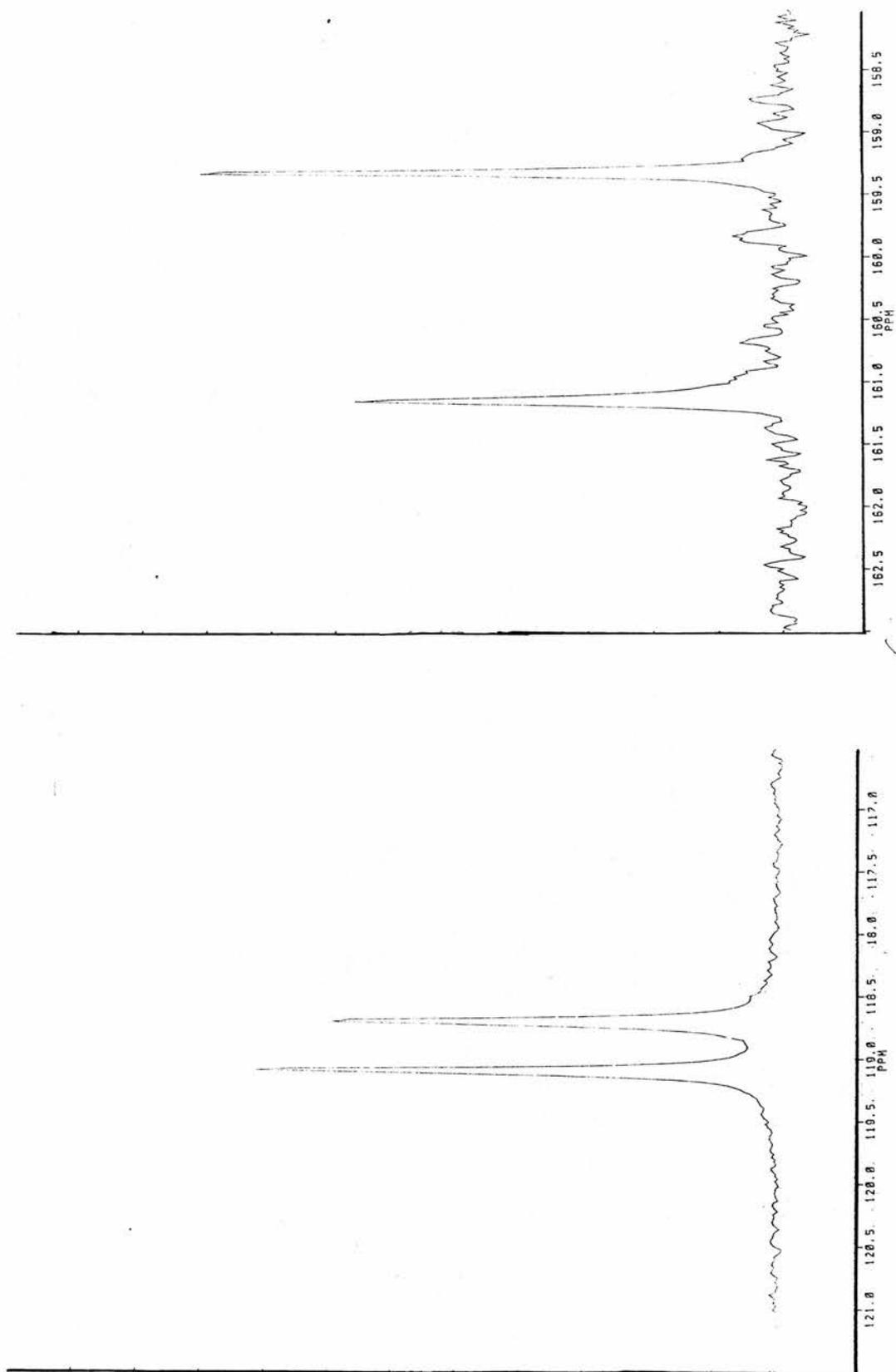


Figure 59 continued:  $^{13}\text{C}$ -NMR spectrum of polymer 8.

