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SYNTHESIS AND PROPERTIES OF NOVEL THERMALLY STABLE POLYMERS

by

Whan-Gi Kim

A thesis submitted to the Faculty of Graduate Studies and Research in
partial Fulfillment of the requirements for the degree of
Doctor of Philosophy

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To my Father, Mother

and Family

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Ph. D. Whan-Gi Kim Chemistry

SYNTHESIS AND PROPERTIES OF NOVEL THERMALLY STABLE POLYMERS

Abstract

Modified biphenols which contain 2,2'-disubstituents on the biphenyl groups and also hydroquinones containing multiple substituents were synthesized in order to prepare novel thermally stable polymers. The structure / properties relationship which were investigated using viscometry, DSC, TG/DTA, TMA, and GPC are discussed.

The prepared polymers (polysulfones and poly(ether ketone)s) exhibit considerably enhanced glass transition temperatures and are soluble in common organic solvents due to the noncoplanar biphenyl rings which increase the disorder along the polymer backbone thereby reducing interchain interactions. The polyesters prepared show poor solubility and their Tg's and Tm's increase considerably over the unhindered polyester analogs due to the chain stiffness.

Polyimides were prepared from the reaction of novel dianhydrides and *m*- and *p*-phenylene diamines. A series of bisanhydrides were prepared via the nitro-displacement reaction of hindered biphenols and N-methyl-4-nitrophthalimide. The polymers exhibit good solubility in common organic solvents and show high Tg's. Blends of polycarbonate and polyimides, prepared from *m*-phenylene diamine, show better miscibility compared to those of polyimides from *p*-phenylene diamine.

The 2,2'-substituted biphenols which can be oxidized to bisphenoxydiradicals are applicable as oxidizing agents for diphenylmethanes and primary alcohols, and also undergo C-O coupling reactions with activated methylene groups. An additional modified biphenol was synthesized for REDOX polymers applications and the properties of these polymers are discussed.

Ph.D. Whan-Gi Kim Chimie

SYNTHÈSE ET PROPRIÉTÉS DE NOUVEAUX POLYMÈRES À STABILITÉ THERMIQUE

Sommaire

Des biphénols qui sont disubstitués-2,2' aux anneaux du biphényle et aussi des hydroquinones qui contiennent une substitution multiple ont été synthètisés pour la préparation de nouveaux polymères à stabilité thermique. Les relations structure/propriétés, étudiés en utilisant la viscométrie, DSC, TG/DTA, et GPC, sont discutés.

Les polymères préparés (polysulfones et poly(éther cétone)s) exibent des températures de transition de verre (Tg) qui sont considérablement augmentées. Ils sont solubles dans des solvants organiques communs à cause de la non-coplanarité des anneaux du biphényle qui augmente le désordre de la chaîne principale du polymère ainsi réduissant les interactions des autre chaînes. Les polymères préparés ont une faible solubilité et leur Tg's et températures de fusion croissent considérablement, relative aux analogues pas encombrés, à cause de la rigidité de la chaîne.

Les polyimides ont été préparés de la réaction de nouvelles dianhydrides et des m- et p-phénylène diamines. Une série de bisanhydrides a été préparée via la réaction de déplacement du groupe nitro de biphénols encombrés et de méthyle-N-nitro-4-phthalimide. Les polymères exibent une bonne solubilité dans les solvants organiques communs et démontrent une haute Tg. Dans les mélanges de polycarbonate et de polyimides, préparés de m-phénylène diamine, démontrent une meilleure miscibilité vis-à-vis ceux de polyimides préparés de p-phénylène diamine.

L'application et propriétés de ces polymères sont discutés. Les biphénols substitués-2,2' peuvent être oxydés au biradical du bisphénoxy qui sont applicables comme agents d'oxydation pour les diphénylméthanes et les alcools primaires et peuvent aussi subir une réaction avec les groupements de méthyènes activés produisant un couplage C-O. Un biphénol additionnel a été synthètisé pour la préparation de polymères à fonction REDOX.

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GLOSSARY OF ABBREVIATION AND SYMBOLS

Å	Angstrom (1 x 10^{-8} cm)
BPA	4,4'-isopropylidenediphenol
Co-salcomine	N,N'-bis-(salicylidene)-ethylenediaminocobalt(II)
DMAc	N,N'-dimethyacetamide
DMF	N,N'-dimethyformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimeter
E'	Young's modulus
FT	Fourier transform
HPLC	high pressure liquid chromatography
GPa	$1\text{x}10^9$ Pascal (1.0 Pa=10 dyn/cm^2=0.000145 psi)
GPC	gel permeation chromatography
IR	infrared
mmol	millimole
Mn	number average molecular weight
mp	melting point
MS	mass spectrum
Mw	weight average molecular weight
Mw/Mn	polydispersity
NMP	N-methylpyrrolidinone
NMR	nuclear magnetic resonance
ppm	part per million
$\tan \delta$	ratio of loss moduli to storage moduli (E'/E")
Tc	crystallizing temperature
Tg	glass transition temperature
TG/DTA	thermogravimetric/ differential thermal analysis
Tm	crystalline melting temperature
TMA	themomechanical analysis
TMS	tetramethylsilane
UV	ultraviolet
ARDEL®	poly(terephthaloyl-4,4'-isopropylidenediphenoxy)
Fortrel®	poly(butylene terephthalate)
Noryl®	Blends of PPO and Polystyrene

PAK	poly(aryletherketone)s
PET	poly(ethylene terephthalate)
PEEK®	poly(etheretherketone)
PEK®	poly(etherketone)
PPO®	poly(phenyleneoxide)
Radel®	poly(oxy-1,1'-biphenyloxy-diphenylsulfone)
Udel®	poly(oxy-4,4'-isopropylidenediphenyloxy-diphenylsulfone)
Ultem®	poly(1,3-phenyl-2,2-bis(phthalimid-4-oxy-phenyl)-propane)
Victrex®	poly(oxy-diphenylsulfone)
λ	wavelength
δ	chemical shift
μ	micro

CHAPTER 1

GENERAL INTRODUCTION

1.1 PLASTICS

As a branch of chemistry, plastics has developed rapidly because they are unique materials with a broad range of properties and an enormous variety of uses [1,2,3]. Most plastics are classified as organic polymers and in general, these polymers consist principally of the elements C, H, N, and O. New families of plastics have appeared on the scene. To satisfy the strong demands to save energy in the construction of vehicles of all kinds, and applications in housing, packing, business machines, and in electronics, medicine and health products, new families of plastics began to appear on the scene and their use has gained more and more momentum. Designing plastic parts for this wide range of uses has become a major activity for designers, architects, engineers, and others who are concerned with product development [1,4]. Figure 1.1 illustrates the important application areas of plastics[1].

The first synthetic plastic was introduced in 1908. Baekeland developed phenolic resins and marketed them under the trade name Bakelite. Bakelite was produced by reacting formaldehyde with phenols[5,6] and the phenol-formaldehyde resins became the standard plastic for telephone receivers, electrical insulators, and handles for cooking utensils. Plastics became significant materials even though the chemistry and structures were not well understood. The concept of a polymer as very large molecule was not fully accepted

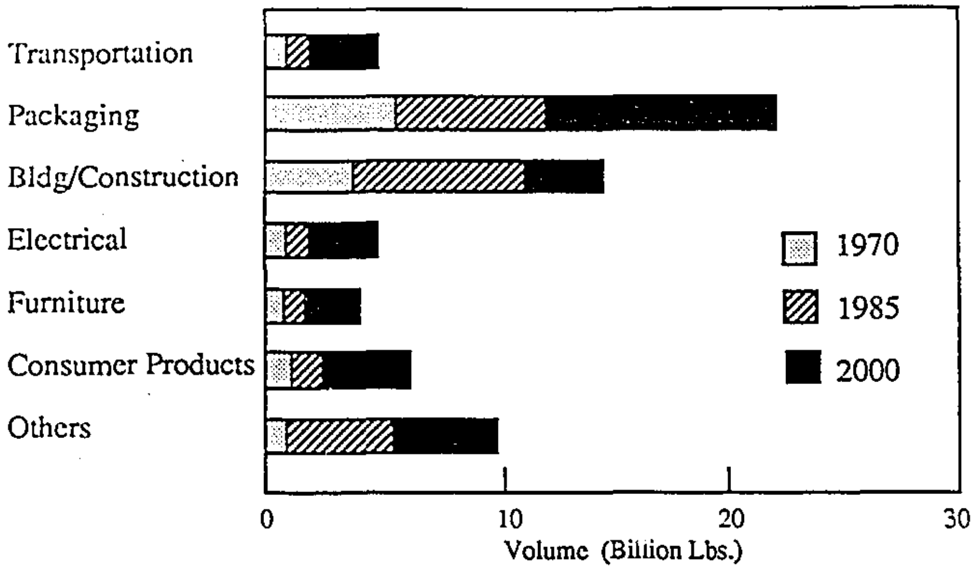


Figure 1.1 Cumulative plastics growth in the U.S. market.

until the 1920's. Since that time, there has been considerable interest in the new synthetic materials and the field has expanded at an accelerated rate. Vinyl monomers and the conditions of their polymerization were the first to be systematically studied and commercial production of several vinyl and diene polymers [7] began in the twenties and their times. Polystyrene, poly(vinyl chloride), synthetic rubber, polyethylene, and nylon appeared on the scene and now are products of immense value and utility [8,9]. An enormous growth of these products occurred because of the readily available and inexpensive monomers available from the petrochemical industry along with a thorough basic understanding of these materials and the development of efficient polymerization processes [10], and the almost universal applicability of the resulting products [1,2].

The last thirty years has seen a flurry of activity in the synthesis of new polymer systems. This interest has developed largely as a result of the increased need for advanced materials to replace metals, glass and ceramics. These new materials were called engineering plastics. Figure 1.2 illustrates a variety of engineering plastics showing their projected

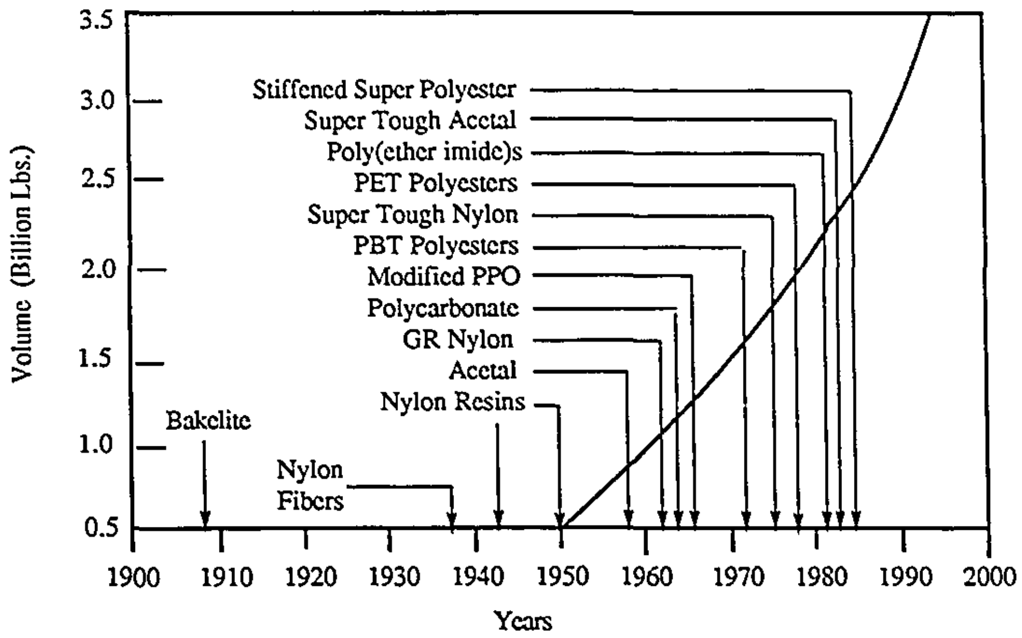


Figure 1.2 Cumulative engineering plastic growth by years

growth [11]. They are thermally stable materials and they possess high glass transition temperatures when amorphous or high crystalline melting temperatures when they are semicrystalline but they are still processable. Most recently polymers have been developed as matrices for composites [12], e.g. aromatic polyesters [13], polyamides [14], polysulfones [15], poly(ether ketone)s [16], polysulfides [17], polyethers [18], polyimides [19], in conjunction with fillers [20], carbon black, silica, and glass fibers. These new materials offer properties far superior to anything available so far with plastics and they open the door to a whole new range of applications. The search for new synthetic plastics is still going on and new uses for the existing ones are constantly being developed, so that the industry is always in a state of change.

1.2 CRITICAL FACTORS IN THE SYNTHESIS OF HIGH MOLECULAR WEIGHT POLYMERS

The capability of a monomer to polymerize depends on various factors [21] such as the reactivity and purity of the monomers, the reaction temperature, solvents, and stoichiometry.

1.2.1 PURITY OF MONOMERS

In all polymerization reactions the purity of the starting materials is of prime importance. Carothers and his associates were pioneers particularly in the synthesis of condensation polymers [22]. They emphasized the importance of the purity of monomers and provided important quantitative analytical methods for determination of end groups. They realized that purities of 99 % or even 99.5 % would still limit the molecular weight of macromolecules, although for most uses the molecular weights attainable would be in the useful range. The usual purification processes that have to be carried out carefully are fractionation, azeotropic and extractive distillation in an inert atmosphere, crystallization, sublimation, and chromatography. Most monomers and solvents must be stored under inert gas , or at low temperatures, even for short periods of time prior to use.

1.2.2 INFLUENCE OF TEMPERATURE AND SOLVENT

Exact temperature control is very important in polymerization, since the rate and degree of polymerization are influenced by the reaction temperature and solvent [23]. The boiling point of the solvent must exceed the boiling point of the low molecular weight reaction product evolved in a condensation polymerization process, *i.e*, if it is a question of the elimination of water then a solvent must be used which boils above 100 °C if it does not form an azeotrope with water. In carrying out polymerization reactions in solution it is also necessary to pay attention to the careful purification of the solvent. With an impure solvent side reactions may take place with the impurities which can lead to the cessation of the growth of the polymer chain. In cationic and condensation polymerization reactions the influence of the solvent is even more pronounced [24]. In certain polymerizations the dielectric constant of the solvent is of importance and the solvent may also have an effect on the steric arrangement of the repeat units. The rate and degree of polymerization decreases with decreasing monomer concentration in homogeneous solution polymerizations in inert solvents. Polycondensation reactions are generally performed at about 20% concentration of the starting components in the solution. The water liberated is then much more easily removed because of the low viscosity of the solution.

1.2.3 REACTION STOICHIOMETRY

An exact stoichiometric balance of the monomers used is critical to obtain high molecular weight polymers in most instances of step polymerization reactions [25]. In order to properly control the polymer molecular weight, it is often necessary to adjust the composition of the reaction mixture slightly away from stoichiometric equivalence, by adding either a slight excess of one bifunctional reactant (0.5-2%) or a small amount of monofunctional reagent [26]. If the nonstoichiometry is too large, the polymer molecular weight will be too low. Important factors in the quantitative effect of the stoichiometric imbalance of reactants on the molecular weight attained are the quantitative effect of any reactive impurities which may be present in the reaction mixture or which are formed by undesirable side reactions.

1.2.4 REACTION CONDITIONS

In most cases molecular oxygen has an influence on the course of polymerization, such as on the initiation and termination reactions of radical polymerizations, on the activation or deactivation of ionic initiators, and on the degradation of the formed polymers in polycondensation reactions [27]. In ionic and condensation polymerization reactions, moisture must be excluded from the reaction mixture since small amount of water reduces the degree of polymerization [28]. The inner walls of a glass apparatus are best freed from moisture by heating under high vacuum. Gases may be dried by freezing out the moisture or by passing them through columns filled with a suitable drying agent. Liquids can be freed from water by use of suitable drying agents or by azeotropic or extractive distillation. Generally reactions or distillations are carried out under a continuous flow of nitrogen or other inert gas to prevent diffusion of oxygen from ambient air into the apparatus.

1.2.5 PURIFICATION AND DRYING OF POLYMERS

Isolation is simplest when the polymer precipitates from the reaction mixture because of insolubility. The polymeric products can be separated by filtration or by centrifugation. If the polymer remains dissolved in the reaction mixture it must be precipitated by addition of a precipitating agent, or the solvent, excess monomer, and any other volatile ingredients are removed by distillation. Careful purification and drying is important not only for proper analytical characterizations but also because the mechanical, electrical and optical properties are strongly influenced by impurities. Moreover, even traces of impurities may cause or accelerate degradation or cause crosslinking reactions [29].

