Novel poly(aryl ether)s containing nitrile groups: synthesis, characterization and cross-linking studies.

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A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science.
To Francesca (and she's earned it!) and Angus,

and to Mum and Dad.
Seek not to know all of the answers, merely to understand the questions.
Acknowledgments

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Abstract

Four novel aromatic difluoride compounds were synthesized for use as monomers in nucleophilic aromatic displacement polymerization reactions. Attempts were then made to polymerize these monomers with a series of bisphenols, using potassium carbonate as a base, in a dipolar aprotic solvent as in equation 1.

\[ \text{L-Ar-L} + \text{HO-Ar-OH} \xrightarrow{\text{K}_2\text{CO}_3, \text{Dipolar aprotic solvent, 160-195°C}} \left( \text{O-Ar-O-Ar} \right)_n \]  

Using the reaction above, several novel poly(aryl ether)s have been produced and some of their physical properties, such as glass transition temperature and thermal stability, have been investigated. The polymers all contain nitrile groups which have potential to form cross-links upon heating, thereby increasing the use temperature and solvent resistance of the resulting materials. This cross linking potential was investigated. Also, polymers containing the 9,10-dicyanophenanthrene moiety were prepared and then reacted with cuprous chloride and phthalonitrile to give poly(aryl ether)s containing copper phthalocyanine groups.
Quatre nouveaux difluorures aromatiques ont été synthétisés à l'usage comme monomères pour la polymérisation utilisant la réaction de déplacement nucléophile des fluors. On a essayé de polymériser ces monomères avec une série de biphénoles utilisant le carbonate de potassium comme base dans un solvant aprotique dipolaire exemplifié dans l'équation 1.

\[
\begin{align*}
F-Ar-F + 2\text{HO-Ar-OH} & \xrightarrow{\text{K}_2\text{CO}_3} \frac{\text{Dipolar aprotic solvent}}{160 - 195^\circ\text{C}} (\text{O-Ar-O-Ar})_n
\end{align*}
\]

Ainsi, plusieurs nouveaux poly(aryl éther)s ont été produits et on a évalué des propriétés physiques, comme la température de transition de verre et leur stabilité thermique. Tous les polymères contiennent les groupes nitrides qui au chauffage, peuvent former des liaisons croisées augmentant la température d'usage et la résistance aux solvants des matériaux qui y résistent. On a étudié ce potentiel de former les liaisons croisées. Aussi des polymères contenant le dicyanophenanthrène-9,10 ont été préparés et puis utilisés comme réactif avec le chlorure de cuivre et phthalonitrile donnant des poly(aryl éther)s solubles et d'une couleur verte très foncée contenant le phthalocyanine de cuivre.
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Chapter One

Introduction

The goals of the research described in this thesis were to prepare some novel polymers and to investigate some of their physical properties. In particular we were interested in synthesizing polymers which initially were soluble in organic solvents and could, after fabrication into the desired shape, be thermally or photochemically cross linked. The resulting polymers would then be insoluble. However, before launching into a detailed discussion of the polymers that were prepared, it is useful to begin by giving a general description of some aspects of polymer chemistry in order to put this work into context.

1.1 What is a polymer?

A polymer may be described as "a substance composed of molecules which have long sequences of one or more species of atoms, or groups of atoms, linked to each other by primary, usually covalent bonds". In other words, polymers are very large, usually linear molecules which are composed of units, or groups of atoms, which are repeated throughout the molecule. These very large molecules are known as macromolecules.

A familiar example of a polymer is polystyrene which is used to make disposable drinking cups, and many other things too. Polystyrene is composed of macromolecules which have the chemical structure depicted in figure 1.1. Macromolecules can be represented in an abbreviated form by enclosing the repeating unit (the monomer) in brackets followed by the letter n. Hence polystyrene can be represented by figure 1.2.

The n denotes the number of repeating units which go together to make up the macromolecule and it is known as the "degree of polymerisation".
Scheme 1.1
The words polymer and macromolecule are often used interchangeably. Another word that is often used in place of polymer is plastic. However, this is not accurate as the word plastic refers to commercial materials which consist of the polymer plus a variety of additives such as stabilizers, colourants, fillers, etc. When the average man on the street hears the word plastic, the words cheap and low quality often spring to mind. The first synthetic polymer to be commercially developed were the phenolic resins (Bakelite) followed by polystyrene and poly(vinyl chloride) and later polyethylene and polypropylene. These polymers were not designed to perform better than the traditional materials, but they were able to replace them in some instances, simply because they were cheaper and were able to perform a function adequately. Today things are different and polymers are being designed to fulfill requirements that cannot be met by metal and ceramics - in applications where unique combinations of strength and impact, chemical and electrical resistance are required.

1.2 Three classes of polymer.

The various types of polymer can be divided into three broad classes - commodity polymers, engineering plastics and specialty polymers and they are discussed in turn below.

1.3 Commodity polymers.

These are the inexpensive polymers that are sold in very large quantities - annual sales run into the billions of pounds. Usually they have very simple chemical structures, most of them, formally, being simple derivatives of polyethylene. They are used in applications where the temperature will not exceed much above ambient, as their glass transition temperatures are usually below 100°C. Examples are polyethylene, polystyrene, polyvinyl chloride and polypropylene, which are prepared by the free radical
polymerisation of ethylene, styrene, vinyl chloride and propylene, respectively (see scheme 1.2).

1.4 Engineering plastics
These materials can be defined as "plastics which lend themselves to use for engineering design such as gears and structural members". They have high Tgs (> 100°C) and therefore can be used at higher temperatures than the commodity polymers. It is usual to restrict the term to polymers that can be processed by injection molding and extrusion methods. This excludes specialty plastics such as fluorocarbon polymers and thermosets such as the phenolic resins. The commodity plastics can also be processed by injection molding techniques but they lack the strength required for use in load bearing applications, especially at temperatures above 100°C. They are also more expensive than commodity polymers and this is because they have more complicated chemical structures. They are often prepared from two or more relatively complicated organic compounds which need to be prepared in very high purity. An example is the polymer known as Udel polysulfone, which is prepared from the reaction between 4,4'-dichlorodiphenyl sulfone and 4,4'-(isopropylidene) bisphenol (BPA) (see scheme 1.1). When compared to the commodity polymer polystyrene, which is prepared from just one simple monomer, styrene, it is easy to understand why the engineering plastics are more expensive.

1.5 Specialty polymers
These are usually very expensive materials which are produced in small quantities. They are used in very specific applications, which require a unique combination of physical properties.
\[ R \overset{C=CH}{H} \rightarrow (R\overset{C-CH_2}{H})_n \]

<table>
<thead>
<tr>
<th>( R )</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>CH3</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Cl</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>( \text{\textbullet} )</td>
<td>Polystyrene</td>
</tr>
</tbody>
</table>

Scheme 1.2
It is very unlikely that a new commodity polymer will be introduced onto the market place in the foreseeable future, mainly due to the massive costs associated with setting up a new manufacturing plant which would make it impossible to compete with the existing commodity polymers. For this reason, research into new polymeric materials focuses on the engineering and specialty plastics, and so does the research of this thesis.

1.6 Nucleophilic aromatic displacement polymerisation

For the past 25 years, the nucleophilic aromatic displacement reaction has been used to prepare high molecular weight polymers that have been used as engineering thermoplastics. Polysulfone and poly(ether ether ketone) (PEEK) are examples of materials that have been produced by this reaction and they have been commercialized by Union Carbide and ICI, respectively. In a nucleophilic aromatic displacement polymerisation, an aromatic dihalide is reacted with an aromatic bisphenol under basic conditions and the halides are displaced by bisphenate anions.

The aim of this research was to synthesize four novel, difluoro-substituted aromatic monomers in which we predicted that the fluoro substituents were displaceable. We then planned to polymerize each of them with five different bisphenols using a nucleophilic aromatic displacement reaction. Scheme 1.3 shows the general conditions and the structures of the monomers. The difluorinated monomers are 2,3-bis(4-fluorophenyl)-2-butenedinitrile (1); 3,6-difluoro-9,10-dicyanophenanthrene (2); 3,3-bis(4-fluorophenyl)-propenoic carbonitrile (3) and bis(4-fluorophenyl)-methylene propane dinitrile (4). The five bisphenols are 4,4'-isopropylidenediphenol (BPA; 5), 9,9-bis(hydroxyphenyl)fluorene (6), 4,4'-(hexafluoroisopropylidene)diphenol (7), 4,4'-biphenol (8) and hydroquinone (9).
Scheme 1.3
The synthesis of poly(aryl ether)s by this type of reaction was first reported by Johnson et al\(^3\) in 1967. Johnson described the polymerisation of an activated, aromatic dihalide by condensation with a dialkali metal salt of a dihydric phenol. The base used to generate the dianion was 50\% aqueous sodium hydroxide and the solvent was a mixture of dimethylsulfoxide (DMSO) and chlorobenzene. The purpose of the chlorobenzene was to azeotrope off the water from the reaction mixture and the DMSO, an aprotic dipolar solvent is essential to solvate the disodium diphenate ion.

Stoichiometry of reagents in the above reaction is very important in two respects. Firstly, the bisphenol and the dihalide must be in exactly 1:1 mole ratio if high molecular weight is to be obtained. If one of the functional groups is present in excess, then low molecular weight polymer chains will be end capped by that functional group and further increase in molecular weight becomes impossible. This is illustrated by the results shown in figure 1.3, in which molecular weight, which is indicated by relative viscosity is plotted against the ratio of dihalide to disodium diphenate.