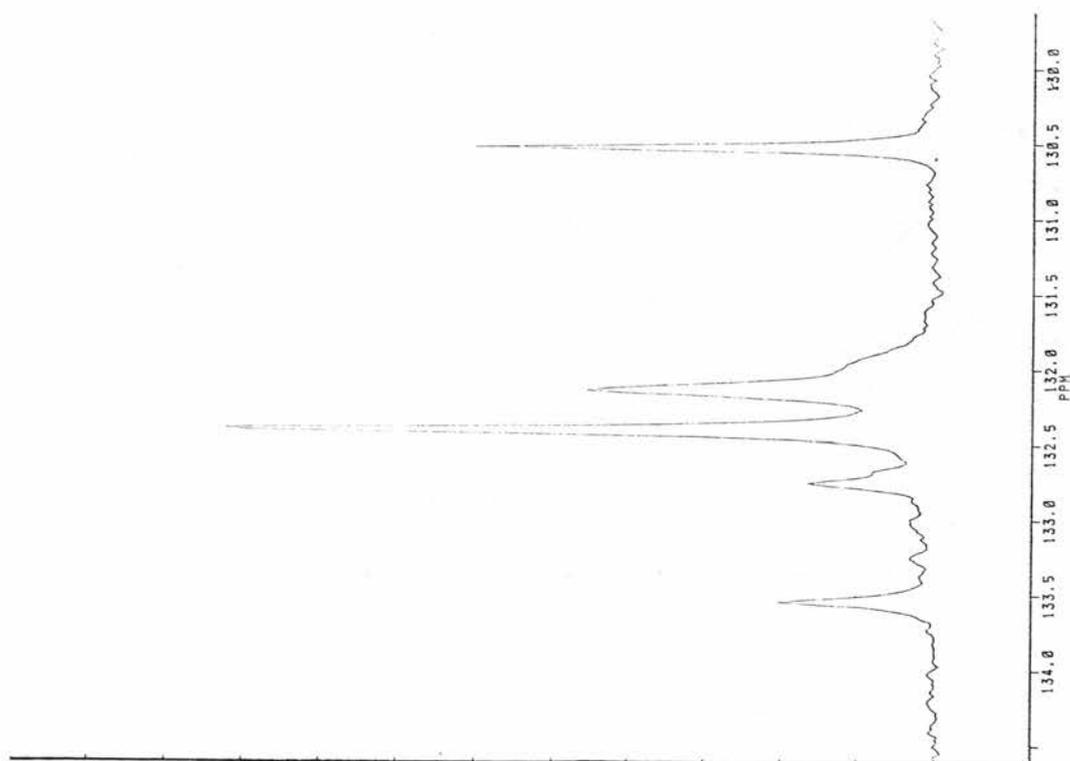


Figure 60:  $^{13}\text{C}$ -NMR spectrum of polymer 21.