1.3 RELATIONSHIP OF STRUCTURE AND PROPERTIES

1.3.1 Tg AND Tm

Polymers can exhibit a number of different phase transformation's and each change is accompanied by differences in polymer properties [30,31]. Two major thermal transitions occur in polymers: the glass transition temperature (Tg), which is associated with local, segmental chain mobility in the amorphous regions of a polymer, and the melting point (Tm), which is associated with the crystalline region of the polymer. The Tm is called a first-order transition temperature, and Tg is often referred to as a second-order transition temperature. The values for Tm are usually 33 to 100% greater than for Tg when expressed in absolute temperature scale. Tg values are typically low for elastomers and flexible polymers and higher for hard amorphous plastics.

The two thermal transitions generally correlate with the flexibility of the chain which is determined by steric effects, chain rigidity, and secondary forces between polymer chains [35,32]. Flexibility is related to the activation energies required to initiate rotational and vibrational segmental chain motions. As flexibility is increased, Tg and Tm tend to decrease. Substituents on polymer backbones restrict chain rotation and encourage rigidity. Thus, polymers containing bulky aromatic substituents tend to be rigid, and show high Tm and high Tg. Secondary forces, due to high polarity or hydrogen bonding, also decrease the mobility of polymer chains and lead to high Tg values. Although Tg and Tm depend similarly on the molecular structure of polymer chains, the variations in the two transition temperatures do not always parallel each other.

1.3.2 SOLUBILITY

There are several factors [33,34] which affect solubility in polymers; van der Waals forces (permanent and induced dipoles, polarizability); geometric regularity (head-to-head vs head-to-tail type monomers, positional isomerism of ring substituents, comonomer length, coaxiality); the number, size and electronic nature of substituents, symmetry (enantiomeric purity, atropism), and hydrogen bonding in amide-containing polymers. Some general strategies to improve the solubility through structural modifications include the use of polar groups along the polymer backbone or pendent groups, large or bulky bridging or pendent groups, and increasing the flexibility along the polymer backbone.

1.3.3 THERMAL STABILITY

Thermal stability correlates with the primary bond energy that exists between the atoms in the chain. The strength of a chemical bond imposes an upper limit on the vibrational energy that a molecule may possess without bond rupture. Since heat increases the vibrational energy, the heat stability is related to the bond dissociation energy of the bond. Bond dissociation energy between two atoms can be determined by measuring the energy of dissociation into atoms or the heat of formation from the elements.

High thermal stability in polymers can be achieved by making full use of resonance stabilization. Resonance stabilization in aromatic and heterocyclic structures [35,36], such as benzene, phthalimide or quinoxaline, contributes substantially to bond strength. The resonance energies of these structures range from 40 to 70 kcal/mol. In addition, polymers may also derive additional stability from secondary forces which may be described in part as the attraction between neighboring chains. These forces have a pronounced effect on the melting point and glass transition temperature. Two of the more important of these forces are dipole-dipole interactions and hydrogen bonding.

1.4 GOALS OF THIS PROJECT

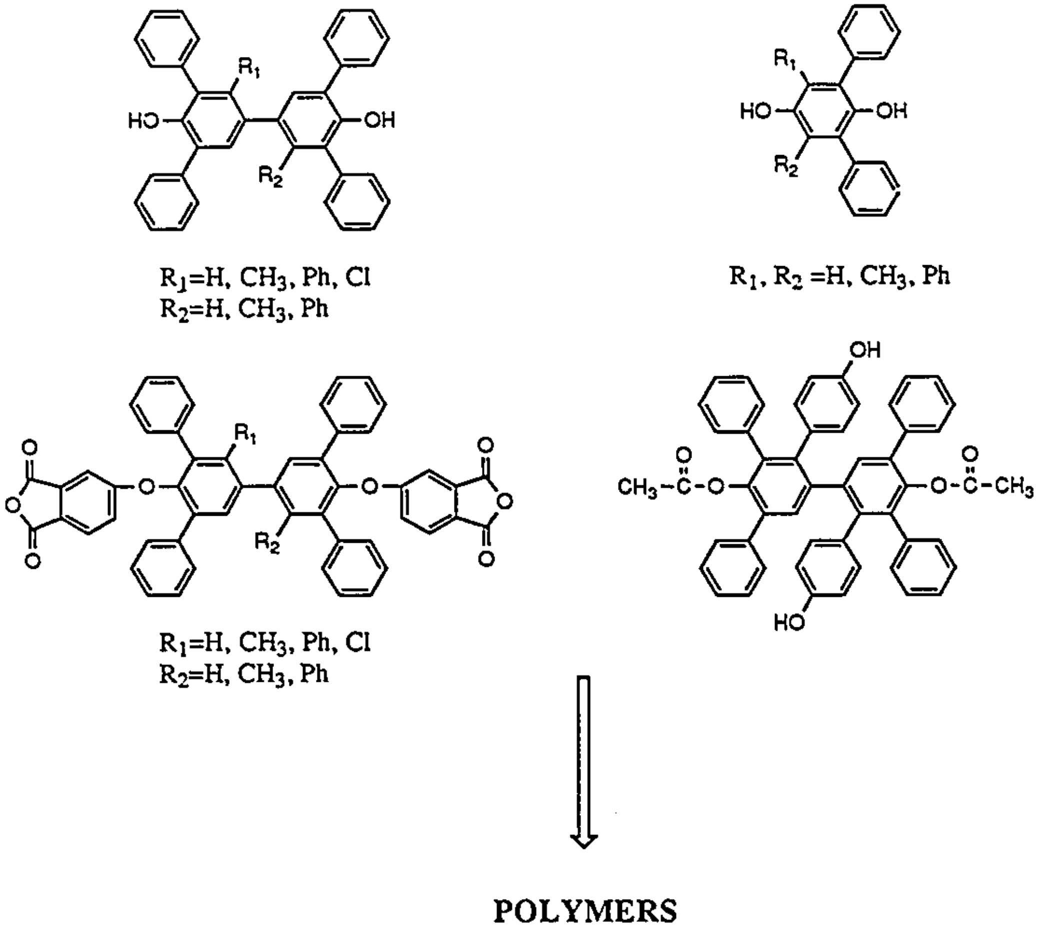
The development of thermally stable polymers [39,40], i.e., those combining the properties of heat resistance and thermal dimentional stability, has for many years been one of the important objectives in the synthesis of high molecular weight compounds. The heat resistance and thermal stability of polymers are determined fundamentally by the strength of intermolecular forces, the presence of cross-links, crystallinity, and so forth. This has been achieved by changing the structure of pendent groups while keeping the structure of the main chain unchanged, or introducing thermally stable groups, such as aromatic groups, into the chain.

The incorporation of ring structures into organic polymer chains has been extensively used for the purpose of chain stiffening. Aromatic rings have been used in particular because of their known thermal stability. However wholly aromatic polymers, without any aliphatic units in the chain, are often infusible and insoluble [37]. The melting points and softening temperatures of such polymers are 300-400 °C or greater, and they start to decompose at even higher temperatures. Therefore their practical use has been delayed by the difficulty, and sometimes even impossibility, of processing them and because of their poor physical and mechanical properties. Structural modifications are required to provide processability and this general approach has in recent years resulted in a number of new commercially available polymers with improved high temperature properties [38].

The goals of this study are the synthesis of thermally stable and processable polymers having high glass transition temperatures which exhibit solubility in common organic solvents. We have designed and synthesized a variety of novel monomers and polymerized them by condensation polymerization reactions (Scheme 1.1).

In chapter 2 the synthesis of a series of hindered biphenols and hydroquinones for use as monomers is presented, and it is shown that pendent phenyl groups in the 2,2' positions can cause non-coplanarity between phenyl rings. The structures and the thermal characteristics of the biphenols are also discussed.

Scheme 1.1



New classes of polysulfones, poly(ether ketone)s and polyesters prepared by condensation polymerization reactions are presented in Chapter 3, 4, and 5. The reactions were carried out at elevated temperatures. It is shown that the polymerizations were very slow because of the steric hindrance of the pendent phenyl rings. The thermal and physical properties were studied by DSC, TG/DTA, and TMA and compared to known polymers. Two of the sought after properties were realized in these polymers, *i.e.* an increase of the Tg and an improved solubility.

Chapter 6 describes the synthesis of a new type of bisanhydride monomers by a nitro displacement reaction using hindered biphenols and N-methyl-4-nitrophthalimide. Polyimides were prepared by the reaction of the bisanhydrides and *p*- or *m*-phenylene diamines by using a two step polymerization reaction. The properties of the polymers were investigated by DSC, TG/DTA, and TMA. The miscibility behavior of blends of polyimides with polycarbonate was investigated by DSC. It is shown that these polymers also exhibited increased Tg's and maintained solubility in common organic solvents.

In Chapter 7 possible applications of the hindered biphenols are discussed. In the presence of oxygen several diphenylmethane derivatives were oxidized to benzophenone under neutral condition. Under basic conditions oxidation of 2,2',3,3',5,5'-hexaphenyl-[1,1'-biphenyl]-4,4'-diol yields a soluble bisphenoxy radical instead of a diphenoquinone because of the steric hindrance provided by the 2,2'-substituents. This radical reacts with diphenylmethane compounds to produce C-O coupled compounds. Primary alcohols were t-butylated and then reacted with the radical to give acetals which are readily converted to aldehydes and the parent biphenols with acid.

Several novel redox polymers are discussed in Chapter 8. Modified hindered biphenols were synthesized and polymerized with methylenebromide, 4,4-difluorodiphenylsulfone, or 4,4'-difluorobenzophenone by condensation polymerization. The polymers were investigated by DSC and TG/DTA.

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CHAPTER 2

MONOMER SYNTHESIS

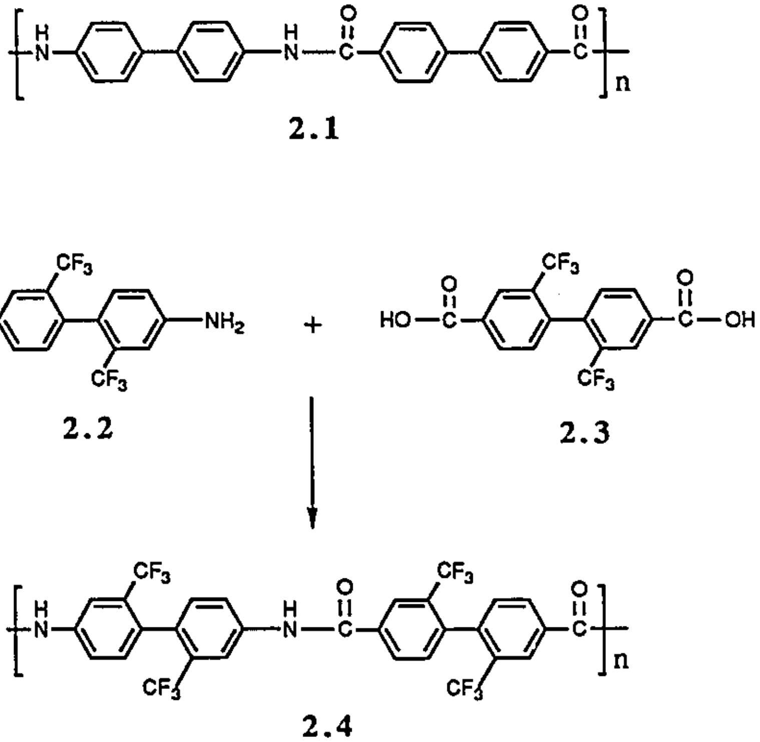
2.1 INTRODUCTION

2.1.1 MONOMERS

Properties, such as melting point, glass transition temperature, thermal stability and mechanical properties, etc., depend on the structure of the monomer unit making up the polymer. Therefore specific monomers when incorporated into polymers are advantageous for tailoring the properties of material for the specific applications. For example, engineering plastics have been discovered which begin to degrade appreciably in vacuum or inert atmospheres only at temperatures of greater than 500 °C [1,2,3], and equally remarkable are their high stability in air which approaches 400 °C for short intervals [4,5]. These improvements in material technology have resulted largely from designing strategically substituted aromatic and heteroaromatic monomer units in the polymer architecture [6,7,8]. However, polymers formed by the direct linking of unsubstituted aromatic or heteroaromatic monomers generally lack the desirable mechanical properties for successful application because often their insolubility, infusibility, and general intractability make their fabrication into useful forms difficult, if not impossible [9,10]. Considerable improvement in mechanical properties while maintaining thermal stability and good solubility may be obtained with various linking groups such as -O-, -S-, SO_2-, -CO-, etc., which are incorporated into the design of specific structural modifications of monomer units along with appropriate substituents.

The polyamide of structure **2.1** is insoluble and infusible [11]. Specific modifications **2.4** on the repeat units of polymer **2.1** have been reported [12] (Scheme 2.1). The monomers, 2,2'-ditrifluoromethyl-[1,1'-biphenyl]-4,4'-diamine **2.2** and its corresponding diacid **2.3** are substituted in the 2,2' positions with trifluoromethyl groups.

Scheme 2.1



2.1

2.2 **2.3**

2.4

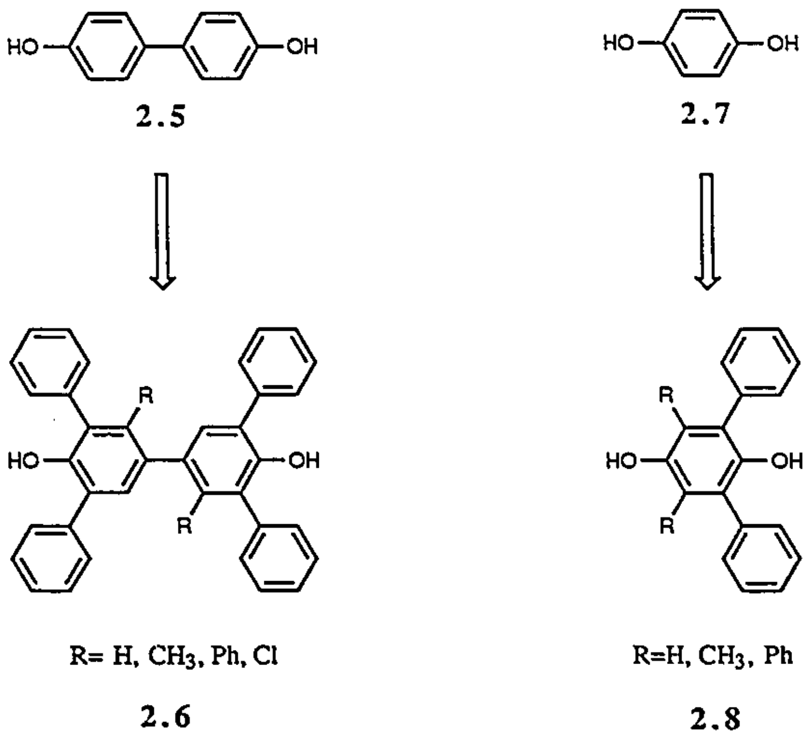
The steric hindrance provided by these groups forces noncoplanality between the rings of the biphenyl moieties which significantly disorders molecular packing and limits hydrogen bonding while maintaining the rodlike conformation of the backbone. These effects contribute to the higher solubility and major changes in spectral and thermal properties and birefringence compared to the unsubstituted biphenyl repeat unit of **2.1**.

A general approach to processability in polymers is to introduce bulky substituents on the polymer backbone which suppress crystallization of the polymer, and improve solubility [13,14]. Bulky substituents can inhibit the vibrational and rotational mobility of an intrinsically flexible chain. Methyl, carboxymethyl and phenyl groups inhibit the segmental mobility of linear macromolecules as shown by increases in the high glass transition temperature and heat distortion. Larger aromatic groups have a stronger influence giving unusual rigidity and remarkably high heat distortion temperatures in the polymers.

2.1.2 STRATEGY AND GOALS

The objective of this section is to describe the synthesis of new classes of monomers **2.6**, **2.8** based on 4,4'-dihydroxybiphenyl **2.5** and hydroquinone **2.7** in order to impart high thermal stability, high glass transition temperatures and solubility in common organic solvents in their corresponding polymers. The first approach is to place bulky substituents, such as, phenyl, methyl, and chloro in the 2,2' positions of 4,4'-dihydroxybiphenyl **2.5** and place phenyl and methyl groups in the 3,5 positions of hydroquinone. The second approach is to phenylate positions 3,3',5,5' on **2.5** and place phenyl groups in the 2,6 positions of hydroquinone **2.7**. Thus the focus is in the synthesis of two novel sets of monomers based on biphenols and hydroquinones containing bulky substituents. All the biphenols exhibit a noncoplanar conformational structure and chirality because the substituents in positions 2,2' of **2.6** or 3,5 positions of **2.8** inhibit conformational changes and lead to difficult or slow crystallization and provide good solubility. In the hindered hydroquinones the phenyl substituents are also twisted with respect to each other which affects solubility.