The second stoichiometric consideration is that the sodium hydroxide must be present in exactly double the amount of the bisphenol. If the hydroxide is present in excess it will react with the dihalide, substituting the halide for -OH. This not only creates an unreactive end group but it also disrupts the stoichiometry of the reaction and results in a lowering of the molecular weight.

1.7 Mechanism

The dihalides in this reaction must be activated by electron withdrawing groups situated at the ortho and/or para positions of the benzene ring on which the halide is attached. This is important because the reaction proceeds via a Meisenheimer complex which is
Figure 1.3

Meisenheimer complex, stabilised by electron withdrawing groups at ortho and para positions.

Scheme 1.4
stabilized by electron withdrawing groups at the \(o\) and \(p\) positions. This is illustrated in figure 1.4.

In contrast, the reactivity of the bisphenol is decreased by the presence of electron withdrawing groups on the phenyl ring. This is because the reactivity of the bisphenol is proportional to the basicity of the anion or the intensity of the negative charge on the phenate ion, which will obviously be reduced by the presence of electron withdrawing groups. As expected, electron donating groups such as alkyl groups increase the reactivity of the bisphenol, hence BPA is very reactive in these reactions.

1.8 Reactivity of the halide

The reactivity of the dihalide depends not only on the electron withdrawing ability of the activating group, but also upon the halide itself. Nucleophilic displacements of aromatic halides which contain strong electron withdrawing groups, such as the nitro group, have been extensively studied\(^4\),\(^5\),\(^11\) and it is known that the order of reactivity is \(F \gg Cl > Br \sim I\). The dramatic difference in reactivities between the fluorides and the rest of the halides is due to the fact that the rate determining step is different for fluoride displacement. In all cases the reaction proceeds in two steps. The first step is the formation of the Meisenheimer complex, and the second step is the expulsion of the halide ion.

In the substitution reactions of chlorides, bromides and iodides, the rate determining step is the formation of the Meisenheimer complex but for fluoride displacement, the Meisenheimer complex is formed rapidly and the rate determining step is the expulsion of the fluoride ion. The formation of the Meisenheimer complex is faster for fluorides for two reasons: a) the other halides have much greater atomic radii and therefore create steric hindrance for the incoming nucleophile and b) the greater electronegativity of the
fluorine atom makes the attack site relatively more positive and therefore more reactive towards nucleophiles.

1.9 Potassium carbonate/DMAc improvement

In 1984 McGrath et al\(^6\) reported an improved method for preparing poly(aryl ether)s in which he used potassium carbonate as the base and dimethyl acetamide as the aprotic dipolar solvent. The original method reported by Johnson was inconvenient for two reasons. Firstly, the sodium hydroxide had to be added in exactly the right amount, which necessitated the addition of the base in an aqueous solution of which the concentration must be known precisely. This might involve a titration prior to the polymerisation. Secondly, the reagents had to be added in two steps. The disodium salt of the biphenate had to be formed first before the dihalide monomer was added, otherwise some of the halide might be displaced by hydroxide. The improved method by McGrath et al solves these problems because potassium carbonate does not cause displacement of aromatic halides, therefore the reagents can all be added at the start of the reaction and it is safe to use a slight excess of the base, negating the requirement of precisely known concentrations of aqueous solutions of NaOH. In McGrath's procedure anhydrous potassium carbonate is added as a finely ground powder. Most of the polymerisation reactions described in this thesis were performed using this improved method.

1.10 Properties of poly(aryl ether)s

The poly(aryl ether)s that are produced in the aromatic halide displacement reactions described above, are classed as engineering thermoplastics. A good example of such a polymer is poly(ether ether ketone) (PEEK) which has the structure shown in scheme 1.5. This polymer was first produced by Imperial Chemical Industries PLC in the late seventies and was commercialized in 1981 under the trade name Victrex. It is produced by condensing 4,4'-difluorobenzophenone with hydroquinone using potassium carbonate.
Scheme 1.5.
as base. In this case the product is highly crystalline and insoluble except at high temperatures in certain solvents. Therefore the reaction must be carried out at about 300°C in diphenylsulphone in order to avoid precipitation of low molecular weight polymer from the reaction mixture.

PEEK has many useful physical properties. It has high temperature resistance, the melt is stable at 400°C for over one hour in the absence of air, which makes melt processing relatively easy. It has good electrical and radiation resistance and excellent chemical resistance, PEEK is insoluble in all common solvents at room temperature. These physical properties are a direct consequence of its chemical structure which is highly aromatic which results in it being very thermo-oxidatively stable. Also the ether linkage is important because it provides flexibility in the polymer chain which is translated to a lowering of the Tg (143°C) which in turn makes processing easier.

1.11 Molecular structure and its affect on Tg

One of the main thrusts in polymer research is to design polymers that will maintain their physical properties at high temperatures. In automotive under the hood applications, the operating temperature might routinely exceed 200°C. To operate under these conditions a polymer must have a high Tg. One method of increasing the Tg of a polymer is to include rigid or bulky groups in the structure. The effects of including bulky groups in a polymer can be seen when comparing the Tgs of polyethylene and polystyrene. Polyethylene, which contains no bulky or rigid groups, has a Tg of -20°C. However, if one of the four hydrogen atoms in the ethylene repeat unit is replaced by a benzene ring, then you have polystyrene which has a Tg of 100°C.

When polymers pass through the Tg from the glassy state to the rubbery state, the molecules attain greater, long range molecular motion. For a polymer to behave like a
glass, the molecular vibrations and rotations must be restricted to very short segments of the molecule. If the polymer is to behave like a rubber then greater freedom of molecular rotation must be allowed. It is estimated that at the Tg as many as 20 to 50 chain atoms are involved in the segmental rotation in which the polymer chain can behave like a skipping rope. This type of rotation obviously requires an input of energy. Even in the simplest most unhindered of molecules, ethane, there is an energy barrier of 3 kcal/mol for the C-C bond rotation. If the hydrogen atoms of ethane are replaced with more bulky groups then the barrier to rotation will increase (e.g., in n-butane, the C2-C3 rotational energy barrier is 5 kcal/mol). It is obvious then that the introduction of bulky groups into a polymer chain should be expected to increase its Tg.

Another factor which affects the rotational movement of a polymer chain is the stiffness of the repeating unit or, conversely, the number of flexible linkages in the repeat unit. The more rigid the polymer chain, the more energy will be required for segmental rotation and therefore the higher the Tg.

In this research polymers were prepared with the very rigid phenanthrene repeat unit, in which three aromatic rings are fused together, and the affect on Tg was observed. Also, the very large, flat phthalocyanine ring system was attached directly to the polymer backbone. It is assumed that this should greatly affect the polymer chains rotational energy barrier and hence the Tg.

1.12 Thermosetting resins
Besides high molecular weight polymers with high Tgs, another class of materials which maintain physical properties at high temperatures are the thermosetting resins (or thermostets). Thermosets are oligomers, or even monomers, which contain reactive groups which, when heated to high temperatures, will react with each other to give a cross-linked
Linear polymer

Cross-linked polymer

Figure 1.4

Scheme 1.6
polymer matrix, as shown in figure 1.4. An object made from such a material is effectively one huge molecule and they will often maintain their physical properties at very high temperatures - sometimes up to their decomposition temperatures which may be over 500°C.

Thermosets are difficult to form by injection molding techniques since they cure during the curing process. Compression molding techniques are commonly used for processing thermosets. A useful property of thermosets is their high resistance to solvents, due to the fact that their highly cross linked structure prevents solvent molecules from entering the polymer matrix. The short comings of thermosets include the fact that they are often very brittle and they may require long cure cycles, which can make them unsuitable for rapid production techniques. Also, once they have been cured, they can not be melted and reused as can thermoplastics. It is conceivable, that high molecular weight polymers containing cross linkable functionalities might produce materials possessing the favorable properties of both thermosets and thermoplastics.

In principle, any chemical reaction that forms a chemical bond can be utilized to form cross links in polymers. However, many bond forming reactions produce small volatile molecules such as water, as a by-product. These small molecules can form voids in the polymer matrix and so weaken the structure of any products made from such materials. It is known that the triple bond can undergo cycloaddition reactions at high temperatures to form aromatic rings as in scheme 1.6. These reactions produce no volatile by-products and so they have excellent potential as cross linking reactions.

The target monomers and polymers in this research all contain nitrile groups and the cross-linkability of the polymers was examined. The incorporation of nitrile groups into monomers and polymers is desirable, not only because they might cross-link but also
because they are very electronegative and therefore activate the difluoride towards nucleophilic attack. Also, the nitrile group is easily converted into other functional groups such as carboxylic acids, esters and amides to give other new polymers.

1.13 Conclusion.

The aims of this research have been stated in the previous pages and a brief summary of the results that were achieved is given here.

-- The four target monomers listed on page 6 were synthesized.
-- Polymers were prepared from three of the four monomers but an attempt to polymerize bis(4-fluorophenyl)-methylene propanedinitrile failed.
-- A preliminary investigation into the cross linkability of all of the polymers was undertaken.
-- The copper phthalocyanine moiety was incorporated into three polymers and their physical properties were investigated.
1.14 Chapter one, references.

Chapter Two.

Monomer Synthesis.

2.1 Preparation of 2,3-bis-(4-fluorophenyl)-2-butenedinitrile (1)

This monomer was prepared via the oxidative coupling of two moles of 4-fluorobenzyl cyanide using a method suggested by Makosza et al$^1$ in which the non-fluorinated analogue was prepared. This is an elegant one step synthesis employing sodium hydroxide as a base, carbon tetrachloride as the solvent and co-reagent and trimethylbenzylammonium chloride as a phase transfer catalyst. See scheme (2.1).