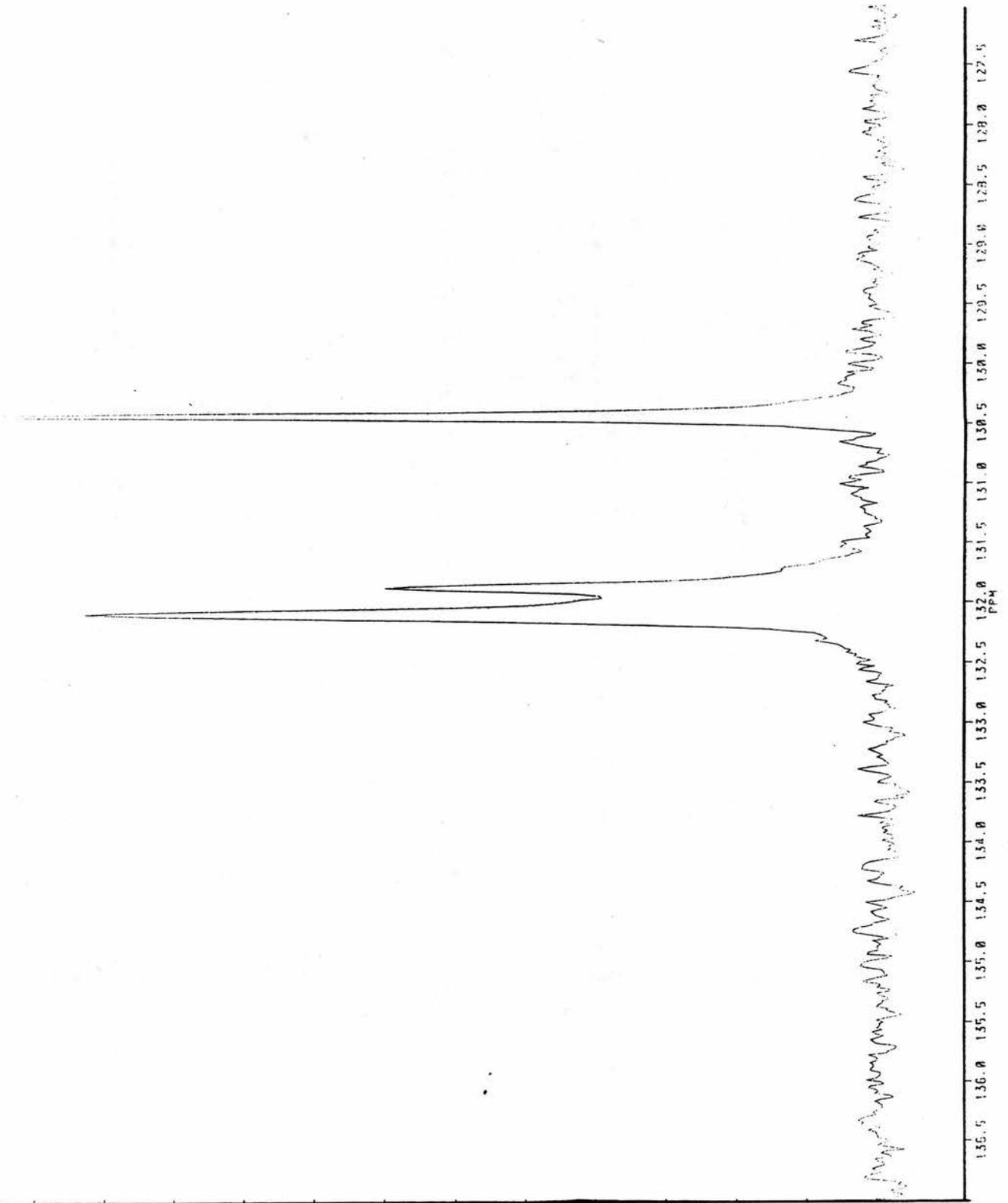


Figure 60 continued:  $^{13}\text{C}$ -NMR spectrum of polymer 21.