Scheme 2.2

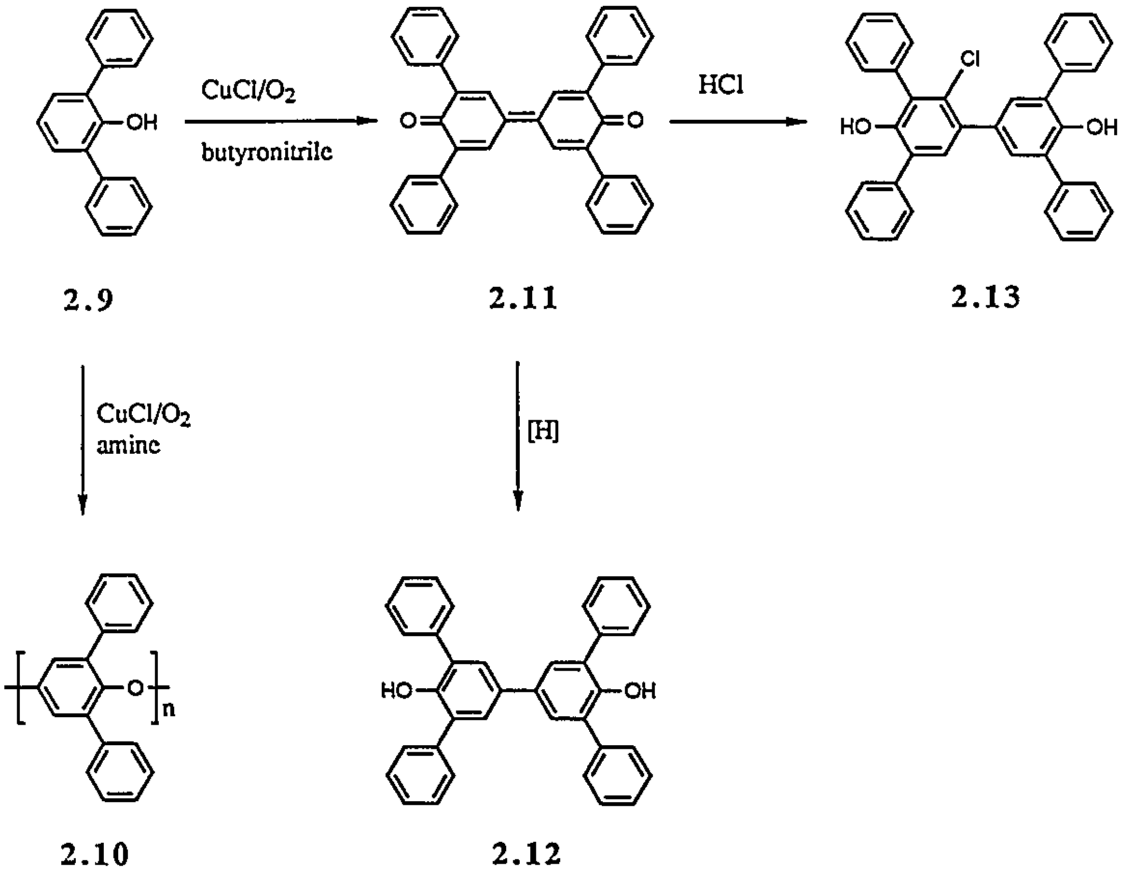


2.2 RESULTS AND DISCUSSIONS

2.2.1 PREPARATION OF BIPHENOLS

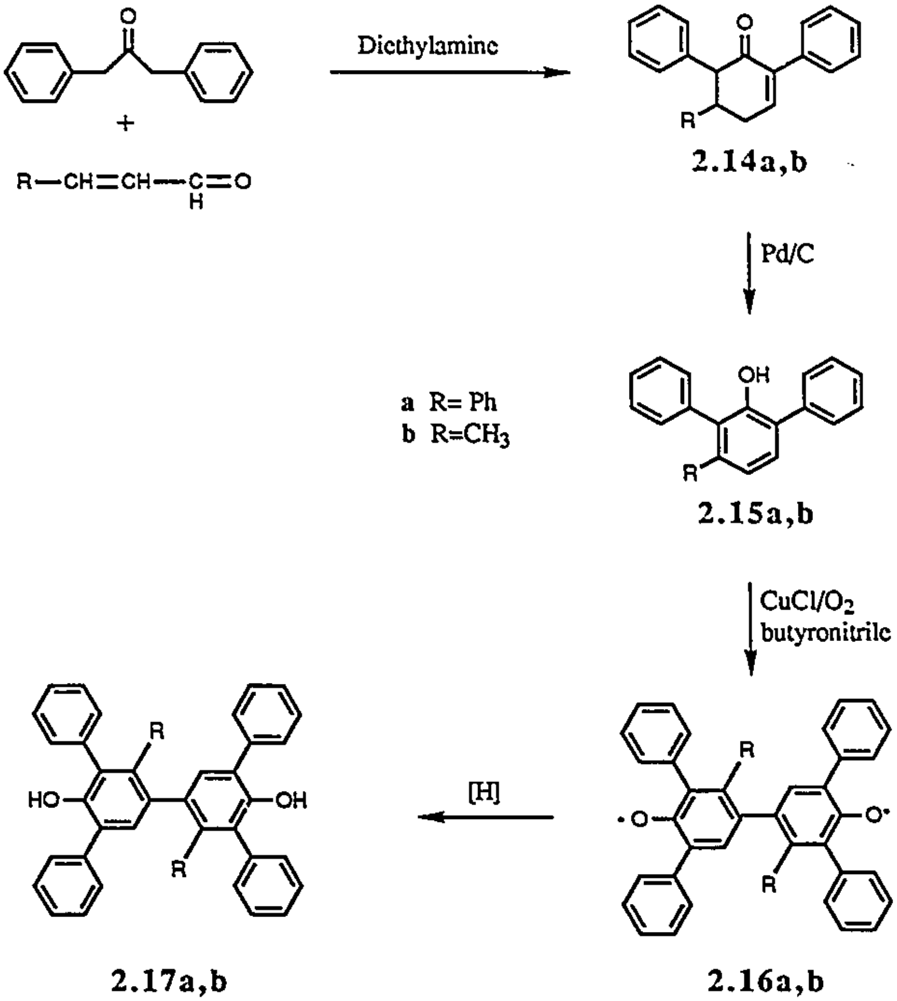
The oxidative coupling of 2,6-diphenylphenol **2.9** with a copper (I) chloride-amine catalyst and oxygen was reported by Hay to yield a high molecular weight poly(phenylene oxide) **2.10** as the product via carbon-oxygen coupling [15]. However, if the oxidation reaction is carried out using a nitrile such as butyronitrile or benzonitrile, as the ligand and solvent in the reaction at 100 °C, the corresponding diphenoquinone **2.11** is obtained in high yield. The diphenoquinone can then be reduced to 3,3',5,5'-tetraphenylbiphenol

Scheme 2.3



2.12 in hot chloroform with hydrazine [16]. The diphenoquinone **2.11** has been shown to react with hydrogen chloride to give the chloro-substituted biphenol **2.13** through 1,4 addition [17]. The 2,3,6-triphenylphenol **2.15a** and 2,6-diphenyl-3-methylphenol **2.15b** have been prepared previously [18] (Scheme 2.4). It was found that because of steric hindrance oxidative carbon-oxygen coupling did not give high molecular weight poly(phenylene oxide)s from these monomers **2.15a, 2.15b.** The condensation reaction of cinnamaldehyde with dibenzylketone in presence of diethylamine afforded a mixture of two compounds with very close retention times in the HPLC and approximate peak ratios of 7 to 3 with an overall yield of 96%. The other component was presumably the isomeric

Scheme 2.4



cyclohexanone which results from an equilibrium with the dienol. The resulting cyclohexenone **2.14a** was followed by dehydrogenation with Pd/C at 260 °C to give 2,3,5-triphenylphenol **2.15a**. This phenol can be oxidatively coupled to the highly hindered 2,2',3,3',5,5'-hexaphenylbiphenol **2.17a** using the procedure we have described for the preparation of diphenoquinones from 2,6-disubstituted phenol [17]. In this case, because of steric hindrance, the central rings cannot be coplanar and presumably the oxidized product exists as a bisphenoxy radical **2.16a** or **2.16b** which in contrast to the diphenoquinones is extremely soluble in nonpolar solvents. From 2,6-diphenyl-3-methylphenol **2.15b** was prepared, using identical methodology from crotonaldehyde and dibenzylketone, the corresponding biphenol **2.17b**.

These biphenols are highly hindered. The molecular models of 3,3',5,5'-tetraphenylbiphenol **2.12** and 2,2',3,3',5,5'-hexaphenylbiphenol **2.17a** are shown in Figure 2.1 and 2.2 were obtained from CHEM 3D [19]. These models indicate that the structures are very rigid and noncoplanar. The effect of substituents at positions 2,2',6',6' on the dihedral angles and the rotational barriers of biphenols is well documented [20].

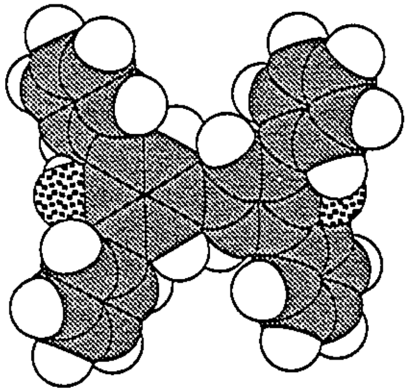


Figure 2.1 Molecular model of **2.12**

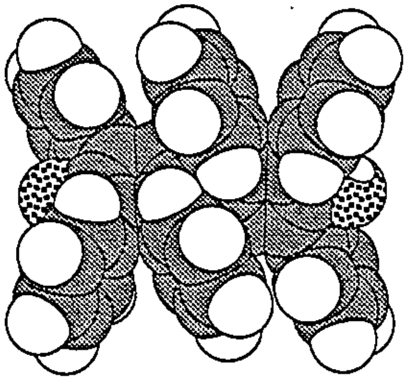


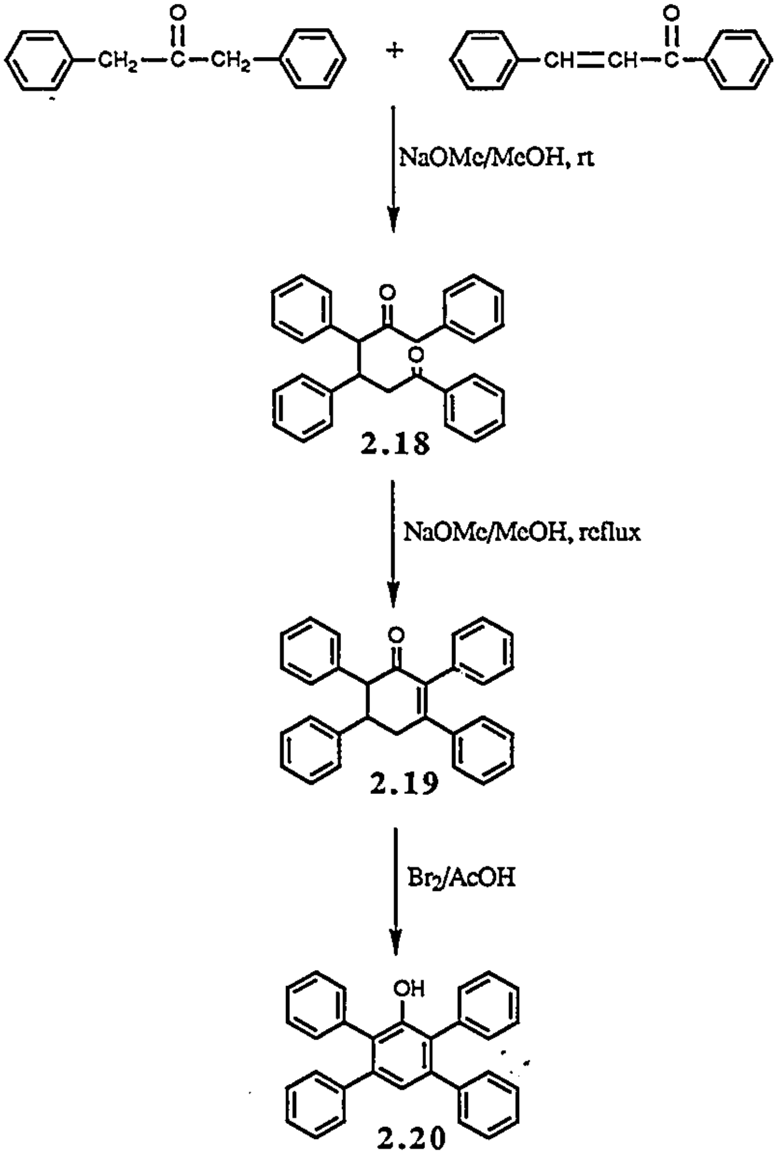
Figure 2.2 Molecular model of **2.17a**

The dihedral angles in these compounds are 90° and rotational barriers are high even when the substituents are relatively small such as in 2,2'-difluoro-6,6'-dimethoxybiphenyl (E_{rot} $\approx$ 35-39 Kcal/mol) [21]. Disubstituted biphenyls are much more difficult to resolve because of their lower rotational barriers, which are in the 18-21 Kcal/mol range for 2,2'-dibromo, 2,2'-diiodo, and 2,2'-ditrifluoromethyl biphenyl [22]. The dihedral angle for biphenyl is 20° in solution [23], whereas 2,2'-disubstituted biphenyls in the vapor phase, in solution, and in the crystalline state range from 60° for 2,2'-difluorobiphenyl to 79° for 2,2'-diiodobiphenyl [24]. From Raman spectroscopy the dihedral angles of biphenyl, 2-methylbiphenyl, and 2,2'-dimethylbiphenyl are 25°, 60°, and 70°, respectively [25]. 3,3',5,5'-Tetraphenylbiphenol shows a slightly twisted conformation of the central biphenyl group as in the dihedral angle of biphenyl, but 2,2',3,3',5,5'-hexaphenylbiphenol has an almost 90° twisted conformation because of the large 2,2'-diphenyl substituents which also interact with phenyl substituents in the positions 3,3',5,5' positions. However, the phenolic hydroxyl groups should be available for the synthesis of poly(aryl ether)s. In 2,2'-methyl-3,3',5,5'-tetraphenylbiphenol **2.17b** and 2-chloro-3,3',5,5'-tetraphenylbiphenol **2.13** the phenylene units in the biphenyl moiety also cannot be coplanar giving a very rigid but very bulky molecule.

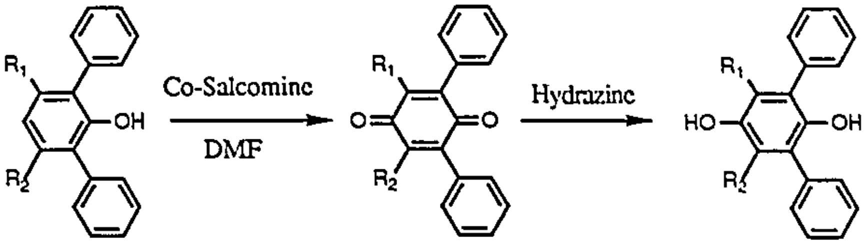
2.2.2 PREPARATION OF HYDROQUINONES

The 2,3,6-triphenylphenol **2.15a** and the 2,6-diphenyl-3-methylphenol **2.15b**, were prepared by condensation with 1,3-diphenylacetone, followed by dehydrogenation of the intermediate cyclohexenone **2.14a,b** (Scheme 2.4). The 2,3,5,6-tetraphenylphenol **2.20** was prepared as in the literature [26] with modifications which increased the yield and minimized the number of steps (Scheme 2.5). The 2,3,5,6-tetraphenyl-2-cyclohexenone **2.19** was synthesized by the Michael addition of 1,3-diphenylacetone and chalcone in methanol in the presence of excess sodium methoxide at room temperature to give 1,3,4,6-tetraphenyl-1,5-hexanedione **2.18** followed by heating with additional sodium methoxide (1 mol) which readily converted it to 2,3,5,6-tetraphenyl-2-cyclohexenone **2.20** via aldolization and dehydration. The 2,3,5,6,-tetraphenylphenol **2.20** was prepared by aromatization of **2.19** with one molar equivalent of bromine in acetic acid. When an excess of bromine was used for the oxidation, the 4-bromo substituted product resulted.