It is thought that the reaction proceeds via chlorination of the anion of fluorobenzyl cyanide to give the chlorobenzyl cyanide (2.1). This species undergoes a second deprotonation and the anion produced attacks a second mole of (2.1) and then dehydrochlorination gives the desired product (see scheme (2.2)). The yield in this reaction is approximately 50%.

It is not known whether or not a mixture of isomers is formed in this reaction but is assumed that the cis isomer is present to some extent. Evidence for this assumption is gained from an observation of the melting point. Compound 1 melts at 194-5°C, but at approximately 130°C a slight movement in the crystals was noticed. This is possibly due to a small amount of the cis isomer melting.

A by-product of this reaction is an unidentified white solid. A mass spectrum shows a fragment weighing 506. $^1$H NMR shows a very complicated spectrum composed exclusively of aromatic protons.
Scheme 2.1

Scheme 2.2

20
2.2 Preparation of 3,6-difluoro-9,10-dicyanophenanthrene

3,6-Difluoro-9,10-dicyanophenanthrene (2) was prepared by the oxidative photodehydrocyclisation of (1) as in scheme (2.3). This reaction of stilbenes is well known and has been reviewed by Blackburn and Timmons. The reaction proceeds via two intermediates, the cis stilbene(2.2) and the dihydrophenanthrene (2.3).

In the final step, in the presence of air or oxygen, the dehydrogenation is accompanied by the formation of hydrogen peroxide. If oxygen is carefully excluded the reaction proceeds no further than 2.3, therefore it is necessary to bubble oxygen into the reaction mixture in order to drive it to completion. Even under these conditions, the reaction can take up to 100 hours. In an attempt to speed the reaction up, an equimolar amount of tetrachloro-1,4-quinone (chloranil) was added according to the procedure of Bendig et al. Chloranil is a much more efficient hydrogen scavenger than oxygen in these circumstances and it had the affect of greatly accelerating the rate of the reaction, which now went to completion in just 10 hours. However, separation of the product from the hydrogenated chloranil was difficult and so the process with oxygen was used routinely.

2.3 Preparation of 3,3-bis-(4-fluorophenyl)-propenionic carbonitrile

3,3-Bis-(4-fluorophenyl)-propionic carbonitrile (3) was prepared using an adaptation of the method of DiBiase et al in which the non-fluorinated analogue was prepared. The reaction involves a condensation of 4,4'-difluorobenzophenone with acetonitrile, using potassium hydroxide as the base and excess acetonitrile as the solvent (scheme 2.4). The product was obtained, after purification, as large colourless cubic crystals melting at 79 - 81°C.

2.4 Preparation of bis-(4-fluorophenyl)-methylene propane dinitrile.
**Scheme 2.3**

\[
\begin{align*}
\text{(1)} & \quad \xrightarrow{\text{U.V. light}} \quad \text{(2)} \\
\xrightarrow{\text{U.V. light}} & \quad \text{KOH} \\
\end{align*}
\]

**Scheme 2.4**

\[
\begin{align*}
\text{KOH} & \quad \xrightarrow{\text{CH}_3\text{CN}} \quad \text{Reflex, 4hrs} \\
\end{align*}
\]
Bis-(4-fluorophenyl)-methylenepropane dinitrile (4) was prepared by a modification of the method used for preparing the non-fluorinated analogue, diphenylmethylenepropane dinitrile\textsuperscript{6}, outlined in scheme 2.5. The product was obtained in a 50\% yield as large white needles.

2.5 Preparation of 9,9-bis(hydroxyphenyl)fluorene

All of the bisphenols used in this research were obtained from commercial sources except for 9,9-bis(hydroxyphenyl)fluorene (6) which was prepared using a modification of the method described by Knebel et al\textsuperscript{7}. In this reaction, fluorenone is condensed with phenol in the presence of Amberlyst 15 and \(\beta\)-mercaptopropionic acid, as in scheme 2.4. Amberlyst 15 is an acidic ion exchange resin which acts as a catalyst and it can be recovered at the end of the reaction. The \(\beta\)-mercaptopropionic acid is a co-catalyst which is added in a minute quantity (less than 0.1 mol\% of the fluorenone). The solvent for this reaction is an additional 1\(\frac{1}{2}\) equivalents of phenol. The reaction proceeds to a 60\% yield after 2 hours at 100°C.
Scheme 2.5

Scheme 2.6
2.6 Chapter two references

Chapter three

Polymerization of monomers

3.1 Use of Huckel Molecular Orbital (HMO) calculations to predict reactivity of monomers

The synthesis of difluorinated monomers obviously involves the use of fluorinated starting materials which are relatively expensive. Therefore it is desirable to be able to predict whether or not a monomer would polymerize before it is actually synthesized. It was found that a HMO computer program\(^1\) is a useful tool for predicting the reactivity of potential monomers. This program\(^1\) is able to calculate the partial charge densities of all of the atoms in a molecule. The partial charge density of the carbon atom to which the fluorine is attached is particularly indicative of the reactivity of a monomer towards nucleophilic displacement reactions, the higher the value the more reactive the monomer. By comparing the partial charge densities of potential monomers with those of monomers that are known to be reactive, a good prediction of the reactivity of the monomer could be made. Chart 3.1 lists the potential monomers that were target molecules in this research, and compares their relevant partial charge densities with those of monomers that are known to polymerize.

Of the four known monomers, 5 and 6 are commercial monomers and are known to react very rapidly. The relevant partial charge densities of these monomers are 0.05 and 0.042 respectively and these values are close to the upper limits for neutral monomers of this type. The other two monomers, 7 and 8, have recently been synthesized in our laboratory (see ref.'s 2 and 3 respectively), and it was found that 7 took 18 hours at 180°C to polymerize to high molecular weight, compared to less than 1 hour for monomers 5 and 6. Clearly 7 is less reactive. Under the same conditions, difluorodiphenylacetylene (8)
Target monomers

1

2

3

4

Known monomers

5

6

7

8

Chart 3.1
takes approximately 8 hours to reach high molecular weight. This would appear to be inconsistent, as the HMO calculations suggest that 7 should proceed faster than 8. This apparent contradiction can be explained by the fact that the phenyl rings in 7 are sterically hindered and are pushed out of the plane of the molecule. Therefore they are not conjugated to the electron withdrawing groups and so it is not fully activated towards nucleophilic substitution.

In conclusion the HMO calculations have proved useful in predicting the reactivity of potential monomers. The four monomers synthesized in this research all have higher partial charge densities than difluorodiphenylacetylene and indeed they have all shown good reactivity in nucleophilic displacement polymerization reactions.

3.2 Polymerisation of 2,3-bis-(4-fluorophenyl)-2-butene dinitrile with various bisphenols.

2,3-Bis-(4-fluorophenyl)-2-butene dinitrile (1) was polymerized with five different bisphenols to yield five novel polymers (1a-e) as shown in scheme 3.1. Polymers 1a to d were prepared using the method described by McGrath et al, using dimethylacetamide (DMAc) and toluene as the solvent system and excess potassium carbonate as the base.

In general high molecular weight polymers were obtained quite quickly, with typical reaction times being 3 hours at 135°C whilst the dianion was forming and the reaction mixture was dehydrating, and then 1 hour at 160°C. The reaction mixture is dehydrated by azeotropic distillation of toluene into a Dean-Stark trap and the temperature is raised from 135 to 160°C by bleeding the toluene from the trap.

Polymer 3e could not be prepared by using the above method because low molecular weight material precipitated out of the reaction mixture within ten minutes of raising the temperature to 160°C. This was evident by the fact that the reaction mixture became light.
Scheme 3.1

Polymer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>X</th>
</tr>
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<tbody>
<tr>
<td>la</td>
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</tr>
<tr>
<td>lb</td>
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</tr>
<tr>
<td>ld</td>
<td><img src="image" alt="ld" /></td>
</tr>
<tr>
<td>le</td>
<td><img src="image" alt="le" /></td>
</tr>
</tbody>
</table>
coloured and cloudy, whereas under normal circumstances, the mixture is a dark, reddish brown and clear throughout the high temperature stage of the reaction.

To overcome the problem of precipitation, polymer 1e was prepared using the reaction conditions described by Andrews\(^5\), in which the solvent DMAc is replaced by tetramethylene sulfone and toluene is replaced by chlorobenzene. The idea behind this modification is that the reaction proceeds at a higher temperature (190°C) and so the material is more likely to remain in solution. The procedure also differs from that of McGrath in that the temperature of the reaction is raised directly to 190°C instead of being maintained at a lower temperature whilst water is azeotroped out of the reaction mixture.

With these two modifications the reaction is completed much faster, polymer 1e being prepared in just one hour in total. Andrews' method was not used routinely for polymerizations because at these higher temperatures there is greater risk of competing side reactions. Evidence of side reactions could be seen by the fact that polymer 1e was much darker in colour than the others in the series.

In all of the polymerizations described above, care must be taken not to allow the reaction to proceed too far, or the polymer becomes completely insoluble, in all solvents, due to cross-linking reactions in the high molecular weight polymer. When this happens, the polymer can not be purified or used in any way and it must be discarded. The "gelling" of the reaction mixture in this manner can happen surprisingly quickly. This is especially true for polymer 1d, where the difference in reaction time between acceptable molecular weight and unusable gel is approximately 10 minutes. To overcome this problem, a 1% excess of the difluoride was used to prepare polymer 1d. This has the effect of limiting
the molecular weight of the polymer by end capping all of the polymer chains with a fluoride and so stopping the reaction.