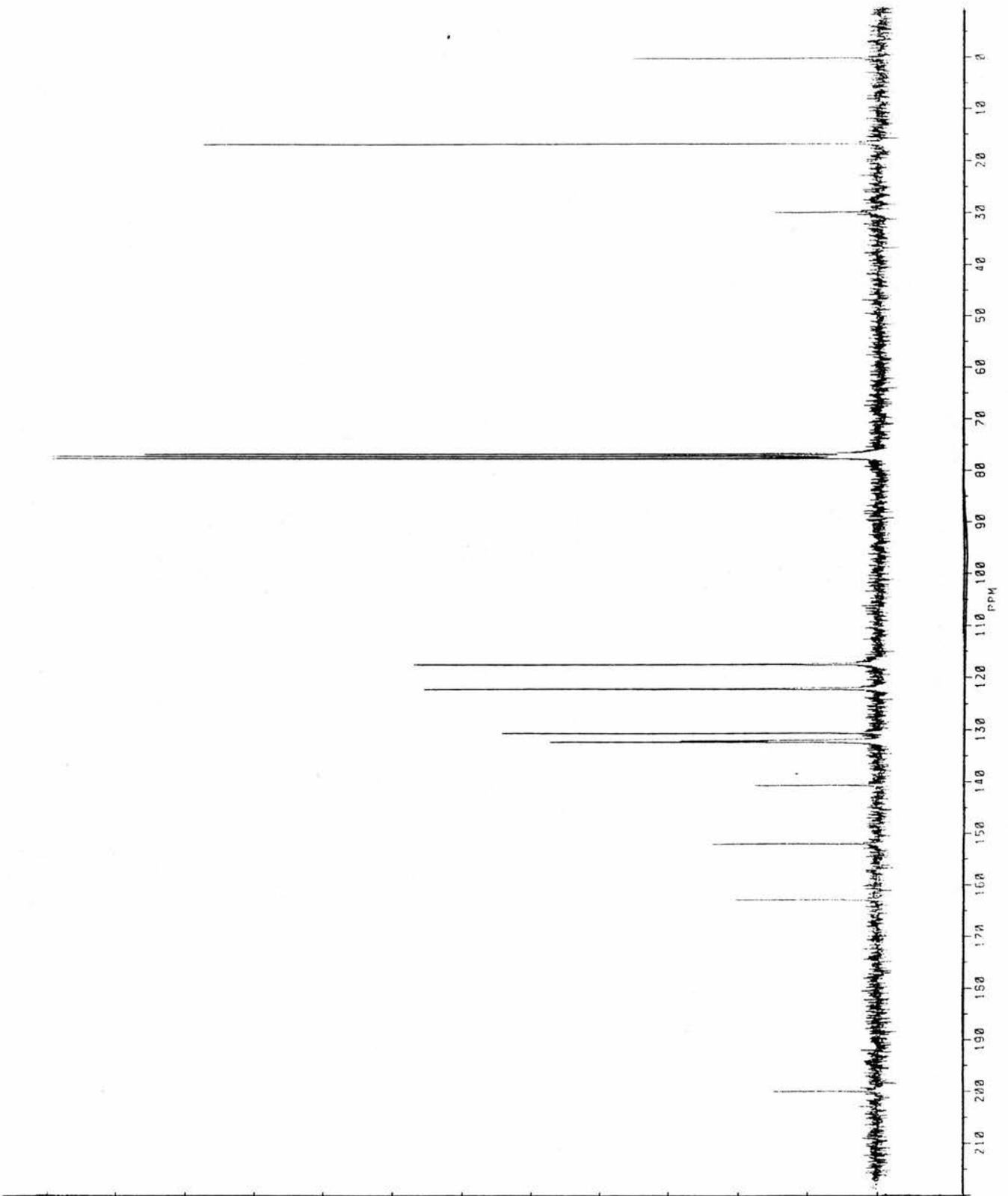
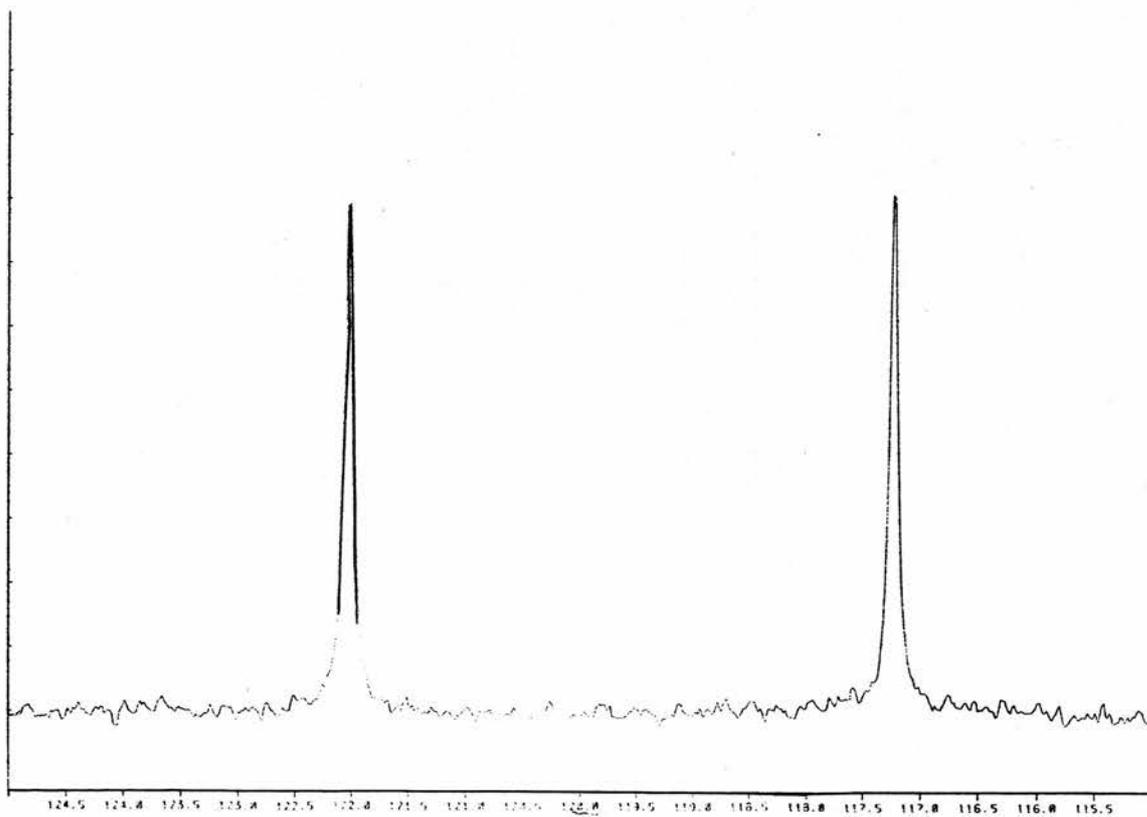
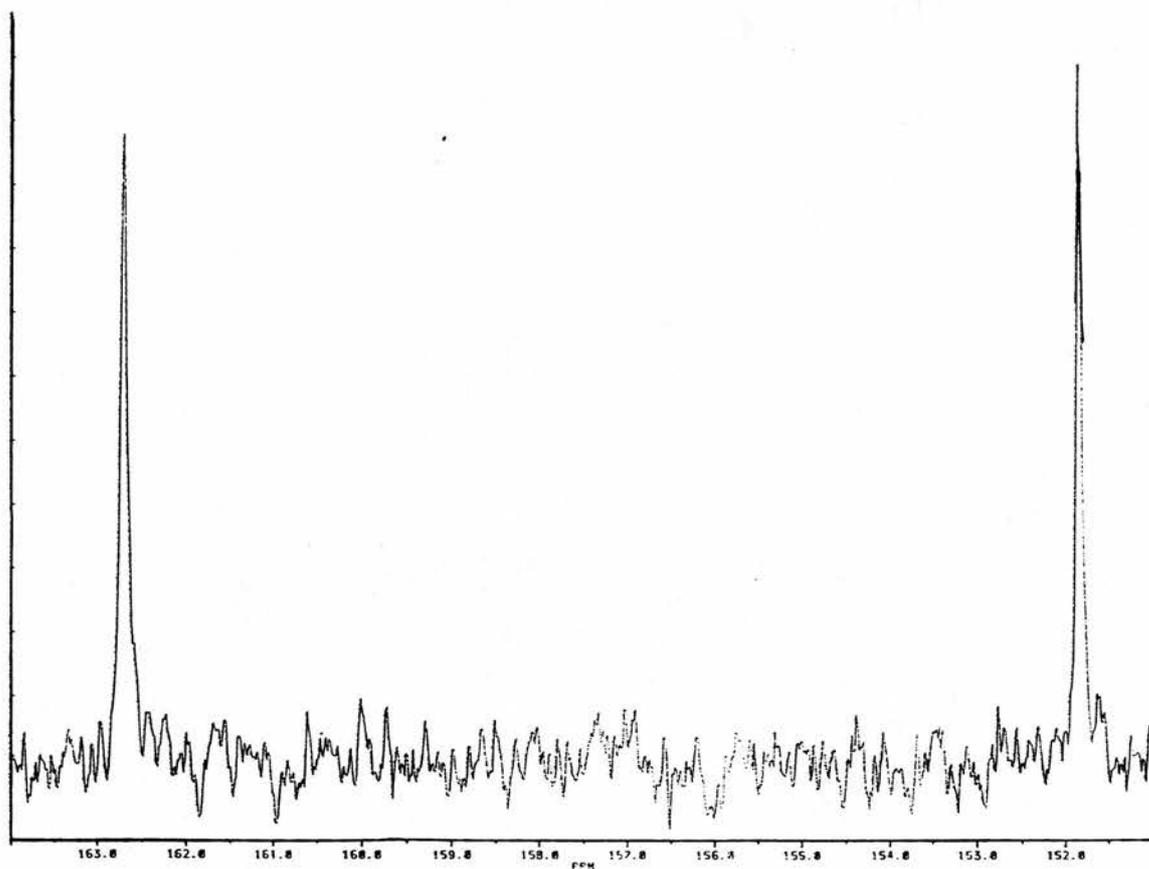


Figure 60 continued:  $^{13}\text{C}$ -NMR spectrum of polymer 21.



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