Scheme 2.5


CH2—C—CH2
O
+
CH=CH—C
O
NaOMe/MeOH, rt
2.18
NaOMe/MeOH, reflux
2.19
Br2/AcOH
OH
2.20

Scheme 2.6



2.21 **2.22**

2.21	2.22	R_1	R_2
a	a	H	H
b	b	CH_3	H
c	c	Ph	H
d	d	Ph	Ph

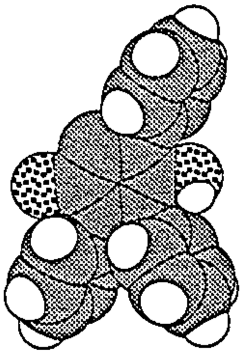


Figure 2.3 Molecular model of **2.22c**

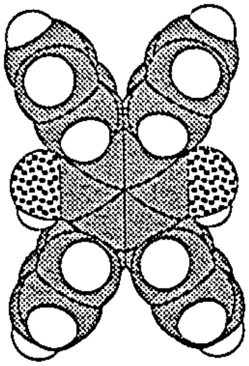


Figure 2.4 Molecular model of **2.22d**

Oxidation of phenols to benzoquinones has been achieved with a variety of oxidants [27, 28]. Recently, a new method of oxidation of 2,6-disubstituted phenols by hydrogen peroxide in the presence of bromine or hydrogen bromide as a catalyst has been reported [29]. However, in the case of highly hindered phenols, such as, 2,3,6-trisubstituted **2.15a,b** or 2,3,5,6-tetraphenylphenol **2.20** we were not able to utilize this method. It is known that 2,6-diphenylphenol **2.9** can be oxidized to 2,6-diphenylbenzoquinone in high yield with oxygen in the presence of N,N'-bis(salicylidene)-ethylenediaminocobalt(II) (Co-salcomine) as a catalyst [30]. This method was applied to the highly hindered phenols **2.9**, **2.15a**, **2.15b**, and **2.20** (Scheme 2.6). N,N'-bis(salicylidene)-ethylenediaminocobalt(II) (Co-salcomine) was prepared using the known procedure [31]. Oxidation of 2,3,5-trisubstituted phenols **2.15a**, **2.15b** was carried out with a catalytic amount of N,N'-bis(salicylidene)-ethylenediaminocobalt(II) and a large excess of oxygen was bubbled into the solution at about 55 °C. The quinones were obtained in 85-90% yields after recrystallization. Oxidation of 2,3,5,6-tetraphenylphenol **2.20** also gives the quinone, however, it was necessary to use a longer reaction time and higher temperature (about 90 °C) compared to the di or tri-substituted phenols. All of the quinones prepared **2.21a**, **2.21b**, **2.21c** and **2.21d** were reduced to the hydroquinones **2.22a**, **2.22b**, **2.22c** and **2.22d** in quantitative yields by treatment with hydrazine in hot chloroform or in a mixture of chloroform and methylene chloride. The molecular models of **2.22c** and **2.22d** show that the structures are very rigid (Figure 2.3 and 2.4). The quinones obtained have colors ranging between orange and red. The ultraviolet-visible spectrum of *p*-benzoquinone shows three bands at 250, 282 and 410 nm. The first two bands, 250 and 282 nm, have been assigned to a $\pi-\pi^*$ transition, while the broad and weak band at about 410 nm has been assigned to a n-π^* transition [32]. The substituted quinones prepared have similar spectra. The 2,6-diphenylquinone **2.21a** and 2,6-diphenyl-3-methylbenzoquinone **2.21b** in chloroform solution show three absorption bands at about 245 nm (strong and sharp), 295 nm (shoulder) and 340 nm (weak and broad). The corresponding 2,3,6-triphenylbenzoquinone **2.21c** and 2,3,5,6-tetraphenylbenzoquinone **2.21d** show changes in the position of two main bands with maxima at about 250 nm (strong and sharp), 360 nm (weak and broad).

2.3 THERMAL ANALYSIS OF BIPHENOLS

The ability of an organic compound to crystallize in several forms is far more frequent than is generally supposed. Polymorphism is thus a phenomenon whose theoretical and practical importance is considerable. The biphenols **2.12**, **2.13**, **2.17a**, and **2.17b** are chiral along the 1,1'-biphenyl axis. Their dissymmetry is molecular in nature, and enantiomer interconversion, in case of tetraphenylbiphenol **2.12**, is possible simply by rotation about the interannular bond rather than by a bond breaking process. In the case of the remaining biphenols **2.13**, **2.17a**, **2.17b** it is impossible to rotate about this bond because of steric hindrance by 2 or 2,2' substituents. The biphenol **2.17a** shows two melting points at 248 °C and 259 °C and the other biphenols **2.12**, **2.13**, **2.17b** have single melting points. A similar behavior has been noted for binaphthyl which forms two crystalline structures (mp 145 and 158 °C) (Figure 2.5) [33] . The low melting form, mp 145 °C, is known from X-ray structural analysis to belong to a centrosymmetric space group with a unit cell consisting of two molecules having R configuration and two having S configuration; i.e., the low melting form is a racemic compound and is, of course, optically inactive [34]. The high melting form, mp 158 °C, is an eutectic mixture of individual R and S crystals rather than a solid solution or a second racemate, and shows optical activity.

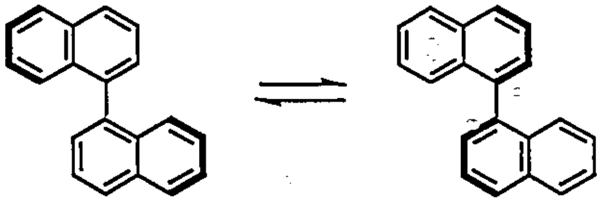

(R)-(-)-1,1'-binaphthyl (S)-(+)-1,1'-binaphthyl

Figure 2.5 Interconversion of binaphthyl

We studied the biphenols by a differential thermal analysis (DTA) in the range of 25 °C to 320 °C at heating rate of 10 °C/min (Figure 2.6 and 2.7). Upon heating, different curves can be obtained according to the history of sample and the speed of the crystal-crystal transformation. A first heat of biphenols **2.12** and **2.17a** shows both endothermic and exothermic peaks. The exothermic peaks may be explained by crystal to crystal transformation (R and S) while biphenols **2.13**, **2.17b** only show endothermic peaks for their melting points. Biphenols **2.12**, **2.13** convert to the glassy states when the biphenols are cooled after the first heat and glass transition temperatures of 84 and 93 °C, respectively appeared during the second heating. During the second heat, the biphenol **2.17b** shows the same thermogram as in the first heat. In the case of biphenol **2.17a** a glass transition temperature was observed at 126 °C followed by an exothermic peak at 192 °C, which may be crystal to crystal transformation, and a single melting point at 265 °C. It has been reported that such a phenomenon affects monotropic as well as enantiotropic systems [35]. These crystals are subsequently transformed into the stable form either while standing in contact with the liquid (either solution or melt) or upon heating of the solid to an appropriate temperature.

Table 2.1 Thermal analysis of Biphenols

Biphenols	1 st-run	2-nd run	Comments
2.12	Texo 153 °C mp 200 °C	Tg 91 °C	glass state (after 1st heating)
2.13	mp 210 °C	Tg 100 °C	glass state (after 1st heating)
2.17a	Texo 171 °C mp 248, 259 °C	Tg 121 °C Texo 192 °C mp 259 °C	two crystals, single crystal (after 1st heating)
2.17b	mp 283 °C	mp 284 °C	single crystal (before and after 1st heating)

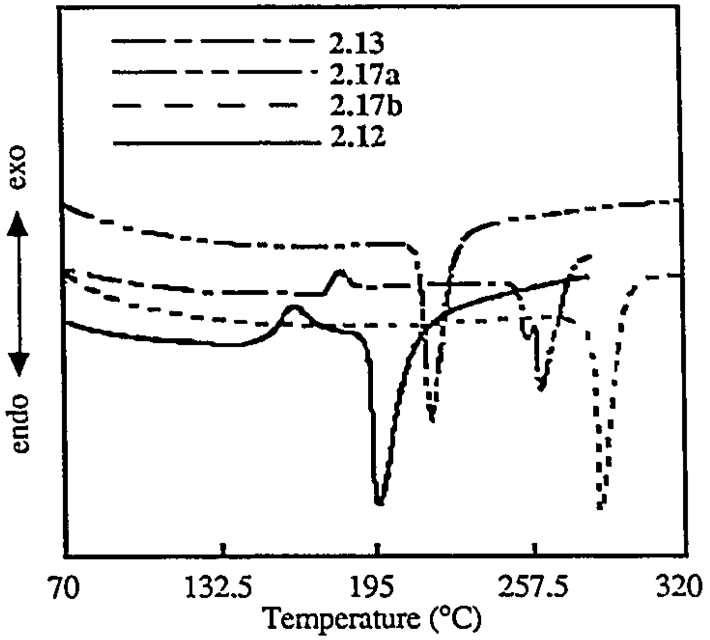


Figure 2.6 DTA traces (1st heating) were performed at a heating rate of 10 °C/min.

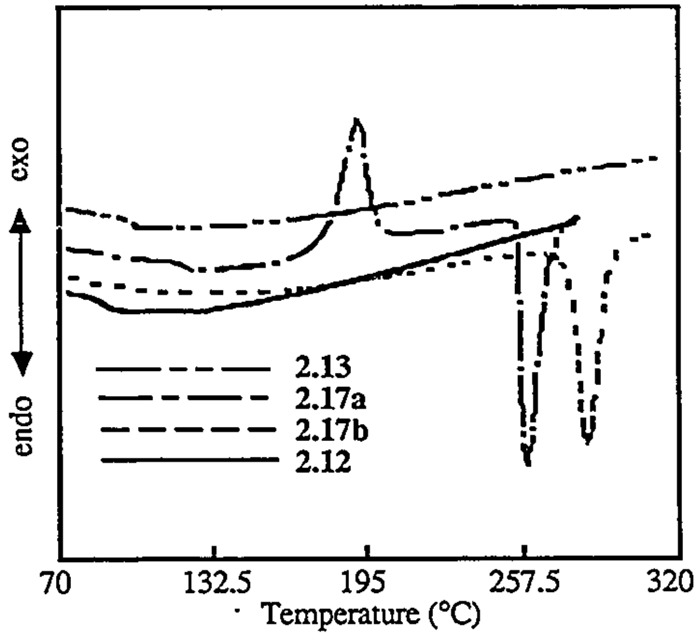


Figure 2.7 DTA traces (2nd heating) were performed at a heating rate of 10°C/min.

2.4 EXPERIMENTAL

General Methods

^{1}H NMR spectra were taken in $CDCl_3$ solution on a Varian XL-200 instrument, and chemical shifts are given in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were recorded on a ZAB 2F HS spectrometer, ion source 240 °C and 70 eV electron impact, direct inlet: *m/z* (assignment). Melting points were determined on a Fisher-Johns melting point apparatus. Elemental analyses were performed by Galbraith Laboratories Inc. UV spectra were performed on a SP 800 Unicam ultraviolet spectrophotometer with a deuterium lamp. In experiments requiring dry solvent, DMF was dried by shaking with 3 Å molecular sieves. Pure 2,6-diphenylphenol was supplied by the General Electric Company. 1,3-Diphenylacetone, butyronitrile and chalcone were purchased from Aldrich Chemical Co.. Common reagents, e.g. copper chloride, sodium methoxide, hydrazine monohydrate (98%) and bromine (Aldrich) were used without further purification.

2.4.1 SYNTHESIS OF BIPHENOLS

3,3',5,5'-Tetraphenylbiphenyl-4,4'-diol (2.12) [16]

A three necked 1 L flask equipped with a mechanical stirrer, a condenser and two adapters for oxygen inlet and outlet was charged with 2,6-diphenylphenol **2.8** (50g, 0.20 mol) and copper (I) chloride (0.5g, 5 mmol) in butyronitrile (500 mL) and heated at 100 °C for 8 h, and the reaction was monitored by HPLC. The mixture was cooled and filtered. The resulting violet product was dissolved in hot chloroform and filtered to remove CuCl. The filtrate was evaporated and the recovered solid recrystallized from chloroform/methanol to yield **2.11** (40g, 82 %); mp 290 °C (lit. 290 °C). The resulting product was reduced with hydrazine (2 mL) in hot chloroform and the color changed to light yellow. The mixture was filtered and the recovered product recrystallized from chloroform/methanol to give the corresponding biphenol **2.12**; mp 198-200 °C (lit. 196 °C).

MS (EI) *m/z* : 490 (M^+).

Elemental analysis (%). Calculated for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 87.98; H, 5.61.

^{1} H NMR (200 MHz, $CDCl_3$) δ 5.42 (s, 2 H, OH), 7.41-7.66 (m, 24 H, ArH).

2-Chloro-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol (2.13)

Biphenol **2.13** was prepared following a literature procedure [17]. In a 1 L three neck round bottomed flask 3,3',5,5'-tetraphenyldiphenoquinone (30g, 61.35 mmol) was dissolved in chloroform (600 mL) and methanol (200 mL) under nitrogen atmosphere at room temperature. Gaseous hydrogen chloride was bubbled into the stirred suspension for 6 h, whereupon the red solution became colorless. The solvents were distilled off to yield a white solid, which was recrystallized in chloroform/methanol; mp 207-210 °C (lit. 208-210 °C).

MS (EI) *m/z* : 524 (M^+).

Elemental analysis (%). Calculated for $C_{36}H_{25}O_2Cl$: C, 82.35; H, 4.80; Cl, 6.75. Found: C, 81.79; H, 5.02; Cl, 6.68.

^{1} H NMR (200 MHz, $CDCl_3$) δ 5.11 (s, 1 H, $C_4O\underline{H}$), 5.48 (s, 1 H, $C_{4'}O\underline{H}$), 7.32-7.74 (m, 23 H, ArH).

2,2',3,3',5,5'-Hexaphenylbiphenyl-4,4'-diol (2.17a)

The literature procedure for the preparation of 2,3,6-triphenylphenol was modified as follows. The 2,3,6,-triphenol **2.15a** was prepared following the known procedure [18]. Diphenylacetone (11.36 g, 54 mmol), cinnamaldehyde (7.14 g, 54 mmol) and diethylamine (5 mL) were stirred slowly at room temperature. The reaction is exothermic, and the product forms a yellow deposit on the side of the flask. The resulting 2,3,5-

triphenylcyclohex-2-enone **2.14a** was recrystallized in ethanol (15.9 g, 91 % yield); mp 131-133 °C. This ketone reacted with 5% Pd on carbon (1 g) on heating to 260 °C for 30 min. The mixture was allowed to cool, the organics were dissolved in hot ethyl acetate and filtered. The white product crystallized during the cooling to yield 2,3,6-triphenylphenol (69 %); mp 164 °C. This phenol **2.15a** (5g) was stirred in butyronitrile (50 mL) with CuCl (0.4 g) while bubbling oxygen at 100 °C for 8h. The reaction mixture was cooled and filtered to remove the catalyst. The filtrate containing a mixture of biphenols and biphenoxyradical was evaporated. The residue was reduced with hydrazine (0.5 mL) in chloroform (50 mL) and acetic acid (10 mL) at reflux temperature. The reaction mixture became colorless, was filtered and the solvent was distilled. The crude product was recrystallized in methanol and chloroform; mp 248, 259 °C.

MS (EI) *m/z* : 642 (M^+).

Elemental analysis (%). Calculated for $C_{48}H_{34}O_2$: C, 89.69; H, 5.33. Found: C, 89.82; H, 5.76.

^{1} H NMR (200 MHz, $CDCl_3$) δ 5.06 (s, 2 H, OH), 6.96-7.37 (m, 32 H, ArH).

2,2'-Dimethyl-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol (2.17b)

Dibenzylketone (100 g, 0.48 mol) and acrolein (33.3 g, 0.48 mol) were stirred with diethylamine (50 mL) at room temperature for 3 h. The crude residue was purified by Kugelrhor distillation under vacuum at 100 °C and recrystallized from methanol to yield 3-methyl-2,6-diphenylcyclohex-2-enone **2.14b** (101 g, 85%); mp 99-101 °C. This ketone (80 g, 0.32 mol) was dehydrogenated in the presence of 4g of 5 wt. % palladium on carbon catalyst for 20 min at 260 °C. The reaction mixture was cooled and extracted with hot ethanol and the catalyst was removed by filtration. The solvent was evaporated under reduced pressure and the recovered solid was recrystallized from hexane to yield 2,6-diphenyl-3-methylphenol **2.15b** (65.1 g, 83%); mp 130-131 °C. ^{1} H NMR (200 MHz, $CDCl_3$) δ 2.12 (s, 3 H, CH_3), 5.01 (s, 1 H, OH), 6.95-7.71 (m, 12 H, ArH). This phenol **2.15b** (50 g, 0.19 mol) was treated with CuCl (3.8 g) and butyronitrile (400 mL). The reaction was heated to 100 °C while bubbling oxygen through for 4 h. A white solid precipitated during the reaction. The heterogeneous solution was cooled and filtered. The precipitate was recrystallized from ethanol and chloroform to yield **2.17b** (44.6 g, 85 %); mp 281-283 °C.

MS (EI) *m/z* : 518 (M^+).

Elemental analysis (%). Calculated for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83. Found: C, 87.21; H, 5.80.

^{1} H NMR (200 MHz, $CDCl_3$) δ 1.87 (s, 6 H, methyl), 4.96 (s, 2 H, OH), 7.23-7.63 (m, 22 H, ArH).