3.3 Physical properties of polymers 1a to e.

The inherent viscosities of all of the polymers were measured, along with the glass transition temperatures, thermal decomposition temperatures (i.e. the temperatures at which the polymers lose 5% of their mass as they are being heated at a rate of 10°C/min., under a flow of nitrogen), the Young’s modulus and tan δ. The results are tabulated in table 3.1.

3.4 Inherent viscosities

Inherent viscosity gives an indication of the molecular weight of the polymer. In general, providing that polymers of similar structure are being compared, the higher the viscosity, the higher the molecular weight. All of the important physical properties of a polymer, such as Tg and thermal stability depend upon the polymer’s molecular weight. In general, as the molecular weight increases, the physical properties improve until they reach a plateau value at which point, further increases in molecular weight will have only a limited effect on the properties (see figure 3.1). It is generally accepted that polymers, with aromatic structures of the type described here, should have an inherent viscosity of approximately 0.3 before they begin to reach a plateau value. The inherent viscosities of polymers 1a-e range from 0.27 to 0.60, with four out of the five having values above 0.3.

In addition to the inherent viscosity, another indication that a polymer is of high molecular weight is given by its ability to form a film. All of the polymers in this series form flexible films when cast from a suitable solvent which means that acceptable molecular weight has been attained.
Table 3.1 Properties of poly(aryl ether)s 1a - e
3.5 Glass Transition Temperatures (Tgs)

The Tgs of these polymers range from 159 to 259°C and this illustrates the effect of having bulky and rigid groups in the polymer chain. As expected, the polymers with the lowest Tgs are those prepared from BPA and 4,4’-(hexafluoroisopropylidene)diphenol (7). These bisphenols contain no bulky groups and they possess the flexible methylene linkage, therefore they keep the Tgs of these polymers low. The polymer with the highest Tg is that prepared from 9,9-bis(hydroxyphenyl)fluorene (6) which is also to be expected as it is by far the bulkiest monomer in the series. Intermediate Tgs were obtained from polymers prepared from hydroquinone and biphenol, which are rigid groups which are not bulky.

3.6 Thermal Stability.

Table 3.1 shows the temperatures at which these polymers lose 5% of their mass when heated under an atmosphere of nitrogen, measured by thermogravimetric analysis. The temperatures range from 414 to 480°C and these are relatively low when compared to other poly(aryl ether)s. This low thermal stability is believed to be caused by the instability of the dicyanostilbene linkage, which has been shown to undergo a chemical reaction at about 300°C. See the later section on cross linking.

The least thermally stable polymer is 1a prepared from BPA. This was expected because this is the only polymer containing aliphatic groups which would be expected to be the least stable entity in these polymers. This is because the most important factor in determining thermal stability is bond strength. In aliphatic systems, the carbon-carbon bond dissociation energy is ~84 kcal/mol and that of the carbon-carbon double bond is ~145 kcal/mol. In aromatic rings, the carbon-carbon bond dissociation energy is between ~180 and 210 kcal/mol, the increase being due to resonance stabilization. Consequently, the most thermally stable polymers are those that are very aromatic such as the aromatic...
Polyimides, polyquinoxalines and polybenzimidazoles are examples of heat resistant, aromatic polymers.
polyimides and polyquinolines, examples of which are given in figure 3.2. It is not surprising then, that the most thermally stable polymer in the series is that prepared from 9,9-bis(hydroxyphenyl)fluorene, 1b, which contains the largest proportion of aromatic bonds in the series.

For a comparison, the thermal stability of polymer 1d was tested under an atmosphere of air. The 5% weight loss occurred at 457°C in air as compared to 454°C in nitrogen. The difference is negligible and so it can be concluded that the decomposition mechanism is similar in both cases.

3.7 Mechanical Properties.
The Young's moduli (E') of the polymers were obtained from thermal mechanical analysis/stress strain measurements. The measurements were performed on thin strips of film cast from chloroform or sym TCE solution. The values range from ~1.5 to 2.4 GPa at 25°C and these values are typical of amorphous poly(aryl ether)s in the glassy state.

Young's moduli were also measured at 100°C to see how well the polymers maintained their physical properties at higher temperatures. In all cases, the value is slightly lower than at 25°C and this is again typical of amorphous polymers in the glassy state. Figure 3.3 illustrates how E' varies with temperature as 1a is heated at 3°C/min. from 25 to 300°C. Figure 3.3 also illustrates tan δ which is another method of measuring the glass transition temperature. Tan δ is the derivative of E' and it peaks at the maximum rate of change of E', as the temperature increases. Therefore the tan δ maximum corresponds to the temperature at which the polymer loses its physical properties, which is the glass transition temperature.
Figure 3.3 Typical TMA/SS thermogram showing Young’s modulus and tan δ of a poly(aryl ether).
In all cases, $\tan \delta$ correlates well with the Tg as measured by differential scanning calorimetry. In most cases, $\tan \delta$ is slightly lower than Tg and this is probably principally caused by the different heating rates used by the two instruments (10°C/min. for DSC and 3°C/min for TMA/SS).

3.8 Crystalline properties of polymer 1e

All of the polymers in this series are completely amorphous except for 1e, the polymer formed from hydroquinone. Although this polymer is amorphous when precipitated from methanol, it crystallized when an attempt was made to cast a film from chloroform. Instead of forming a flexible film like the rest of the polymers, small, brittle, opaque flakes developed. Interestingly, even though the polymer was completely soluble in its amorphous form, after crystallizing it was completely insoluble in chloroform.

Further evidence of crystallinity comes from DSC analysis - see figure 3.4. Thermogram A shows the Tg of an amorphous sample of 1e to be 177°C. Thermogram B is of a crystalline sample of 1e. It is significant that the Tg at 177°C is virtually undetectable and instead there is a large melting point endotherm at 293°C. The relative sizes of the endotherms for Tg and Tm gives an approximate indication of the percentage of the polymer that is in the crystalline form, and so it can be seen that the majority of the polymer is crystalline when cast from chloroform. Thermogram C is of the second heating of the "crystalline" polymer and it shows a Tg at 206°C but no indication of a Tm. This means that the polymer does not crystallize when cooled rapidly from the melt, and this is normal behavior for crystalline polymers, which often require hours at elevated temperatures to crystallize.
Thermogram A showing Tg of 1e after the usual precipitation from methanol
Thermogram B showing Tm of 1e after crystalizing from chloroform
Thermogram C showing an absence of a Tm and an elevated Tg after a second heating of the crystalized polymer

Figure 3.4 Thermograms showing the Tm of polymer 1e, and also the Tg before and after cross-linking.
The other significant observation from thermogram C is that the Tg of le has increased by 27°C. This is a result of a cross linking reaction that occurs at elevated temperatures and it is discussed in the next section.

3.9 Cross-Linking

One of the main reasons for preparing polymers la-e was to see if they would cross link, in order to render the materials insoluble and increase their use temperature. There are several examples in the literature, of cross linking systems in which the nitrile group is used\(^8\text{-}^{10}\), and the use of acetylenes (the other main triple bond containing species) is well known\(^11\). However, the dicyanostilbene moiety has not been reported as being useful for this purpose.

Samples of polymers la - e were maintained at 300° C for 30 minutes, then cooled and their Tgs were measured. In all cases their Tgs increased (by between 2 and 24°C, see table 3.2) and this is a typical result of a cross-linking reaction. Cross-linking was confirmed qualitatively by the fact that polymers which had been subjected to such treatment were no longer soluble in any common solvents, instead they merely swelled like a gel. On prolonged exposure to elevated temperatures the Tg continued to increase, but the intensity of the endotherm decreased until at a limiting value the Tg endotherm was no longer visible. At this point the system is very highly cross linked. This is shown in figure 3.5.

In another experiment designed to show the affects of the cross linking reaction, thin strips of films of the polymers were sandwiched between two glass plates and baked in a vacuum oven at 300°C for 1 hour and other samples for 4 hours. Then they were cooled and their Young's moduli and tan δ's were measured. The results are displayed in table 3.3 and it can be seen that in all cases, the Young's modulus increases for the heat treated
### Table 3.2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ °C</th>
<th>$T_{g2}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>159</td>
<td>183</td>
</tr>
<tr>
<td>1b</td>
<td>259</td>
<td>261</td>
</tr>
<tr>
<td>1c</td>
<td>164</td>
<td>187</td>
</tr>
<tr>
<td>1d</td>
<td>192</td>
<td>221</td>
</tr>
<tr>
<td>1e</td>
<td>179</td>
<td>191</td>
</tr>
</tbody>
</table>

$T_{g2}$ is the $T_g$ after the polymer has been cured at 300°C for 30 minutes.

**Figure 3.5** $T_g$ of 1a increases as cure time (at 300°C) increases from zero to 60 minutes.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>E' at 25°C</th>
<th>E' at 100°C</th>
<th>Tan δ °C</th>
<th>E' at 25°C</th>
<th>E' at 100°C</th>
<th>Tan δ °C</th>
<th>E' at 25°C</th>
<th>E' at 100°C</th>
<th>Tan δ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>1.89</td>
<td>1.68</td>
<td>157</td>
<td>2.09</td>
<td>1.80</td>
<td>186</td>
<td>2.08</td>
<td>1.48</td>
<td>202</td>
</tr>
<tr>
<td>lb</td>
<td>2.44</td>
<td>2.06</td>
<td>247</td>
<td>2.51</td>
<td>2.15</td>
<td>257</td>
<td>2.17</td>
<td>1.69</td>
<td>268</td>
</tr>
<tr>
<td>lc</td>
<td>1.54</td>
<td>1.37</td>
<td>165</td>
<td>1.66</td>
<td>1.40</td>
<td>201</td>
<td>1.12</td>
<td>0.53</td>
<td>217</td>
</tr>
<tr>
<td>ld</td>
<td>2.10</td>
<td>1.55</td>
<td>188</td>
<td>1.99</td>
<td>1.22</td>
<td>204</td>
<td>1.94</td>
<td>1.11</td>
<td>226</td>
</tr>
<tr>
<td>le</td>
<td>1.95</td>
<td>1.53</td>
<td>173</td>
<td>2.42</td>
<td>1.95</td>
<td>215</td>
<td>1.46</td>
<td>0.59</td>
<td>226</td>
</tr>
</tbody>
</table>

Table 3.3 Tan δ's and Young's modulii of la - e before and after baking for 1 and 4 hours at 300°C.
polymers and also their tan δ's are higher. It was also noticed that after heat treatment the films were fingernail creasable, which means that they could be folded through 180° and then back on themselves through 360° without breaking, whereas before the heat treatment they were brittle and most could not withstand one fold. This is a good, qualitative indication of a significant increase in molecular weight along with an increase in toughness. The experiment was extended further and the samples were baked at 300°C for four hours. Again, in all cases the tan δ of the polymers rose significantly but surprisingly the Young’s moduli all fell (see table 3.3) This reduction in Young’s modulus may be an indication of a decomposition of the polymer, which is also suggested by a marked darkening of the material. It is interesting to note that even after baking for four hours, the films were still creasable (i.e. they did not break if folded back on themselves through 180°).

3.10 Solid state $^{13}$C NMR

It is very difficult to determine the type of reaction that occurs when these polymers are cured because they are insoluble in all solvents and so the usual spectroscopic analysis is impossible. However, solid state $^{13}$C cross polarization magic angle spinning NMR has been employed and the results are displayed in figure 3.7. The two spectra are of polymer $1a$, before heat treatment and after being heated for 120 minutes at 300°C. Notice that the spectra are virtually identical, indicating that a major change in the composition of the material has not taken place. The only observable difference is that, after heating, the peak at 121 ppm (the nitrile carbon) disappears, which shows that the nitrile group is involved in the cross linking reaction. Unfortunately, no clue is given as to the fate of the nitrile group and the nature of the bonds formed during the cross linking reaction. Extensive studies on model compounds would be required to clarify this.

3.11 IR studies on polymer film
Figure 3.7 Solid state 13C NMR of 1e before (top) and after (bottom) curing at 300°C for 2 hours.
Figure 3.8 IR spectra of le before (top) and after (bottom) curing at 300°C for 2 hours.
The other spectroscopic technique available to study this cross linking reaction is infrared spectroscopy performed on polymer films. Figure 3.8 shows the IR spectra of a film of 1a before and after being heated at 300°C for four hours. The polymer films were approximately 70μm thick and they gave very intense absorption peaks. This thickness was necessary in order to clearly observe the weak nitrile peak at 2219 cm\(^{-1}\). The two spectra are very similar to each other, suggesting that no major structural changes have taken place. However, the nitrile peak of the cured sample is less intense than that of the uncured sample giving further evidence (to that provided by solid state \(^{13}\)C NMR) that the nitrile group is involved in the cross linking reaction.

The other major changes in the IR spectrum are the appearance of a weakly absorbing peak at 1737 cm\(^{-1}\) and the disappearance of a strongly absorbing peak at 780 cm\(^{-1}\) but it is difficult to formulate a satisfactory explanation for these changes.

3.12 Copolymer of polysulfone and (1a)

Probably the greatest potential use for cross linkable monomers such as 1, is not as a homopolymer but when used in a small percentage as a comonomer. This is because as a fully cross linked homopolymer the material might tend to be very brittle and unusable. However, if present in a copolymer at a concentration of c.a. 10%, it might have the effect of raising the glass transition temperature and imparting greater solvent resistance to a polymer such as polysulfone. To explore this possibility, a copolymer of 20% of 1 and 80% difluorodiphenyl sulfone was prepared with BPA. The polymer (1.1a) had a Tg of 178°C and a TGA(N\(_2\)) of 421°C and these values fall between those of 1a and polysulfone.

To test its cross linking behavior, the Tg of 1.1a was measured after having been cured at 300°C for 0, 30, 60 and 120mins. The Tgs of these samples were 177, 181, 197 and
198°C respectively. Unlike the homopolymer of dicyanostilbene, the copolymer retained a definite Tg even after being cured for 2 hours. This means that the material is not completely cross linked and so it should retain some flexibility and not be too brittle.

3.13 Polymerisation of 3,6-difluoro-9,10-dicyanophenanthrene (2)

Owing to the difficulties of preparing and purifying large quantities of 3,6-difluoro-9,10-dicyanophenanthrene (2) only one homopolymer (2a) was prepared. It was polymerized with bisphenol A under the usual reaction conditions, to yield a high molecular weight polymer after 3 hrs at 135°C and 1 hr at 160°C. This is an interesting polymer because to our knowledge this is the first reported case in which a monomer containing the phenanthrene unit has been polymerized to give a poly(aryl ether). Poly(aryl ether)s in which phenanthrene forms part of the repeat unit have been reported by Wang and Zhang. Wang and Zhang synthesized such polymers by using an intramolecular cyclisation of 2,2'-dibenzoylbiphenyl units after an initial polymer had been formed (see scheme 3.3). A series of polymers were obtained with high Tgs and excellent solvent resistance. However they were unable to produce the same results by polymerizing 9,10-Bis(4-fluorophenyl)phenanthrene because this monomer was not sufficiently activated towards nucleophilic displacement reactions. This fact was proved in a model reaction in which the phenanthrene did not react with potassium 3,5-di-tert-butylphenoxide in NMP at 180°C over 24 hours.

3.14 Glass transition temperature.

The Tg of 2a is 250°C and this is quite high for a poly(aryl ether) containing such a high percentage of BPA, which is a flexible unit which usually keeps the Tg of a polymer low. For example, the Tg of 2a is 90°C higher than that of the stilbene analogue 1a. This high Tg can be explained by the very rigid nature of the phenanthrene repeat unit which causes
Inherent viscosity = 0.33
Tg = 250°C
TGA(N₂) = 492°C
TGA(air) = 495°C

**Figure 3.9**

**Scheme 3.2**

**Scheme 3.3**
the rotation of polymer chain segments (necessary for the onset of Tg) to require a lot of energy.

3.15 Thermal stability
The 5% weight loss in nitrogen (and air) occurs at 492°C (and 495°C), therefore it is significantly more stable than the stilbene analogue (414°C). In fact the thermal stability is very similar to that of polysulfone prepared under the same conditions (492°C) and so we might conclude that in both cases the weak link is the BPA unit.

3.16 Cross linkability.
When heated up to 400°C this polymer shows no sign of cross linking; there is no increase in the Tg and it was still soluble in sym TCE. Keller has reported a cross linking system involving phthalonitrile containing systems which can be considered analogous to the 9,10-dicyanophenanthrene system in 2a. However in Keller's case an amine additive was needed to catalyze the cross linking reaction, the products of which were thought to be triazine and phthalocyanine units. (see scheme 3.2). Future work might consist of catalyzing a cross linking reaction of 2a using, for example, 4,4'-methyleneedianiline as the amine catalyst.

3.17 Polymerisation of 3,3-bis-(4-fluorophenyl)-propenoic carbonitrile.
3,3-Bis-(4-fluorophenyl)-propenoic carbonitrile (3) was polymerized, under the standard reaction conditions, with the five bisphenols listed in scheme 3.1 to give the five polymers 3a - e. The physical properties of these polymer are given in table 3.4 All of the polymerizations proceeded smoothly in DMAc, with high molecular weight being obtained after 3hrs at 135°C followed by 3hrs at 160°C.

3.18 Physical properties of polymers 3a - e
**Table 3.4 Properties of poly(aryl ether)s 3a - e**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Inherent viscosity</th>
<th>Tg °C</th>
<th>TGA(N$_2$) °C</th>
<th>TGA(air) °C</th>
<th>E' at 25°C GPa</th>
<th>E' at 100°C GPa</th>
<th>Tan δ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.91</td>
<td>165</td>
<td>435</td>
<td>-</td>
<td>2.47</td>
<td>1.87</td>
<td>162</td>
</tr>
<tr>
<td>3b</td>
<td>0.31</td>
<td>243</td>
<td>491</td>
<td>-</td>
<td>2.38</td>
<td>1.84</td>
<td>239</td>
</tr>
<tr>
<td>3c</td>
<td>1.09</td>
<td>175</td>
<td>452</td>
<td>-</td>
<td>2.07</td>
<td>0.56</td>
<td>174</td>
</tr>
<tr>
<td>3d</td>
<td>0.50</td>
<td>185</td>
<td>480</td>
<td>503</td>
<td>2.10</td>
<td>1.11</td>
<td>182</td>
</tr>
<tr>
<td>3e</td>
<td>1.54</td>
<td>161</td>
<td>505</td>
<td>-</td>
<td>2.14</td>
<td>1.97</td>
<td>162</td>
</tr>
</tbody>
</table>

3a, X=  

3b, X=  

3c, X=  

3d, X=  

3e, X=  

**Polymer**  

**Inherent viscosity**  

**Tg °C**  

**TGA(N$_2$) °C**  

**TGA(air) °C**  

**E' at 25°C GPa**  

**E' at 100°C GPa**  

**Tan δ °C**

Dipolar aprotic solvent

K$_2$CO$_3$
Polymers 3a-e are white or light yellow and have inherent viscosities in the range of 0.31 to 1.54. Three of the polymers have viscosities of over 0.9 but in those cases the yields were below 30%, much of the reaction mixture having gone to ultra high molecular weight and becoming insoluble.