2.4.2 SYNTHESIS OF HYDROQUINONES

N,N'-Bis-(salicylidene)-ethylenediaminocobalt(II) (Salcomine)

The salcomine was prepared following the literature procedure [31]. To a solution of salicylaldehyde (1.1 mol) in ethanol (100 mL) was added dropwise ethylenediamine (0.55 mol) in ethanol (40 mL) while stirring at room temperature. Immediately a yellow precipitate was formed. After the addition was completed stirring was continued for 1/2 h at 80 °C. Then the reaction product was filtered, washed with cold ethanol, and dried. The Shiff base was obtained in 96 % yield; mp 125-127 °C (lit. 125-125.5 °C).

To a solution of the imine (0.5 mol), sodium hydroxide (1 mol), and sodium acetate (2.5 g) in boiling water (1.5 L) there was added while stirring $CoCl_2 \cdot 6H_2O$ (0.5 mol) in water 250 mL). The reaction was heated on a water bath and a red-brown precipitate was formed. The reaction product was filtered, washed with water (3 x 250 mL) and ethanol (2 x 100 mL), and dried in vacuum at 100 °C. The salcomine was obtained in 93 % yield.

2,6-Diphenyl-1,4-quinone (2.21a)

The 2,6-diphenylphenol (20 g, 82.20 mmol) was dissolved in DMF (150 mL) and the solution was heated to 45 °C. N,N'-bis-(salicylidene)-ethylenediaminocobalt(II) (2.0 g, 6.15 mmol) was added as a catalyst and oxygen gas was bubbled through the solution for 4 h. After cooling, the mixture was poured into crushed ice (250 mL) containing 4 N hydrochloric acid (15 mL). The orange-red precipitate was filtered, washed with water (3 x 100 mL) and dried in vacuum. The crude 2,6-diphenyl-1,4-benzoquinone **2.21a** was recrystallized from n-butanol (89% yield); mp 135-137 °C.

MS (EI) *m/z* : 260 (M^+).

Elemental analysis (%). Calculated for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65; Found: C, 82.94; H, 4.58.

λmax ($CHCl_3$) 246 nm, 296 nm, 340 nm.

2,6-Diphenylhydroquinone (2.22a)

The quinone **2.21a** (15 g, 57.6 mmol) and hydrazine (1 mL, 30 mmol) were heated in chloroform (150 mL) until the solution was colorless. The mixture was filtered and the chloroform was evaporated. The residue was recrystallized from toluene to give the title compound (95% yield); mp 180-181 °C.

MS (EI) *m/z* : 262 (M^+).

Elemental analysis (%). Calculated for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.76; H, 5.42.

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.65 (s, 1H, -OH unhindered phenol), 4.83: (s, 1H, -OH hindered phenol), 6.93-7.42 (m, 12 H, aromatic H).

2,6-Diphenyl-3-methyl-1,4-benzoquinone (2.21b)

The reaction was carried out using a procedure similar to that for **2.21a** using N,N'-bis-(salicylidene)-ethylenediaminocobalt(II) (2.5g, 7.69 mmol) at a temperature of 55 °C for 6

h. The crude product **2.21b** was recrystallized from acetone and methanol (85 % yield): mp 94-96 °C.

MS (EI) *m/z* : 274 (M^+).

Elemental analysis (%). Calculated for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.15; H, 5.04.

λmax ($CHCl_3$) 246nm, 294nm, 336nm.

2,6-Diphenyl-3-methylhydroquinone (2.22b)

The reduction of 2,6-diphenyl-3-methyl-*p*-benzoquinone **2.21b** was accomplished with hydrazine in hot chloroform. The resulting product was recrystallized from benzene (92 % yield); mp 149-151 °C.

MS (EI) *m/z* : 276 (M^+)

Elemental analysis (%). Calculated for $C_{19}H_{16}O_2$, C, 82.58; H, 5.84. Found: C, 82.05; H, 5.80.

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 3 H, $-CH_3$), 4.67 (s, 1 H, -OH, unhindered), 4.84 (s, 1 H, -OH, hindered), 6.83-7.68 (m, 14 H, aromatic H).

2,3,6-Triphenyl-1,4-benzoquinone (2.21c)

A procedure similar to that for **2.21a** using DMF (200 mL), N,N'-bis-(salicylidene)-ethylenediaminocobalt(II) (3.5g, 10.76 mmol) and a reaction temperature of 55 °C for 10 h was used. After recovery, the crude product **2.21c** was recrystallized from acetone (83 % yield), mp 156-157 °C.

MS (EI) *m/z* : 336 (M^+).

Elemental analysis (%). Calculated for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.57; H, 4.73.

λmax ($CHCl_3$) 246nm, 352nm.

2,3,6-Triphenyl-hydroquinone (2.22c)

Reduction of 2,3,6-triphenylbenzoquinone **2.21c** with hydrazine produced in chloroform the title compound which was recrystallized in methanol and chloroform (94% yield); mp 153-154 °C.

MS (EI) *m/z* : 338 (M^+).

Elemental analysis (%): Calculated for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36; found: C, 85.32; H, 5.29.

^{1} H NMR (200 MHz, $CDCl_3$) δ 4.68 (s, 1 H, -OH unhindered), 4.84 (s, 1 H, -OH hindered), 7.03-7.67 (m, 16 H, aromatic H).

2,3,5,6,-Tetraphenyl-2-cyclohexenone (2.19)

A previous procedure was modified as follows [26]. In methanol (220 mL) were dissolved 1,3-dibenzylketone (20.0 g, 95.11 mmol) and chalcone (benzalacetophenone) (20 g, 96.03 mmol). Then, sodium methoxide (5.2 g, 96.26 mmol) was added slowly. The mixture was stirred at room temperature for 1h under a nitrogen atmosphere. The suspension was treated with additional sodium methoxide (5.2 g, 96.26 mmoles) and methanol (100 mL) to give the ring closed product **2.18**. The mixture was heated at reflux for 3 h under nitrogen. During the reaction a white solid precipitated out of solution. The reaction mixture was cooled to room temperature and the resulting product was collected on a filter funnel and recrystallized from benzene-petroleum ether (91% yield), mp 158-159 °C (lit. 159-160 °C).

2,3,5,6-Tetraphenylphenol (2.20)

A procedure similar to that used previously was followed [26]. The 2,3,5,6-tetraphenyl-2-cyclohexenone (20 g, 49.94 mmol), acetic acid (400 mL) and bromine (7.9 g, 49.94 mmol) were heated to 70 °C for 7 h until the reaction mixture became colorless. A solid precipitated on cooling. The product was filtered and recrystallized from benzene-petroleum ether (80 % yield). mp 270-273 °C (lit. 272-273 °C).

MS (EI) *m/z* : 398 (M^+).

^{1} H NMR (200 MHz, $CDCl_3$) δ 5.30 (s, 1H, -OH), 7.17-7.38 (m, 21 H, aromatic H).

2,3,5,6-Tetraphenyl-1,4-benzoquinone (2.21d)

The procedure was essentially the same as used for **2.21a**. In DMF (500 mL) were dissolved 2,3,5,6-tetraphenylphenol (16 g, 40.15 mmol) and N,N'-bis-(salicylidene)-ethylenediaminocobalt(II) (4.5 g, 13.83 mmol). The reaction was then heated to 90 °C and oxygen was bubbled through the solution for 30 h. The mixture was added slowly to crushed ice water (1 L) containing 4 N HCl (50 mL) with stirring. The resulting crude product **2.21d** was recrystallized from chloroform-methanol, mp 317-318 °C.

MS (EI) *m/z* : 412 (M^+).

Elemental analysis (%): Calculated for $C_{30}H_{20}O_2$: C, 87.36; H, 4.89. Found: C, 87.36; H, 4.87.

λmax ($CHCl_3$) 250 nm, 370 nm.

2,3,5,6-Tetraphenylhydroquinone (2.22d)

Reduction of 2,3,5,6-tetraphenyl-*p*-benzoquinone **2.21d** with hydrazine in a mixture of chloroform and methylene chloride for 7 h gave 2,3,5,6-tetraphenylhydroquinone which was recrystallized from chloroform, mp 323-325 °C.

MS (EI) *m/z* : 414 (M^+).

Elemental Analysis (%). Calculated for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.71; H, 5.20.

^{1} H NMR (200 MHz, $CDCl_3$) δ 4.77 (s, 2 H, -OH), 7.07-7.13 (m, 20 H, aromatic H).

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CHAPTER 3

POLYSULFONES

3.1 INTRODUCTION

Aromatic polysulfones have achieved an excellent position among other thermoplastic polymers by virtue of their superior properties, such as thermal stability, high heat distortion temperatures, chemical inertness, electrical performance and flame retardancy [1,2,3]. Most aromatic poly(ether sulfone)s and related structures are amorphous resins and are soluble in common organic solvents. Since Udel® polysulfone resin [4] was commercialized by Union Carbide in 1966, the family of polyethersulfones have been extensively developed and studied. At present, many grades of these polymers are marketed under different names, such as, Udel® and Radel® (Amoco Co) [5], Victrex 720P® [6] and Victrex (ICI)® [6] etc. Commercial and related polysulfones [7,8] are listed in Table 3.1.

3.1.1 STRUCTURAL CHARACTERISTICS

The characteristic feature of poly(ether sulfone)s is the highly stable diarylsulfone groups. The sulfur atom is in its highest state of oxidation and the highly electronegative sulfone group in the para position (Figure 3.1) imparts to these resins excellent oxidative and thermal stability [9]. Poly(ether sulfone)s range in properties from moldable materials up to those that are intractable because of the high stiffening effects of the sulfone unit.

Table 3.1 Commercial and Related Poly(ether sulfone)s

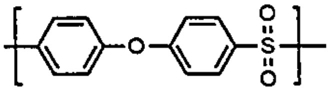
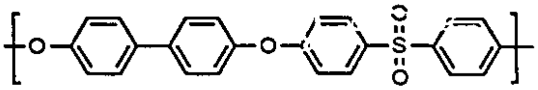
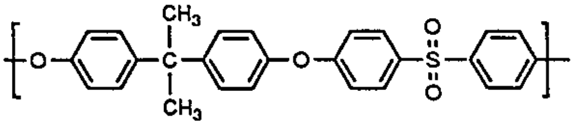
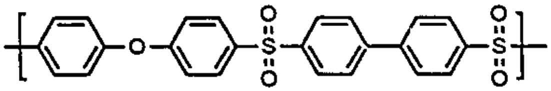
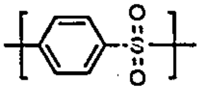
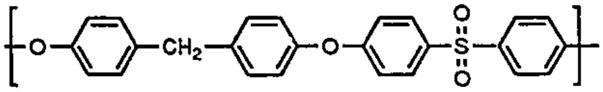
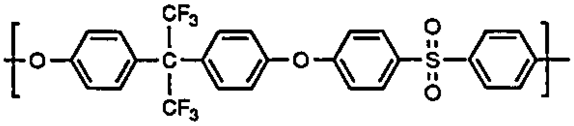
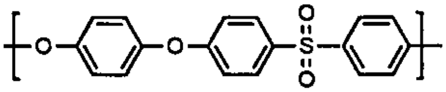
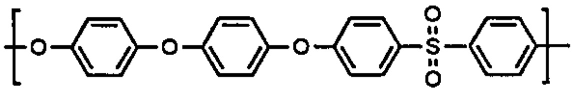
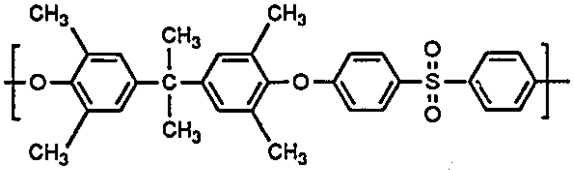
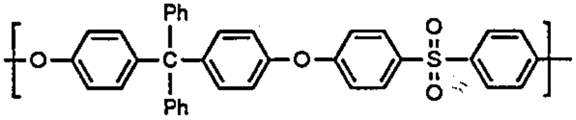
Polymers	Trade name/ Producer	Structure	T_g (°C)
3.1	Victrex (ICI)		230
3.2	Radel (Amoco Co)		232
3.3	Udel (Amoco Co)		190
3.4	720P (ICI)		250
3.5			-
3.6			180
3.7			205
3.8			210
3.9			180
3.10			235
3.11			230

Figure 3.1 The resonance structure of polyethersulfone

The presence of flexibilizing groups in the repeat unit is often desired for ease of processability. Ether groups in the above polymers (Table 3.1) contribute additional desirable properties. These links permit rotation of the adjacent chain sections, thereby improving the toughness of this class of resins and lowering the Tg. The isopropylidene group in Udel® 3.3 improves melt processability. High strength and modulus are imparted by the phenyl substituents in the backbone of the polymer. The linkages connecting the benzene rings are hydrolytically stable, therefore the polymers are resistant to degradation by moisture, aqueous acid and alkaline environments [10]. Polysulfone films are transparent, strong and rigid with high heat deflection temperatures. Their flammability ratings and smoke density ratings are among the best for thermoplastic resins [1,2].

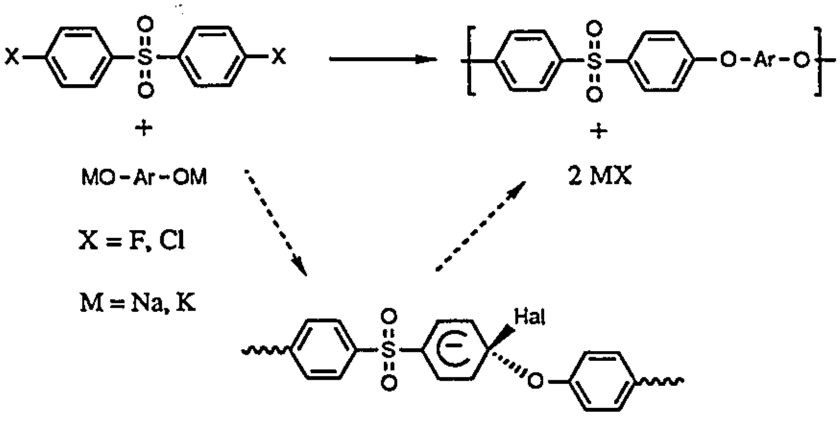
3.1.2 SYNTHESIS OF POLYARYLETHERSULFONES

Aromatic poly(ether sulfone)s can be produced by two different routes. In polyetherification the sulfone groups are present in the monomers and the ether linkages are formed in the polymerization step by a nucleophilic substitution reaction (Scheme 3.1). In polysulfonylation (Scheme 3.3) the aryl ethers are coupled through sulfone linkages by an electrophilic substitution reaction.

3.1.2.1 POLYETHERIFICATION

Aromatic poly(ether sulfone)s [7,11] are formed by nucleophilic aromatic displacement of halogen activated by the highly electron withdrawing sulfone group and salts of dihydroxyaromatic compounds prepared by reaction with NaOH or KOH. The nucleophilic displacement reaction of activated aromatic halides has been widely studied using a variety of phenol derivatives. The reaction proceeds via a Meisenheimer complex where the sulfone group acts to stabilize the negative charge from the ring [12] (Scheme 3.1). Aromatic halide reactivity and phenoxide basicity are strongly influenced, in opposite senses, by both the electron affinity and the position of aromatic substituents, and by their conjugative, inductive and steric effects. Electron withdrawal towards the sulfone groups is highly effective when the halogen is positioned ortho or para to the sulfone moiety. Attack on the ortho-halogen is likely to be subject to steric hindrance. Thus, halogen displacement would be expected to decrease in the order para>ortho>meta and F (312) >> Cl (1) > Br (0.74) > I (0.35) [13,14]. The formation of high molecular

Scheme 3.1

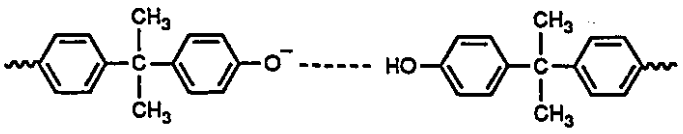


Meisenheimer complex

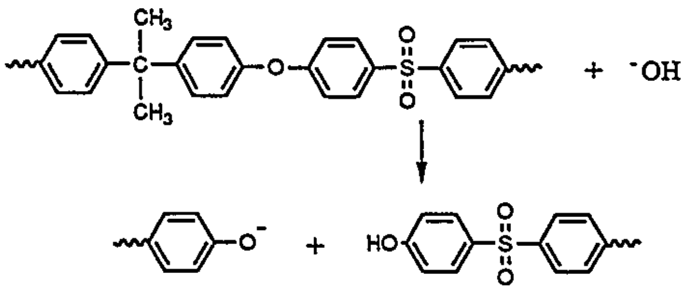
weight polymers depends on the accelerating effect of specific polar aprotic solvents, which are believed to selectively solvate the cations, thereby producing naked phenolate anions which have become more reactive. The solvents must be stable under the conditions of reaction and be capable of dissolving both the reactants and the polymer. Dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), N,N'-dimethyformamide (DMF) and N,N'-dimethylacetamide (DMAc) are commonly used polar aprotic solvents whereas, tetramethylene sulfone (sulfolane), is useful when high reaction temperatures are required [15].