The Tgs range from 161 to 243°C which is very similar to those of 1a-e. This is not surprising as monomers 1 and 3 have very similar molecular weights and structures and should impart a similar degree of flexibility into a polymer chain. Interestingly, none of the polymers are crystalline. This is surprising as one might have expected 3e to show some crystallinity as did 1e and also PEEK which has a very similar structure (see scheme 1.5). The probable reason for the lack of crystallinity in 3a-e is the unsymmetrical nature of the monomer 3. This lack of symmetry causes the monomers to bond together in two different ways, head to head or head to tail, in a random manner. This causes irregularity in the polymer chain which in turn disrupts the formation of crystallites.

No evidence of cross-linking was observed when these polymers were heated in a DSC up to 400°C. After such treatment their Tgs remained unchanged and the polymers remained soluble in chloroform. As with 2a, future work may consist of catalysing cross-linking reactions using an amine catalyst such as 4,4'-methyleneedianiline.

3.19 Polymerisation of bis-(4-fluorophenyl)-methylene propanedinitrile

Attempts to polymerize bis-(4-fluorophenyl)-methylene propanedinitrile (4) were unsuccessful. As the reaction progressed, an unusual deep purple colour very quickly (within 15 min.) developed and this was accompanied by a moderate build up in molecular weight. However, as the reaction progressed still further, the molecular weight
decreased and within 1 hour after dehydration the molecular weight had dropped to a very low value since no polymer precipitated out on addition to methanol.

An attempt was made to polymerize 4 using the sulfolane/chlorobenzene conditions, in the hope that high molecular weight polymer could be obtained quickly and the reaction halted before the polymer decomposed. After 1 hr at 190° C, molecular weight had started to build up but after a further 30 min it had reduced dramatically. At no point was high molecular weight polymer formed.

It seems obvious that 4 is reactive enough to polymerize but a competing reaction is destroying the polymer before it has a chance to go to high molecular weight. In an effort to discover the nature of the competing reaction, a model reaction in which 4 was refluxed in DMAc and toluene, with and without potassium carbonate was followed using HPLC. One gram of 4 was refluxed in DMAc (4ml) and toluene (2ml) at 135° C. After one hour, HPLC showed only 4 and toluene and no other peaks, proving that 4 is stable at reflux. Then potassium carbonate was added and the reaction mixture went purple immediately. After 30 min. HPLC showed that two new peaks had developed, representing approximately 1 and 2% of the reaction mixture. The larger peak appeared, from its retention time, to be 4,4'-difluorobenzophenone, which might have been produced from a reaction between 4 and potassium carbonate. The presence of 4,4'-difluorobenzophenone itself would not cause a problem, as it is a very reactive monomer. However, the other product of the benzophenone producing reaction is probably the potassium salt of malononitrile which might be nucleophilic enough to compete with the bisphenoxide nucleophile. After 8 hrs at reflux the mixture had fused to a gel and the reaction was abandoned.
3.20 Chapter three, references

1. HMO program from Trinity Software, P.O. Box 960, Campton N.H., 03223, U.S.A.
Chapter Four

Polymers containing copper phthalocyanine

4.1 Introduction

Polymers in which the copper phthalocyanine (CuPc) moiety is attached to the polymer backbone have been prepared and some of their physical properties have been examined. Copper phthalocyanine was first described in 1934 by Linstead et al. and its structure is shown in Scheme 4.1. Interest in phthalocyanine compounds developed after the chance discovery of iron phthalocyanine in 1928, during the industrial production of phthalimide at Scottish Dyes Ltd. This process involved passing ammonia through molten phthalic anhydride contained in an iron vessel. After such a process, a small amount of a deep blue, very stable, crystalline substance (iron phthalocyanine) was observed.

Linstead demonstrated that many different metals would combine with phthalonitrile to form metal phthalocyanines and since then, phthalocyanines containing virtually every metal in the periodic table have been prepared. Over 5000 phthalocyanine compounds are now known and it is estimated that approximately three research articles and patents relating to them are published each working day. By far the most common and commercially successful is the copper derivative, which amongst other things, is the 2nd most popular pigment or toner, in terms of the amount produced, with 16 million lb being produced in the US in 1987. Besides colourant applications patents have been issued for a wide variety of uses such as oxidation catalysts, fuel cell electrodes in batteries, a catalyst in the formation of ammonia from nitrogen and hydrogen, a hemoglobin substitute, the photoconducting layer in the target area of a television camera tube, in cigarette filters to catalyze the removal of nitrogen oxides from cigarette smoke, and many other uses too.
Scheme 4.1

Scheme 4.2
With so many uses for the various phthalocyanines, it may be assumed that a high performance polymer incorporating such a group in its backbone, might have several potential uses. To our knowledge, no other poly(aryl ether)s incorporating the phthalocyanine moiety have been reported and so this thesis presents the first such case. A 1990 review\(^2\), citing 3000 references on the applications of phthalocyanines, discusses several types of polymer but they are mostly three dimensional thermosetting networks. In these insoluble materials, each phthalocyanine moiety connects together four polymer chains, as in scheme 4.2.

Copper phthalocyanine (CuPc) can be easily prepared by heating phthalonitrile with cuprous or cupric chloride in the melt or in quinoline or a mixture of quinoline and trichlorobenzene\(^4\) (scheme 4.1). In this work, the copper phthalocyanine moiety was incorporated into three copolymers containing 10, 20 and 30% of 3,6-difluoro-9,10-dicyanophenanthrene (2) (polymers numbered 2.1a, 2.2a and 2.3a in table 4.1) by heating them at 200°C with excess phthalonitrile and cuprous chloride in quinoline to give polymers 2.1pc, 2.2pc and 2.3pc, as shown in scheme 4.3. During this reaction, free copper phthalocyanine is produced which can be separated from the polymer by dissolving the mixture in chloroform and filtering off the phthalocyanine. This gives complete separation because copper phthalocyanine is very insoluble in chloroform and all other common organic solvents. The polymers are a deep green / blue colour and they can be cast into flexible black films which are deep green by transmitted light. Other physical properties of these polymers and the parent polymers are listed in table 4.1.

4.2 Do polymers 2.1 - 2.3pc contain copper phthalocyanine?

The most convincing evidence to suggest that polymers 2.1 - 2.3pc contain the copper phthalocyanine moiety is their intense blue / green colour and their visible spectra. Figure 4.1 shows the visible spectra of 2.2pc. The absorption maximum at 672nm is very close
Scheme 4.3
<table>
<thead>
<tr>
<th>Polymer</th>
<th>%Phenanthrene/Phthalocyanine</th>
<th>°C</th>
<th>°C</th>
<th>Inherent viscosity</th>
<th>E' at 25°C</th>
<th>E' at 100°C</th>
<th>Tan δ</th>
</tr>
</thead>
<tbody>
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<td></td>
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Table 4.1

![Visible spectrum of 2.2pc](image)

Figure 4.1 Visible spectrum of 2.2pc. Marked wavelengths from left to right are at 610, 622, 656 and 672nm.
to that of copper phthalocyanine which occurs at 678nm. Slight differences in
wavelengths are to be expected because the aromatic chromophores are slightly different
since one of the benzene rings in copper phthalocyanine is replaced by a phenanthrene
ring system in these polymers.

The striking difference between the spectrum of CuPc and that of the polymers is the fact
that the polymer spectra show heavy absorption throughout the visible region whereas in
the CuPc spectrum there is virtually no absorption in the green region. This heavy
absorption is especially apparent in the spectrum of 2.1pc and in fact it can be seen with
the eye that this polymer is blacker when compared to 2.2pc and 2.3pc. This black colour
suggests that there are some other coloured species, or by-products present in the
polymer, but what they are exactly is not known. That polymer 2.1pc contains more by-
products than the other two phthalocyanine polymers can probably be explained by the
fact that this polymer was allowed to react with phthalonitrile for four hours, whereas the
other two were reacted for just 1 hour. Therefore, in order to limit the formation of by-
products the reaction time should be limited to 1 hour.

Other evidence for the existence of the CuPc moiety comes from elemental analysis of
2.1pc which shows the presence of 1.23% copper, compared to a theoretical amount of
1.30%. Therefore one might assume a conversion of ~ 90 - 95% of the 9,10-
dicyanophenanthrene units.

4.3 Glass transition temperatures.
The Tgs of the parent copolymers 2.(1-3)a are 195, 200, and 206°C respectively. These
values are almost identical to those calculated using equation 4.1 (where \( w_1 \) and \( w_2 \) are
the weight fractions of the two monomers and \( Tg_1 \) and \( Tg_2 \) are the glass transition
temperatures), which are 195, 201 and 207°C respectively. Equation 4.1 is designed to
calculate the Tg of a random copolymer and therefore it suggests that the two monomers in the copolymers 2.(1-3)a are fairly randomly distributed.