For a reaction carried out with a strong base, such as sodium hydroxide, the exact stoichiometric amount is required to achieve high molecular weight polymer [16]. The presence of excess base is deleterious because under the reaction conditions polymer degradation may occur (Scheme 3.2). A deficiency of alkali not only disturbs the

Scheme 3.2



Hydrogen bonded complex under deficient base condition

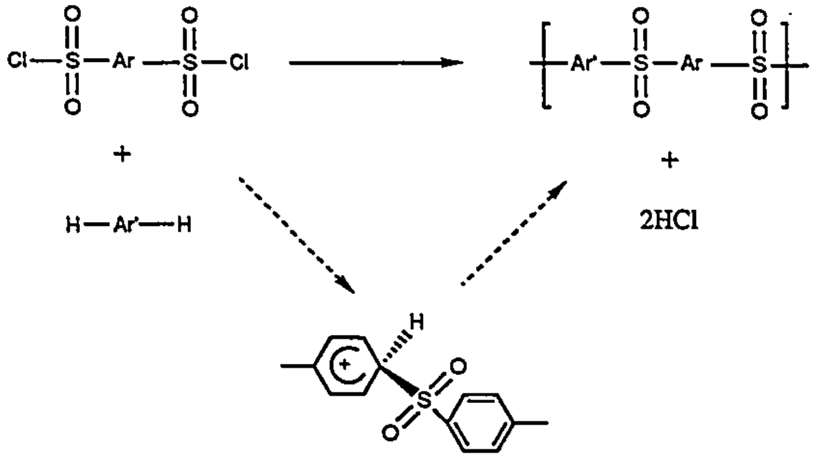


Cleavage of the activated ether linkage under excess base condition stoichiometry of the bisphenols to dihalo-compounds but excess of undeprotonated phenol gives rise to hydrogen bonding with concomitant deactivation of sodium phenolate. Tayor *et al* [17]. have developed a new method of preparation of poly(ether sulfone)s by employing potassium carbonate (K_2CO_3) in DMAc successfully to obtain high molecular weight polymers without side reactions and improved solubility of bisphenate under mild basic conditions. This reaction was carried out under nitrogen atmosphere. Anhydrous conditions were maintained by continuously removing water as an azeotrope with toluene.

3.1.2.2 POLYSULFONATION

Polysulfonylation routes to poly(arylene sulfone)s follow two different reaction routes, polycondensation of bischlorosulfonyl compounds with aromatics and self-polycondensation of monosulfonyl chlorides. Electron-releasing alkyl groups activate the aromatic nucleus towards electrophilic attack, whereas electron-withdrawing sulfonyl and acyl groups tend to hinder electrophilic attack of acid halide by deactivating the substrate. Multiple sulfonylations and acylations are, therefore, almost completely suppressed by the first linked sulfonyl or acyl moiety unless drastic reaction conditions or activated aromatic substrates are involved. The poly(aryl sulfone)s are formed by sequential reactions of the arylsulfonyl chloride groups with a second aromatic nuclus. This is a typical electrophilic aromatic substitution [18] in which the aromatic substrate is attacked by the arylsulfonylium cation and hydrogen is displaced as a proton. The sulfonylation mechanism proceeds in two stages as shown in Scheme 3.3 : attack of the sulfonylium cation $ArSO_2^+$ on the aromatic substrate with formation of an intermediate complex which subsequently loses a proton. It is assumed that the effective sulfonylating agent is the sulfonylium salt generated by the action of a Lewis-acid catalyst on the sulfonyl halide. The reaction is similar to the Friedel-Crafts acylation. The key to development of sulfonylation as a polymerization process [19] was the discovery that, unlike the acylation reaction which requires equimolar amounts of aluminum chloride or other strong Lewis acid, sulfonylation can be accomplished with catalytic amounts of $FeCl_3$, $SbCl_5$ or $InCl_3$ [20]. This is important as it eliminates side reactions, helps considerably with the problem of catalyst removal from the polymers and minimizes costs. The reactions are carried out in the melt or in suitable inert solvents such as acetonitrile. Successful application of the polysulfonylation reaction to polymer synthesis requires a high degree of para coupling. Chain branching or any substantial degree of ortho coupling without branching results in brittle products [21]. The polysulfonylation reactions can be applied to most compounds having two or more aromatic rings, e.g. biphenyl, diphenyl ether, naphthalene.

Scheme 3.3



Intermediate complex

3.1.3 STRATEGY AND GOALS

The methodology for increasing the glass transition temperature is the design of a rigid backbone using hindered substituents, and for maintaining solubility, the use of flexible kinks between the rigid backbones units [8,22]. Table 3.1 lists a number of poly(ether sulfone)s derived from a variety of biphenols. The polymers **3.3**, **3.6**, **3.7**, and **3.9** contain flexible ether or isopropyl links which reduce the glass transition temperature, whereas polymers **3.2**, **3.8** derived from the *p,p* '-biphenol or hydroquinone result in a very rigid system with a high glass transition temperature. The larger the substituent group, the greater the increase of glass transition temperature. For instance, the highly phenylated polymers synthesized by Stille via Diels-Alder polymerization [23] and the hindered polyethersulfones **3.10** derived from tetramethylbisphenol A studied by McGrath *et al* [24], in which the phenyl and methyl groups make chain rotation difficult results in a significant increase of glass transition temperature while retaining good solubility. The rigid polyesters [25] derived from trifluoromethyl-substituted biphenol are amorphous and maintain good solubility because of the 2,2'-substituents which provide non-coplanarity between the phenyl rings.

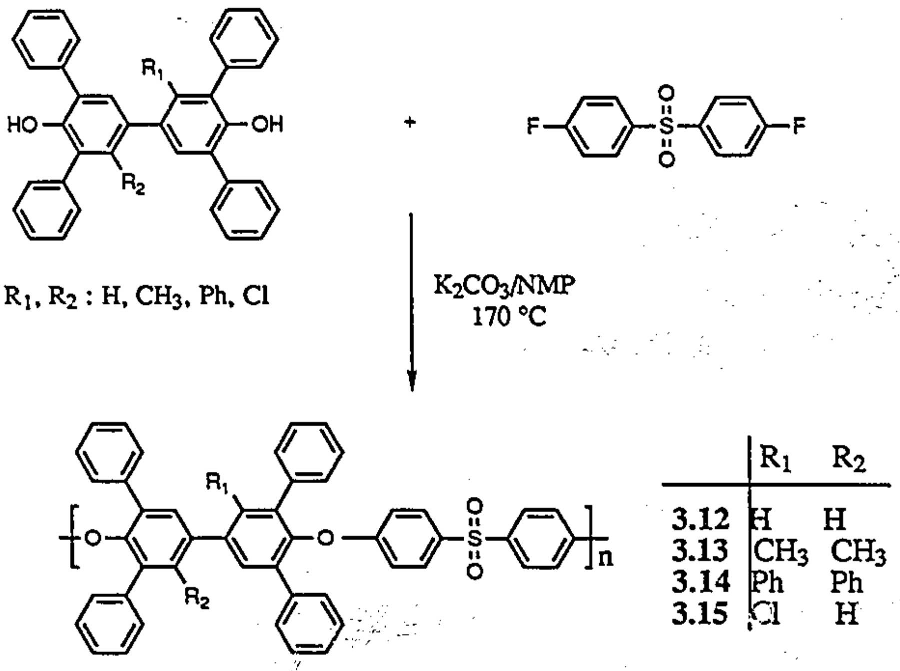
In this section we report the investigation of poly(ethersulfone)s of high molecular weight prepared from a wide variety of hindered biphenols (**2.12**, **2.13**, **2.17a** and **2.17b**) and hydroquinones (**2.22a**, **2.22b**, **2.22c** and **2.22d**) by reaction with 4,4'-difluorodiphenylsulfone via a nucleophilic aromatic displacement reaction in polar aprotic solvents in the presence of potassium carbonate. The solubility, glass transition temperatures, thermal stability and mechanical stability of the polymers will be discussed.

3.2 PREPARATION OF POLYSULFONES

3.2.1 PREPARATION OF POLYSULFONES FROM BIPHENOLS

Three dimensional molecular models indicate that hindered biphenols (**2.12**, **2.13**, **2.17a**, and **2.17b**) and hydroquinones (**2.22a**, **2.22b**, **2.22c**, and **2.22d**) possess highly hindered structures. However the phenolic hydroxyl groups should be sufficiently accessible to act as nucleophiles. We were able to prepare high molecular weight

Scheme 3.4



R_1, R_2 : H, CH_3, Ph, Cl

	R_1	R_2
3.12	H	H
3.13	CH_3	CH_3
3.14	Ph	Ph
3.15	Cl	H

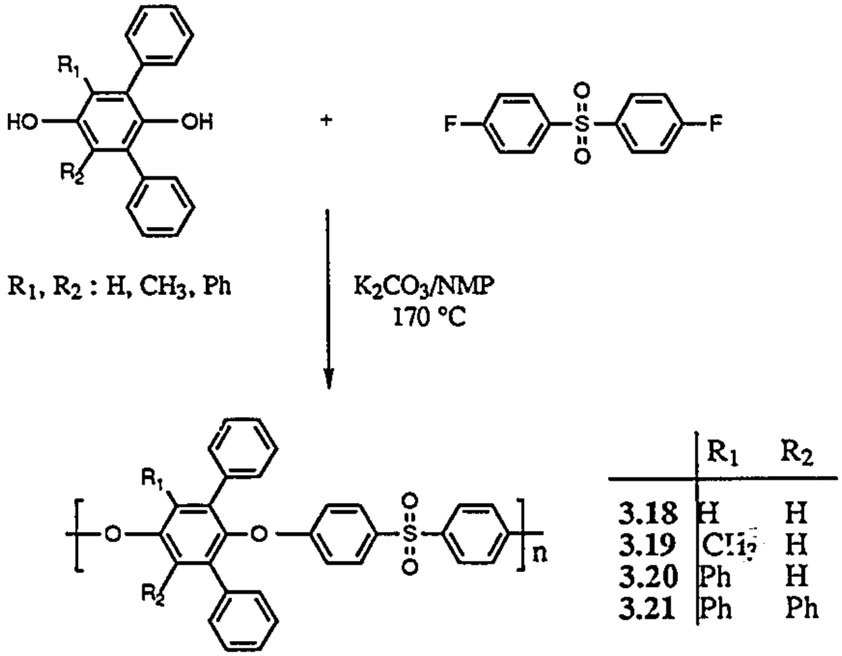
polymers by reacting the biphenols with 4,4'-difluorodiphenyl sulfone using potassium carbonate as the base in NMP. The reactions were slowly heated at 150 °C until no further water was collected as the azeotrope with the added toluene. Toluene was then removed and the temperature maintained at 170 °C. The copolymers were prepared using a 1:1 ratio of 2,2'-substituted biphenols (**2.17a** and **2.17b**) and 3,3',5,5'-

tetraphenylbiphenol (**2.12**) with 4,4'-difluorodiphenylsulfone under the same conditions. The polymerization reactions with these highly hindered biphenols, because of steric crowding by the 3,3',5,5'-tetraphenyl substituents, are very slow requiring as long as two days to attain reasonable molecular weights and yields were generally 85-90 %.

3.2.2 PREPARATION OF POLYSULFONES FROM HYDROQUINONES

With these highly hindered hydroquinones the polymerizations were carried out under the same conditions as with the hindered biphenols. The reactions required long reaction times (7-40 h) to achieve reasonable molecular weight polymers in high yield (85-90%). Polymers **3.18**, **3.19**, and **3.20** prepared from the 2,6- and 2,3,6-substituted

Scheme 3.5



	R_1	R_2
3.18	H	H
3.19	CH$_3$	H
3.20	Ph	H
3.21	Ph	Ph

hydroquinones **2.22a**, **2.22b**, **2.22c** are completely amorphous. However the poly(ether sulfone) **3.21** from 2,3,5,6-tetraphenylhydroquinone **2.22d** is semi-crystalline and precipitates out of solution during the polymerization, even in tetramethylene sulfone at 220 °C after 2 h. The polymerization reactions with 2,6-diphenyl-3-methylhydroquinone **2.22b** proceed much faster and this effect can be explained in part by the lower acidity of the phenolic moiety influencing the rate [26]. Substitution of methyl groups for hydrogen or phenyl groups would decrease the acidity of the hydroquinone and hence increase the nucleophilicty of the anion. The size of the methyl group is also smaller than a phenyl group which reduces steric hindrance of the hydroxyl group thereby increasing the rate of reaction.

3.3 RESULTS AND DISCUSSION

3.3.1 SOLUBILITY AND PROPERTIES

Most of the polyethersulfones derived from hindered biphenols and hydroquinones are amorphous and soluble in common organic solvents such as methylene chloride, chloroform, NMP and DMSO at room temperature. However polymer **3.21** obtained from the symmetrically substituted hydroquinone **2.22d** is not soluble in common organic solvents even at high temperature, but is soluble in hot benzophenone and diphenylsulfone.

The polymers derived from biphenols and hydroquinones have inherent viscosities ranging from 0.13-0.83 and 0.31-0.98 dL/g, respectively. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) in chloroform solution using polystyrene standards. These polymers had molecular weights (Mw) in the range of 11,300-213,900 and a polydispersity (Mw/Mn) of 1.69-5.18. The viscosity of polymer **3.21** could not be measured because of the poor solubility.

3.3.2 Tg AND Tm OF HOMOPOLYMERS AND COPOLYMERS

The thermal behavior (Tg, Tm, and Tc) of the polymers was investigated by differential scanning calorimetry (DSC). Most polymers show high glass transition temperatures which can be attributed to the phenyl substituents in the 3,3'- and 5,5'- positions, which increase the difficulty of chain rotation (Table 3.2 and Figure 3.2). The polymer **3.14** shows a lower Tg, presumably because it is low molecular weight. The polymer **3.13** from biphenol **2.17b** which contains two methyl groups in 2,2'-positions has a Tg of 284 °C which is 52 °C higher than that of Radel **3.2** (Tg=232 °C) [5] and also 49 °C higher than the polymer **3.10** derived from 3,3',5,5'-tetramethyl BPA (Tg=235 °C) [23]. Tg's of the prepared copolymers **3.16, 3.17** determined from DSC are in agreement with calculated values (see Table 3.2). These values are approximately at the middle points of the two homopolymer's glass transition temperatures.

The Tg's of polymers derived from the hindered hydroquinones increase gradually with addition of substituents, in the order, H < methyl < phenyl < diphenyl, in the 5- or 5, 6-positions as shown in Table 3.3. The highest Tg value of 265 °C was obtained for polymer **3.21** which contains four phenyl substituents on the phenyl ring. The tetraphenyl substituted polymer **3.21** is semicrystalline and the DSC showed Tg (265 °C), Tc (300 °C), and Tm (411 °C). The Tg of polymer **3.21** did not increase as much as we expected, perhaps due to the low molecular weight of the polymer. The glass transition temperature of polymer **3.18** derived from hydroquinone **2.22a** only increased about 17 °C compared to that of the unsubstituted polysulfone **3.8** (Tg=210 °C) [27].

3.3.3 THERMAL STABILITY

Thermooxidative stability of the polymers was studied using thermogravimetric analysis (TGA). The properties of the homo polymers and copolymers prepared are summarized in Table 3.2 and Table 3.3. Most of the polymers show excellent thermal stability at high temperature in air and nitrogen atmosphere. The homopolymers containing methyl substituents in the 2,2' positions of the biphenol have lower thermooxidative stability with 5% weight loss at about 452-470 °C compared to the completely aromatic polymers which have 5 % weight loss above 510 °C (Figure 3.3). The copolymers (**3.16**, **3.17**) also showed relatively low thermooxidative stability because of the effect of methyl groups in polymer **3.16**, and probably very low molecular weight in polymer **3.17**.

In polymers derived from the hydroquinones, the polymer **3.19** containing methyl substituents on the arylene also has a lower thermooxidative stability with 5% weight loss at about 450 °C. The wholly phenylated polymers **3.18**, **3.20**, and **3.21** have higher thermooxidative stability with 5 % weight loss temperatures in the range of 505 to 540 °C.

3.3.4 MECHANICAL PROPERTIES

Transparent and tough polymer films were cast from chloroform solution (100 mg/5 mL). Their mechanical properties were measured by thermomechanical analysis (TMA). The polymer films maintained their excellent dimensional stability over a wide range from ambient temperature to their Tg as shown in the TMA curves (Table 3.4 and Figure 3.4). The glass transition temperatures obtained by themomechanical analysis were in agreement with those obtained from DSC. The Young's moduli are in the range of 1.48

to 2.11 GPa at room temperature and 1.05 to 1.82 GPa at a temperature 40 °C below the polymer glass transition temperatures.