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\]

Equation 1

The Tgs of the phthalocyanine polymers are also close to 200°C, ranging from 199 - 202°C. It is surprising that the Tgs have not significantly increased on incorporation of the phthalocyanine group because one would have expected the large, flat phthalocyanine ring system to have severely hindered segmental chain rotation and thereby raise the Tg. One explanation may be that the phthalocyanine rings stack together to form crystalline regions that completely prevent segmental chain rotation. This would also explain the fact that the Tgs of the three phthalocyanine polymers are very similar because the DSC is measuring the Tg of what is essentially polysulfone because the phenanthrene units are mostly locked into crystalline regions. Phthalocyanines are highly crystalline compounds that have no melting point, instead they sublime at over 500°C. This absence of a melting point would explain why no Tm is observed in DSC analysis up to 400°C.

An alternative argument might say that such rigid crystalline regions would act like cross-links and therefore should increase the Tg, but this is contrary to what is observed. The reality of the situation is that the effects of incorporating such rigid systems into a polymer have not been fully investigated and so it is not possible to formulate a good explanation of the observed Tgs. The situation is further complicated by the fact that it is known that there are some other, unidentified moieties present in the polymers, as indicated by their visible spectra. In this light it is obvious that further work is needed in this area.

4.4 Thermal stability.
The 5% weight loss temperatures for the parent copolymers are slightly lower than those for the corresponding homopolymers, ranging from 439 - 470°C. After incorporation of the phthalocyanine system, these temperatures are slightly raised to between 470 and 482°C. A modest increase such as this is be expected because CuPc system is very heat stable and has been shown to be stable at temperatures up to 900°C in vacuo. However, to expect a massive increase in stability would be unreasonable because the polymer backbone is largely unchanged.

4.5 Mechanical properties.

The Young’s moduli of the phthalocyanine polymers are higher than that for the parent copolymers by approximately 0.5 to 0.9 GPa. It is well known that crystalline polymers tend to have higher Young’s moduli than those of amorphous polymers and so the observed Young’s moduli appear to fit the theory of semi-crystallinity outlined under the discussion of glass transition temperatures above.

After the first measurement of tan δ of 2.1pc (in which the temperature was raised to 300°C) the strip of film appeared to be largely unaffected (i.e. it had not stretched unduly) and so it was subjected to a second run. Although tan δ remained unchanged, the Young’s modulus at elevated temperatures was markedly improved, the new values being 1.53GPa at 100°C, 1.48GPa at 150°C and 1.04GPa at 190°C (compared to initial values of 1.37GPa at 100°C and 0.50GPa at 150°C). These are remarkable increases in circumstances where a decrease is expected (a decrease is expected because after the first run, the strip of film is stretched and so the cross sectional area is reduced). The suggested explanation is that when the temperature is raised above the Tg during the first tan δ measurement, more phthalocyanine units are able to move and stack and thereby increase the stiffness of the polymer for the 2nd measurement of tan δ.
4.6 Conclusion

There are two aspects concerning these phthalocyanine polymers that are not easily explained. Firstly, when they are heated to 300°C they become insoluble and their Young's moduli increases. Both of these observations suggest that cross-linking has occurred. However, cross-linking is usually accompanied by an increase in Tg but this is not observed here. Also, from what is known of the structure of the polymers, there are no functional groups that are capable of forming cross-links. The second unexplained observation is that there is not an increase in Tg after the phthalocyanine groups have been added. Usually, large, rigid groups such as these will cause a significant increase in Tg.

Clearly, further work is needed in this area. Most importantly, a polymer must be prepared from monomers which contain the phthalocyanine moiety, so that we can be more certain of the structure of the polymers. A suggested route for the preparation of these monomers is given at the end of this thesis.
4.7 Chapter four, references


5. i.b.i.d. p 31.

Chapter 5.

Experimental

5.1 Materials
All reagents were used as obtained from suppliers, without further purification unless otherwise stated.

5.2 Characterization.
Melting points were measured on a Fisher - Johns melting point apparatus. Thin layer chromatography (t.l.c.) was performed on Whatmann PE SIL G/UV plates. Flash chromatography was done on silica gel 60 from BDH. Proton nuclear magnetic resonance (\(^{1}H\text{-NMR}\)) and carbon nuclear magnetic resonance (\(^{13}C\text{NMR}\)) spectra were obtained in chloroform \(_d\) solution or dimethylsulphoxide \(_d\) (DMSO - d\(_6\)) solution at 200 MHz (50 MHz for \(^{13}C\text{NMR}\)) on a Varian Gemini 200 NMR spectrometer. Chemical shifts are reported in \(\delta\) (ppm) down field from tetramethylsilane (TMS). Elemental analysis were obtained from Guelph Chemical Laboratories Ltd., Ontario. Mass spectra (electron impact) were recorded at 70ev with a direct insertion instrument.

Chemical reactions were routinely followed by high performance liquid chromatography (HPLC), using a Milton Roy instrument, a Spherisorb ODS2 reverse phase column (250 x 4.6mm; 5mm) and methanol as the eluent at a flow rate of 1.0 ml per min., with a u.v. detector set at 254nm.

The glass transition temperatures (Tgs) of polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min. with nitrogen purging at 50ml/min.. The Tg values were obtained from the third scan and are taken at the point of maximum
inflection. Polymer weight loss data was obtained using a Seiko 220 TG/TGA instrument, using a heating rate of 10°C/min. with nitrogen or air purging at 200ml/min. For all DSC and TGA measurements, the samples were dried in a vacuum oven at 75°C for at least 24 hrs and then pressed into a pellet under a pressure of 5 tons. Young's Modulus and tan δ measurements were obtained using a Seiko TMA/SS 120 instrument, using a strip of cast film (length = 5mm, width = 2mm, and thickness = -0.1mm).

Inherent viscosities were obtained using a calibrated Ubbelohde 1(165) viscometer, at 25°C, in chloroform or 1,1,2,2-tetrachloroethane (sym TCE) solutions (5g/l). A waterbath with a Julabo heater was employed to control the temperature.

Photochemical reactions were performed using an Hanovia medium pressure mercury lamp powered by an Hanovia 7830 transformer, both supplied by Ace Glass Incorporated. The photochemical apparatus was cooled using a "Flexi-cool" refrigeration coil supplied by FTS Systems Incorporated.

5.3 Film casting.
Typical procedure: The polymer (150mg) was dissolved in chloroform or sym TCE (2 - 3ml) and the solution filtered through a tissue paper plug, directly into a circular glass template (diameter = 3.5ml) located on a smooth glass plate. The system was covered with a watch glass and allowed to stand until the solvent had evaporated (approximately 48hrs at 25°C for chloroform and 100°C for sym TCE). The resulting films were then dried in a vacuum oven at 75°C for 24hrs before using.

5.4 Synthesis of monomers
2,3-bis(4-fluorophenyl)-2-butenedinitrile. A solution of 4-fluorobenzyl cyanide (30g, 0.222mol.) in carbon tetrachloride (100ml) was added slowly, over a period of 30
minutes, to a rapidly stirring mixture of 40% aqueous sodium hydroxide (100ml; 1mol), carbon tetrachloride (100ml) and trimethylbenzylammonium chloride (TMBA; 0.6g; 0.003mol). The mixture was maintained at room temperature overnight, after which time a precipitate had formed which was collected by filtration and washed with water and chloroform. The organic layer of the mother liquor was washed successively with dilute hydrochloric acid, 5% aqueous sodium bicarbonate and water and then dried over magnesium sulphate. The dried solution was filtered and then evaporated to a paste which was triturated with ethanol to give a second crop of product, which was combined with the first. The material was recrystallised from ethanol to yield small white needles. Yield = 50%: m.p. 194 - 195° (EtOH); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.17-7.29 (m, 4H), 7.78-7.89 (m, 4H); \(^13\)C NMR (50 MHz, DMSO-d\(_6\)) \(\delta\) 116.74 (d, \(J\) = 22.4Hz), 116.76 (s), 124.81 (s), 128.59 (d, \(J\)l=3.4Hz), 131.73 (d, \(J\)l=9.1Hz), 163.87 (d, \(J\)l=250.6Hz); MS (EI) \(m/e\) 266 (100, M\(^+\)); Analysis calc'd for C\(_{16}\)H\(_8\)N\(_2\)F\(_2\): C, 72.17; H, 3.03; N, 10.52; found: C, 71.98, H, 2.80; N, 10.48.

3,6-difluoro-9,10-dicyanophenanthrene. A solution of 2,3-bis-(4-fluorophenyl)-2-butene dinitrile, in chloroform (20g/l), was placed in a photochemical reaction vessel fitted with a water cooled quartz immersion well, a water condenser and a gas inlet needle (see figure 5.1). The mixture was irradiated with a medium pressure mercury lamp, for a period of 2-3 weeks, 8 hours per day. At the beginning of each day the reaction mixture was sparged with oxygen for 15 minutes. The reaction was monitored using HPLC and it was stopped when the product peak ceased to increase. Throughout the irradiation the mixture was maintained at room temperature by means of an external cooling bath. The whole apparatus was enclosed in a box as a protection against U.V radiation.