3.4 CONCLUSION

New classes of polysubstituted biphenols containing methyl, phenyl, or chloro substituents in the 2,2' positions and hindered hydroquinones (di, tri, and tetra-substituted) containing methyl, or phenyl substituents were polymerized with 4,4'-difluorophenylsulfone in NMP in the presence of excess anhydrous potassium carbonate. The polymerization rates are low because of steric hindrance due to the pendent phenyl or methyl groups on the biphenols or hydroquinones. The amount of time required for the reaction to reach completion is approximately 5 times that for unhindered biphenols or hydroquinones. The polymers are amorphous and exhibit good solubility in common organic solvents. The pendent phenyl groups and the 2,2' substituents affect the properties of polymers, but polymer **3.21** derived from the tetraphenyl substituted hydroquinone **2.22d** is semicrystalline and not soluble in common organic solvents. The polymers show significantly increased Tg's compared to the unsubstituted polymers. The methyl substituted homopolymer and copolymers exhibit lower thermooxidative stability than those of the corresponding polymers having pendent phenyl groups. Films cast from these polymers exhibit excellent dimensional stability in the temperature ranges from room temperature to close to their glass transition temperatures.

3.5 EXPERIMENTAL

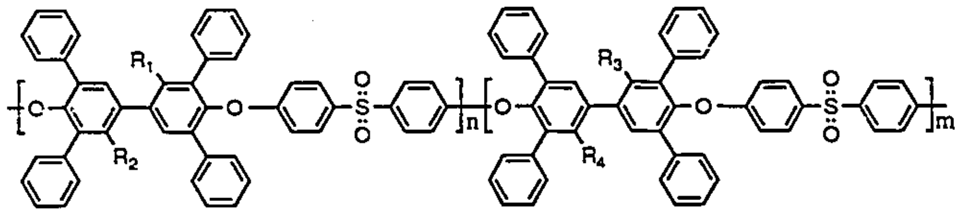
General Polymerization: Synthesis of 3.13

To a 50 mL three-necked round-bottom flask, fitted with a condenser, Dean-Stark trap and nitrogen inlet, were added 4,4'-difluorodiphenylsulphone (0.64g, 2.5 mmol) and 2,2'-dimethyl-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol **2.17b** (1.30g, 2.5 mmol) in N-methyl-2-pyrrolidinone (NMP) (5 mL). Toluene (3 mL) was added along with potassium carbonate (3.25 mmol). The reaction mixture was stirred vigorously and heated to reflux at 150 °C. The reflux was maintained for 4 h until no more water droplets separated. Toluene was then removed continuously from the Dean-Stark trap until the temperature rose to about 170 °C. The reaction temperature was maintained for 50 h. At this time the solution was very viscous. The reaction was checked by using high pressure liquid chromatography (HPLC) to demonstrate the absence of starting materials. The solution first became yellow (65 °C), then green, and finally dark green. The reaction mixture was cooled to 110 °C and NMP (3 mL) was added to dilute the highly viscous solution. The mixture was precipitated in methanol containing 4 wt. % HCl solution to give a white fibrous polymer (85 % yield). The ^{1}H NMR of this polymer showed a methyl peak at 1.9 ppm and the spectrum showed the expected 5:1 ratio of hydrogens (phenyl to methyl).

Polymer characterization

Inherent viscosities were measured using a Ubbelohde viscometer at a concentration of 0.5 g/dL in $CHCl_3$ at 25 °C. Molecular weights of polymers were determined relative to polystyrene standards by gel permeation chromatography (GPC) in $CHCl_3$ as solvent on a Waters 510 HPLC with a set of four µstyragel columns (500, 10^4, 10^5, and 100 Å) in series and a UV detector. Differential scanning calorimetry (DSC) and themogravimetric analyses (TG) were performed with a Seiko 220 DSC at a heating rate of 20 °C/min with a gas flow rate of 50 mL/ min and a Seiko 220 TG/DTA instrument at a heating rate of 10 °C/min with a gas flow rate of 200 mL/min respectively under nitrogen and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument from 25 °C to 350 °C with a heating rate of 3 °C/min in static air. The polymer films for the mechanical analyzer were cast from chloroform solution (100 mg/5mL) on a glass plate (3 cm diameter) by evaporation of solvent at room temperature for 48 h and dried at 100 °C for 24 h. Film thickness was measured with a micrometer.

Table 3.2 Physical and Thermal Properties of Polysulfones of Biphenols



Polymers	R_1	R_2	R_3	R_4	Tg[a]/Tg[b] (°C)	TGA[c](°C) N_2/Air	ηinh[d] (dL/g)	Mw[c]/10^3	Mw/Mn
3.12	H	H	H	H	261	535/525	0.33	59.3	2.00
3.13	CH_3	CH_3	CH_3	CH_3	284	501/475	0.83	213.9	5.18
3.14	Ph	Ph	Ph	Ph	256	553/531	0.18	36.4	2.29
3.15	Cl	H	H	Cl	273	535/526	0.19	44.5	1.69
3.16	CH_3	CH_3	H	H	277/272	495/480	0.42	89.4	2.09
3.17	Ph	Ph	H	H	253/258	505/475	0.13	11.3	3.03

[a] Tg was determined by DSC at heating rate 20 °C/min under nitrogen (50 mL/min).

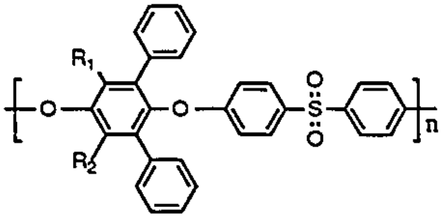
[b] Tg was calculated from the equation $1/Tg^{AB}=w_A/Tg^A + w_B/Tg^B$.

[c] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min).

[d] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

[c] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

Table 3.3 Physical and Thermal Properties of Polysulfones of Hydroquinones



Polymers	R_1	R_2	r.t*(h)	Tg^a(°C)	Tc(°C)	Tm(°C)	TGA^c(°C) N_2/Air	ηinh^d	$Mw^e/10^3$	Mw/Mn
3.18	H	H	20	227			508/504	0.98	68.5	2.4
3.19	CH_3	H	7	235			473/449	0.94	51.6	2.5
3.20	Ph	H	40	240			515/511	0.31	31.1	2.1
3.21	Ph	Ph	2	265	300	441	505/502	-	-	-

[a,c,d,e] Footnotes are identical to those in Table 3.2.

* Reaction time

Table 3.4 Mechanical Properties of Polysulfones

Polymers	Y.M[a](GPa)	Tg[b](°C)(DSC)	Tg[c](°C)(TMA)
3.12	1.61	261	260
3.13	1.67	284	280
3.16	1.48	277	270
3.18	2.02	227	218
3.19	1.97	235	228
3.20	2.11	240	231

[a] Young's Modulus measurement was performed on Seiko TMA/SS at room temperature.

[b] Temperatures were recorded from DSC results.

[c] Temperatures were recorded where the tan δ curve shows a maximum.

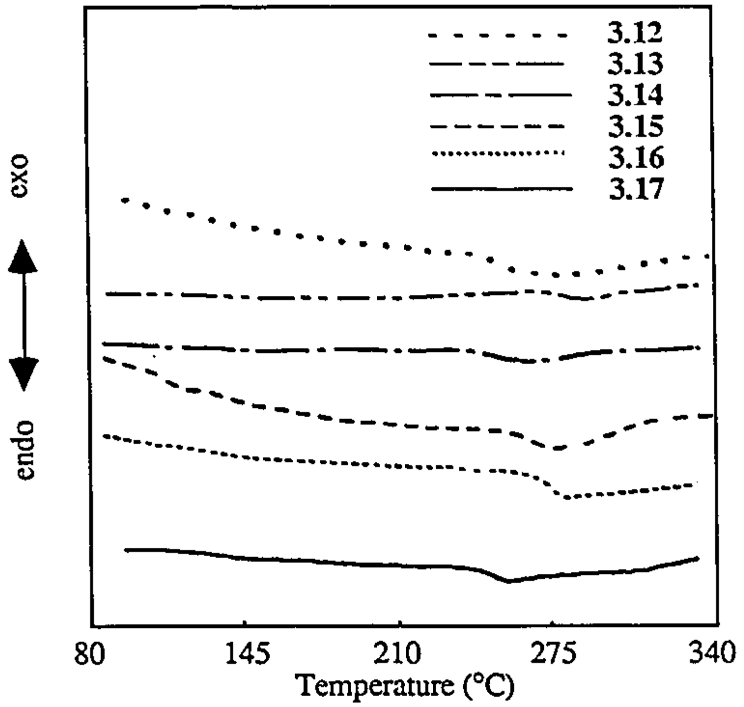


Figure 3.2 DSC analysis of polymers 3.12-3.17 under an atmosphere of nitrogen.

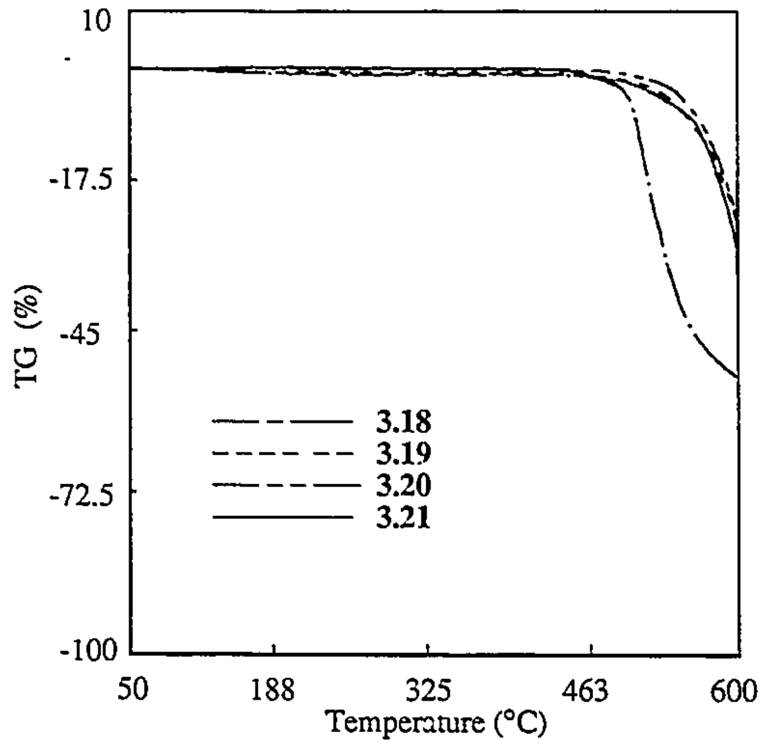


Figure 3.3 TGA thermogram (weight loss vs temperature) for polymers **3.18-3.21** under an atmosphere of air.

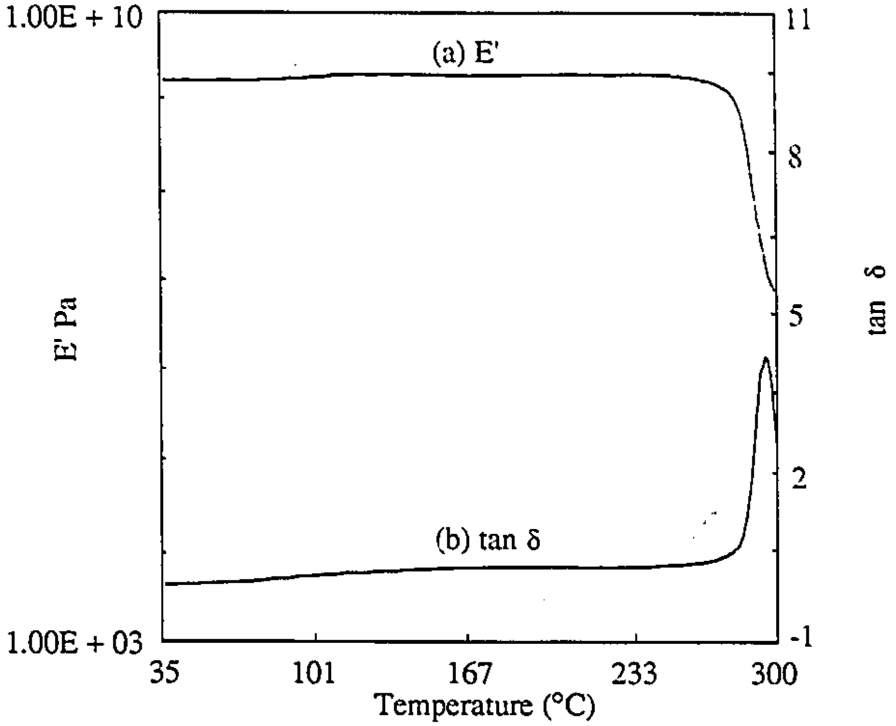


Figure 3.4 Thermomechanical analysis for polymer **3.13**: (a) modulus (E') vs temperature; (b) tan δ vs temperature.

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CHAPTER 4

POLY(ETHER KETONE)S

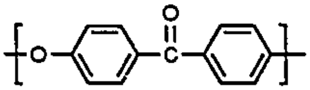
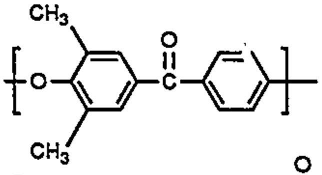
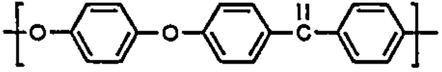
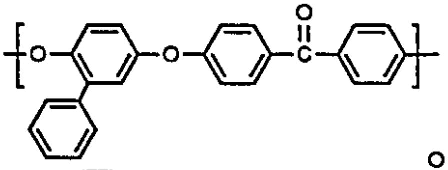
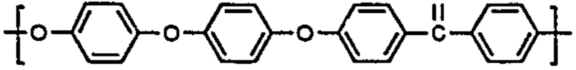
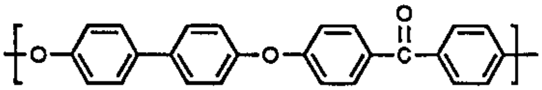
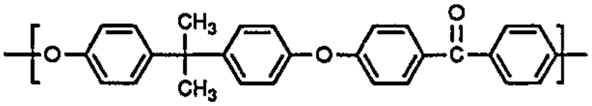
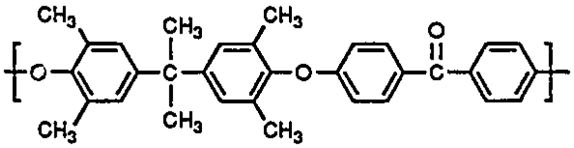
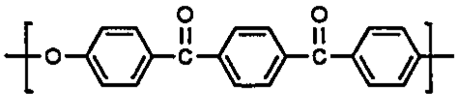
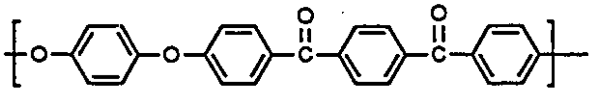
4.1 INTRODUCTION

Poly(aryl ether ketone)s (PAK) are a desirable class of polymers which are attracting increasing interest. Most of the wholly aromatic poly(ether ketone)s are crystalline or semi-crystalline polymers [1,2,3]. They are insoluble in common organic solvents and only soluble at room temperature in some concentrated acids such as sulphuric, methanesulphonic or hydrofluoric acid. Close to the polymer melting points (250-367 °C, see Table 4.1) they dissolve in rather unusual solvents such as diphenylsulfone or benzophenone. Their desirability stems from their excellent thermal stability and mechanical properties, low flammability giving low levels of smoke and toxic gases (e.g. CO, etc.), and their resistance to attack by solvents, which is especially important [4,5]. A polymer marketed as Stilan (RTM) by the Raychem Corporation is referred to as PEK® [6], and Victrex PEEK® (RTM) is produced commercially by ICI [7]. High molecular weight poly(aryl ether ketone)s (PAK) have been successfully synthesized by electrophilic condensation or nuclephilic displacement reaction. Table 4.1 lists commercial and related poly(ether ketone)s [2,8,9,10].

4.1.1 SYNTHETIC ROUTES TO POLY(ETHER KETONE)S

The insolubility of poly(ether ketone)s presented a major synthetic problem because it

Table 4.1 Commercial and Related Poly(ether ketone)s

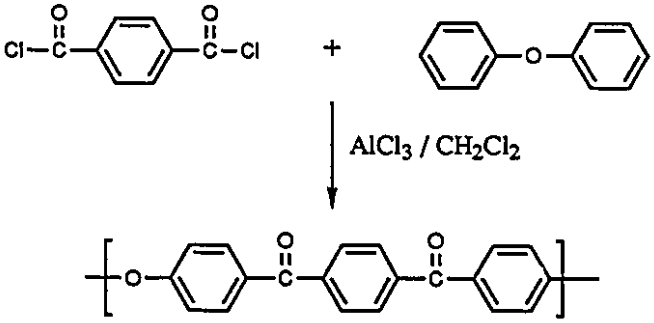
Polymer	Trade name/ Producer	Structure	Tg(°C)	Tm(°C)
4.1	Stilan(RTM) (Raychem)		154	367
4.2			235	-
4.3	Victrex PEEK (ICI)		144	335
4.4			154	-
4.5			150	315
4.6			167	416
4.7			155	248
4.8			235	-
4.9			-	384
4.10			154	358

limited the molecular weight that could be obtained before the growing chains crystallized out from the polycondensation system. This is the main reason why commercial development of the poly(ether ketone)s lagged behind that of the poly(ether sulfone)s. Indeed, polymerization reaction conditions suitable for preparing poly(ether sulfone)s can be used to prepare amorphous poly(ether ketone)s which are soluble at lower temperatures.