At the end of the reaction the mixture was evaporated to dryness and the solid recrystallised to constant melting point from acetone to give very fine beige needles: m.p 297°C (Acetone); \(^1\)H NMR (200 MHz, DMSO-d\(_6\)) \(\delta\) 7.84 (m, 2H), 8.21 (m, 2H), 8.76
Figure 5.1 Diagram of apparatus used for photochemistry
3,3-Bis-(4-fluorophenyl)-propionic carbonitrile. A mixture of powdered potassium hydroxide (85%; 3.30g; 0.05mol) and acetonitrile (50ml) was refluxed under N₂ for 2 h. A solution of 4,4'-difluorobenzophenone (10.91g; 0.05mol) in acetonitrile (30ml) was then added in a stream. The mixture immediately turned deep red. After 4 hrs at reflux the reaction was quenched by pouring onto crushed ice and then it was extracted with ether (3 x 75ml). The combined ether extracts were washed with water until neutral and then with sat. brine, and then dried over magnesium sulphate. The dried solution was filtered and then evaporated to yield a brown oil which was purified by flash chromatography (hexane: ethyl acetate, 4:1) and recrystallised from ether/hexane (3:1), to yield large, colourless, cubic crystals. Yield = 51%. : mp 79-81°C (Et₂O); ¹H NMR (200 MHz, CDCl₃) δ 5.65 (s, 1H), 7.00-7.19 (m, 4H), 7.22-7.32 (m, 2H), 7.36-7.46 (m, 2H); ¹³C NMR (50 MHz, DMSO-d₆) δ 96.53 (s), 116.11 (d, J₁=21.9), 118.21 (s), 130.87 (d, J₁=8.8), 131.75 (d, J₁=8.5), 133.53 (d, J₁=3.4), 134.57 (d, J₁=3.1), 159.79 (s), 163.08 (d, J₁=247.8), 163.70 (d, J₁=249.5); MS (El) m/e 241 (100, M+); Analysis calcd for C₁₆H₆F₂N₂: C, 72.73; H, 2.29; N, 10.60; found: C, 72.67; H, 1.88; N, 10.66.

Bis-(4-fluorophenyl)methylene propane dinitrile. 4,4'-Difluorobenzophenone (10.91g; 0.05mol), malononitrile (3.96g; 0.06mol), ammonium acetate (3.2g), glacial acetic acid (9.6ml) and anhydrous benzene (30ml) were placed in a 3 neck r.b. flask fitted with a Dean Stark trap and refluxed. After 48 hrs, the amount of water collected in the trap had ceased to increase and the reaction was cooled and poured into a mixture of ether (100ml) and water (100ml) and stirred rapidly for 20 mins. A precipitate formed which was
removed and discarded. The aqueous layer of the mother liquor was washed with ether (2 x 75ml) and the washings combined with the original organic layer and then washed successively with 5% HCl (100ml), 10% aq. sodium bicarbonate (100ml), water (100ml) and sat. brine (100ml) and then dried over magnesium sulphate. The solution was then evaporated to dryness and the solid recrystallised to constant melting point from ethanol/water (5:1). Yield = 52%: mp 131-133°C (EtOH/H2O); ¹H NMR (50 MHz, CDCl₃) δ 7.12-7.21 (m, 4H), 7.39-7.48 (m, 4H); ¹³C NMR (50 MHz, DMSO-d₆) δ 82.34 (s), 114.43 (s), 116.38 (d, J=22.2), 132.51 (d, J=3.0), 133.45 (d, J=9.2), 164.73 (d, J=252.6), 171.94 (s); MS (EI) m/e 266 (100, M⁺); Analysis calcd for C₁₆H₈N₂F₂: C, 72.18; H, 3.03; N, 10.52; found: C, 72.24; H, 2.44; N, 10.39.

9,9-Bis(hydroxyphenyl)fluorene. This compound was prepared according to the procedure outlined by Knebel et al in US Patent 4,931,594, except that Amberlyst 15 was used instead of Amberlyst 16. Yield = 60%.

5.5 Polymerizations

Typical procedure: 2,3-Bis-(4-fluorophenyl)-2-butene dinitrile (1.0000g; 0.00376mol) and bisphenol A (0.8574g; 0.00376mol) were carefully weighed, accurate to 4 decimal places and transferred to a 50ml, 3-neck r.b. flask, together with potassium carbonate (0.675; 0.00488mol). Any material that became stuck to the mouth of the flask or the weighing paper was washed into the flask using the solvents, DMAC (10ml) and toluene (5ml). The flask was fitted with a Dean Stark trap filled with toluene and refluxed for 3hrs (reflux temp. = 135°C). The Dean Stark trap was then drained of toluene and any water that had co-distilled, and the remaining toluene in the flask was allowed to distill over. The reaction temperature then increased to 160°C and after 1-3 h the viscosity of the mixture increased dramatically and the reaction was stopped by adding the mixture dropwise to methanol/water (4:1: 200ml). Beads of polymer formed which were
recovered by filtration, dried in air and redissolved in chloroform (20ml). The chloroform solution was filtered through a plug of celite and again precipitated in methanol/water. A fibrous, yellow polymer was obtained and filtered and dried in vacuum at 75°C for 24 h.

Typical yield = 75%.

5.6 Preparation of polymer 1e

Polymer 1e was prepared in a manner similar to that described above except for the following changes. The solvents used were sulpholane (instead of DMAC) and chlorobenzene (instead of toluene). The temperature was raised to 190°C immediately, the chlorobenzene being allowed to distill out into an empty Dean Stark trap.

5.7 Preparation of phthalocyanine containing-polymers

A copolymer containing the 9,10-dicyanophenanthrene moiety (0.8g) was dissolved in quinoline (10 - 20ml). For each equivalent of the dicyanophenanthrene moiety, 40 equivalents of 1,2-dicyanobenzene were added along with 20 equivalents of cuprous chloride. The mixture was warmed to 200°C whereupon a vigorous exothermic reaction ensued. After 1hr the exotherm had subsided and the reaction was cooled and the mixture added dropwise to methanol, to yield black beads. The beads were purified by redissolving in chloroform, filtering through celite, and reprecipitating into methanol to yield green fibrous polymer which was dried in the oven at 75°C.

Typical yield = 75%.
Contributions to knowledge.

Chapter two describes the synthesis and characterization of 4 novel difluorinated molecules with potential for use as monomers in polymerisation reactions.

Chapter three describes the synthesis and characterization of two series' of five novel polymers prepared from 2,3-bis-(4-fluorophenyl)-2-butenedinitrile and 3,3-bis-(4-fluorophenyl)-propenoic carbonitrile and another polymer prepared from 3,6-difluoro-9,10-dicyanophenanthrene. The cross-linkability of these polymers has been investigated and a new thermally cross-linkable system has been discovered.

In chapter four, some copolymers prepared from 3,6-difluoro-9,10-dicyanophenanthrene, difluorophenyl sulfone and BPA were prepared, characterized and then reacted with excess phthalonitrile and cuprous chloride to give some novel, soluble phthalocyanine containing polymers. This is the first reported case of phthalocyanine being incorporated directly into the backbone of a poly(aryl ether)s.
Future work.

In chapter two, the cross linking reaction of polymers containing the dicyanostilbene moiety was investigated using solid state $^{13}$C NMR. After heating the polymer the disappearance of the nitrile carbon atom was clearly observed but a product peak could not be seen. This is probably because the product peak is hidden under some other peaks - perhaps the aromatic peaks - and it is in too low a concentration to be seen. Therefore it would be useful to prepare some $^{13}$C enriched dicyanostilbene in order to enhance the visibility of the product peak. A possible route might make use of 4-fluorobenzylbromide and $^{13}$C enriched carbon dioxide to prepare, via the Grignard reaction, $^{13}$C enriched 4-fluorophenyl acetic acid (6.1 in scheme 6.1). 6.1 can easily be converted to the 4-fluorobenzyl cyanide which is the precursor to the stilbene monomer.

\[
\begin{align*}
\begin{array}{c}
\text{Br} & \xrightarrow{\text{Mg, Ether}} & \text{MgBr} \\
\text{F} & \xrightarrow{1. \text{SOCl}_2} & \text{F} \\
\text{F} & \xrightarrow{2. \text{NH}_3} & \text{F} \\
\text{F} & \xrightarrow{3. \text{P}_2\text{O}_5} & \text{F} \\
\text{N} & \xrightarrow{40\% \text{NaOH}} & \text{F} \\
\text{CCl}_4, \text{TMBA}
\end{array}
\end{align*}
\]

Scheme 6.1
Chapter four describes how a polymer can be reacted with 1,2-dicyanobenzene to produce polymers containing the phthalocyanine moiety. In an analogous reaction, it might be possible to react polymer 1a - e (chapter 2) with aryl fumaronitriles or maleonitriles to a polymer containing tetraazaporphyrins groups, via Linstead's template cyclization\(^2\). See scheme 6.2.

Also in chapter four, from the appearance of the visible spectra of the phthalocyanine polymers (2.(1-3)pc), it seems that some other unidentified moieties are present. These unknown quantities make it difficult explain the behavior of these polymers at elevated temperatures. In particular, the polymers appear to cross-link when raised to 300°C but there are no identified functional groups that would react under such conditions. In order to clarify matters, it would be useful to prepare a monomer containing copper phthalocyanine and then to polymerize it with BPA and difluorodiphenyl sulfone. In this way, the structure of the polymer would be known with greater certainty than that of the polymers described in chapter four. An obvious structure for a suitable phthalocyanine containing monomer is that prepared in the two step reaction outlined in scheme 6.2. In the first step, 9,10-dicyanophenanthrene is reacted with two equivalents of BPA using the familiar nucleophilic displacement reaction to give 6.2, which could then be converted to the phthalocyanine by reacting with phthalonitrile and cuprous chloride.

References.


Scheme 6.1

1. BuOH/BuO'/Mg²⁺, 120°C, 18h
2. CHCl₃/AcOH, 100°C, 15min

Scheme 6.2
Scheme 6.3