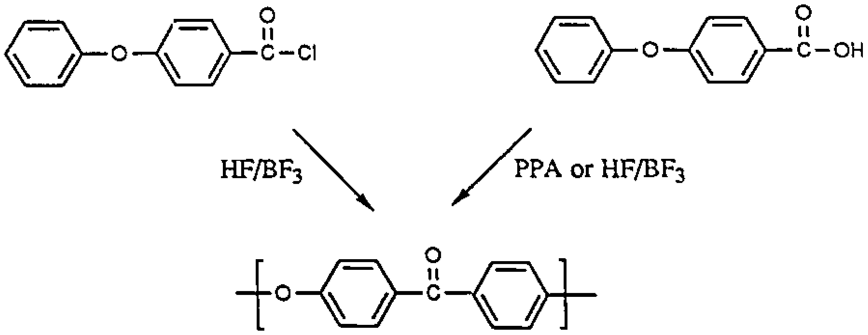
4.1.1.1 ELECTROPHILIC SUBSTITUTION ROUTE

The first attempted synthesis of a completely aromatic poly(ether ketone) was reported at DuPont by Bonner [11] who obtained a polymer of low molecular weight by Fridel-Crafts polymerization using nitrobenzene as solvent and aluminum chloride as catalyst. Polymerization by the AlCl3-catalyzed acylation method has since been extensively used [12,13]. Jansons [14] reported a study, consisting of numerous examples, in which AlCl3 in methylene chloride (and other chlorinated solvents) in conjunction with a Lewis base proved to be effective in giving high molecular weight polymers (Scheme 4.1). The preferred Lewis bases are dimethylformamide, lithium chloride and ammonium chloride. It

Scheme 4.1



Scheme 4.2

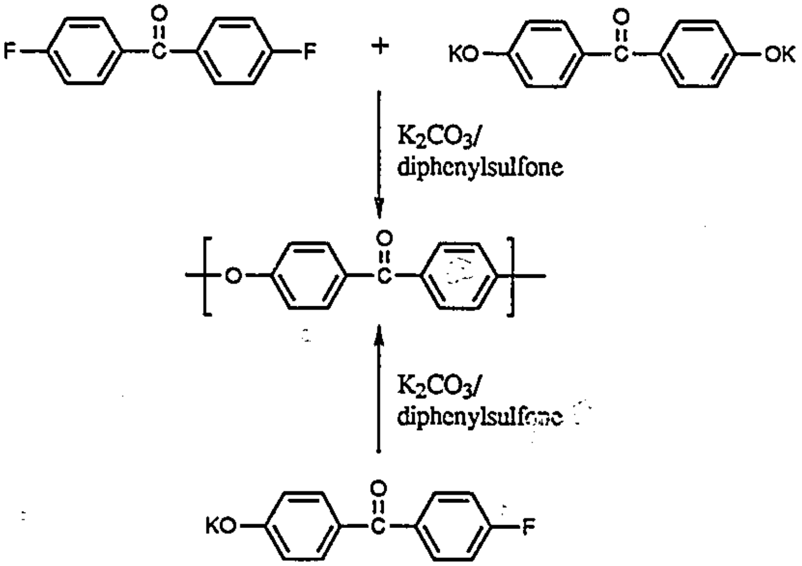


was claimed that the complex formed from $AlCl_3$ and a Lewis base could either act as a solvent or as a swelling medium for the polymer. This reaction required using a large excess of $AlCl_3$ (2.6-5.6 mol per mol of reacting acid chloride group) to obtain high molecular weight. The self-condensation of *p*-phenoxybenzoyl chloride or *p*-phenoxybenzoic acid is a suitable method for manufacture of polyketones by the HF/BF_3 route [15,16]. In addition, strong acids such as trifluoromethanesulfonic acid as a solvent-catalyst combination which is capable of protonating the carbonyl group, can be used (Scheme 4.2). This method has been developed for the production of high molecular weight polymers, but it is not ideal for industrial application due to cost, handling and disposing of acids. PEK also has been prepared from *p*-phenoxybenzoic acid, using polyphosphoric acid as solvent and catalyst [17] (Scheme 4.1). The synthesis of poly(etherketone)s from phosgene and diphenyl ether in carbon disulfide/ $AlCl_3$ does not produce high molecular weight polymers [12].

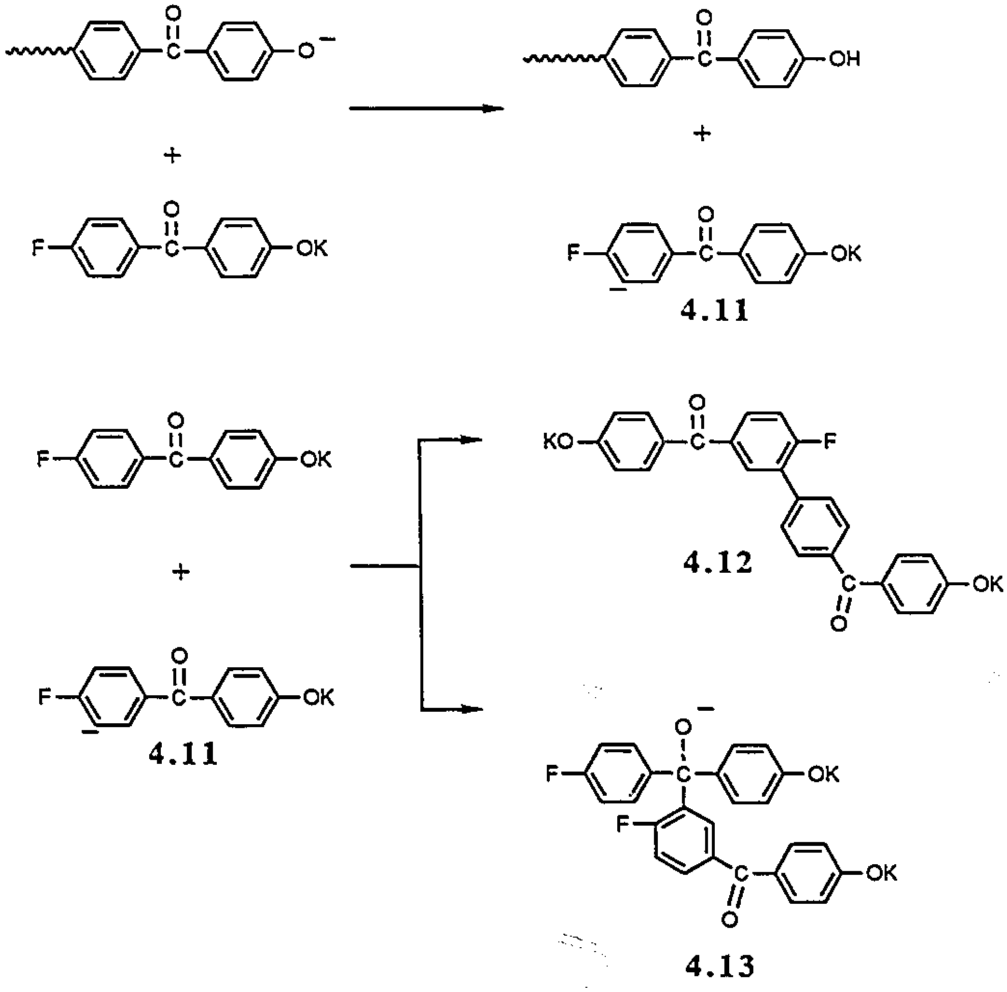
4.1.1.2 NUCLEOPHILIC DISPLACEMENT ROUTE

The initial development of PAK's by nucleophilic displacement took place concurrently with that of the poly(ether sulfone)s and the first nucleophilic displacement polymerization was reported by Rose *et al* [18] in 1967. Rose obtained a low molecular weight polymer by reacting the disodium salts of bisphenol A with 4,4'-dichlorobenzophenone in DMSO with a catalytic amount of copper oxide. At the same time Johnson [8] also synthesized PAK's from the reaction of bis(4-fluorophenyl)ketone and the dipotassium salt of bis(4-hydroxyphenyl)ketone but obtained only low molecular weight polymer because of crystallization of the oligomers which separate from the reaction mixture. The major factors affecting the synthesis of high molecular weight poly(ether ketone)s in nucleophilic displacement polymerization, besides chemical reactivity, are the choice of a suitable solvent and the exclusion of air and water. Crystalline poly(ether ketone)s generally require a solvent which can be used at higher temperatures without decomposition of monomer and solvent. High temperature polar aprotic solvents are required because of their ability to dissolve the alkali biphenate as well as the growing polymer chains under anhydrous conditions. The reactivity of 4,4'-dichlorobenzophenone is considerably lower than 4,4'-difluorobenzophenone or 4,4'-dichlorodiphenyl sulfone. However, with the difluorobenzophenone, a high molecular weight poly(ether ketone) was

Scheme 4.3



Scheme 4.4

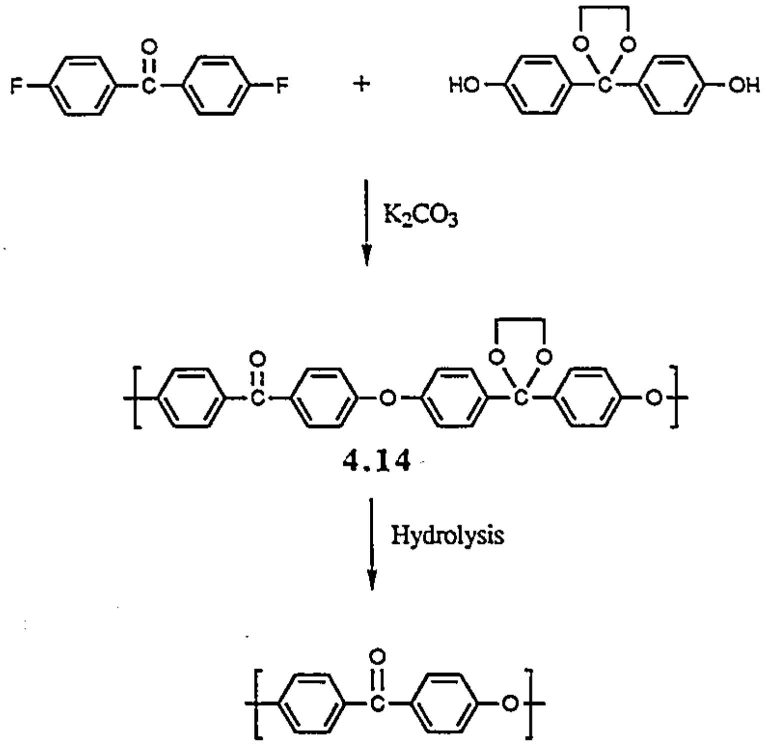


prepared in diphenylsulfone at 320 °C [1,19] (Scheme 4.3). Poly(ether ether ketone) (PEEK) [20] is commercially produced by the reaction of hydroquinone and 4,4'-difluorobenzophenone in the presence of anhydrous potassium or sodium carbonate as a catalyst in diphenylsulfone as solvent to give high molecular weight polymer. Another synthetic route using a single difunctional monomer, the potassium salt of 4-fluoro-4'-hydroxybenzophenone, gave a low molecular weight polymer [4,21]. In this system side reactions occurred, such as chain branching by proton abstraction to give the carbanion **4.11** (Scheme 4.4). The carbanion **4.11** can attack one of two reactive sites, the position ortho to the fluoro substituted carbon **4.12** and the carbonyl group **4.13** to produce a branched polymer. Therefore, this self-condensation polymerization is not a desirable route to synthesize high molecular weight polymer.

4.1.2 STRATEGY AND GOALS

Our objective is the synthesis of amorphous, high molecular weight, thermooxidatively stable poly(ether ketone)s with high glass transition temperatures. Bonner reported the first preparation of a poly(ether ketone) by aluminum chloride catalyzed acylation of diphenyl ether with an aromatic diacid chloride. The reaction failed to produce high molecular weight polymer because the product came out of solution prematurely. Since then, significant progress has been made in synthetic methodology to produce high molecular weight polymers. Several systems have been described in which soluble high molecular weight poly(aryl ether ketone)s are initially formed which can subsequently be converted to the semicrystalline poly(ether ketone). Kelsey [22] has utilized the ketals of 4,4'-dihydroxybenzophenone to form poly(ether ketal ketone) which can then be hydrolyzed to the poly(ether ketone). The cyclic ketal derived from ethylene glycol was the preferred monomer (Scheme 4.5). McGrath [23] utilized the ketimine of the benzophenone to form soluble amorphous polymers which could then be hydrolyzed and Sogah [24] utilized monomers that contained bulky t-butyl groups which could be subsequently removed. An amorphous poly(ether ketone) **4.4** has been synthesized containing a phenyl substituent on the arylene ring which has good solubility in organic solvents. Although the solubility was improved, the glass transition temperature was only slightly increased (Tg=154 °C) compared to poly(ether ether ketone) (PEEK) **4.3** [1] (Tg=146°C). Methyl group substituted PEK 4.2 [25] was reported as an amorphous poly(ether ketone). Although the polymer showed a high Tg of 235 °C, its thermal stability was inferior to the wholly aromatic poly(ether ketone). For example, its temperature at 5% weight loss was 480 °C,

Scheme 4.5



which was lower than wholly aromatic poly(ether ketone). Hergenrother [26] has utilized the very bulky 9,9-bis(4-hydroxyphenyl)fluorene containing methyl substituents in the 3- and 5- positions to synthesize amorphous poly(ether ketone)s with high Tg's and Wang [27] has made the corresponding phenyl-substituted polymers. The polymers are amorphous with Tg's as high as 262 °C and show high thermal stability.

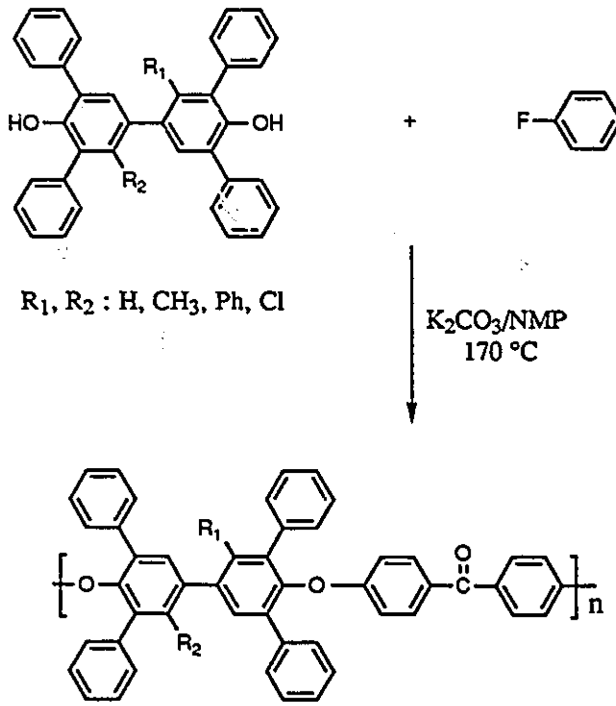
In this section we describe the synthesis of poly(ether ketone)s from hindered biphenols **2.12**, **2.13**, **2.17a**, **2.17b**, and asymmetrically substituted monomers, 2,6-diphenylhydroquinone, 2,3,5-trisubstituted hydroquinones **2.22a**, **2.22b**, **2.22c**, and the symmetrically substituted monomer 2,3,5,6-tetraphenylhydroquinone **2.22d**. Their properties are discussed.

4.2 POLYMER PREPARATION

4.2.1 PREPARATION OF POLY(ETHER KETONE)S FROM BIPHENOLS

We were able to successfully prepare high molecular weight poly(ether ketone)s from biphenols **2.13**, **2.17a**, and **2.17b** by reaction with 4,4'-difluorobenzophenone using potassium carbonate as the base in N-methyl-2-pyrrolidinone (NMP) [28]. The poly(ether ketone)s were amorphous. However, the synthesis of the corresponding poly(ether ketone) **4.15** by reaction with biphenol **2.12** and 4,4'-difluorobenzophenone was unsuccessful because the resulting polymer is highly crystalline and precipitates out of solution during the polymerization reaction. Copoly(ether ketone)s **4.19** and **4.20** were

Scheme 4.6



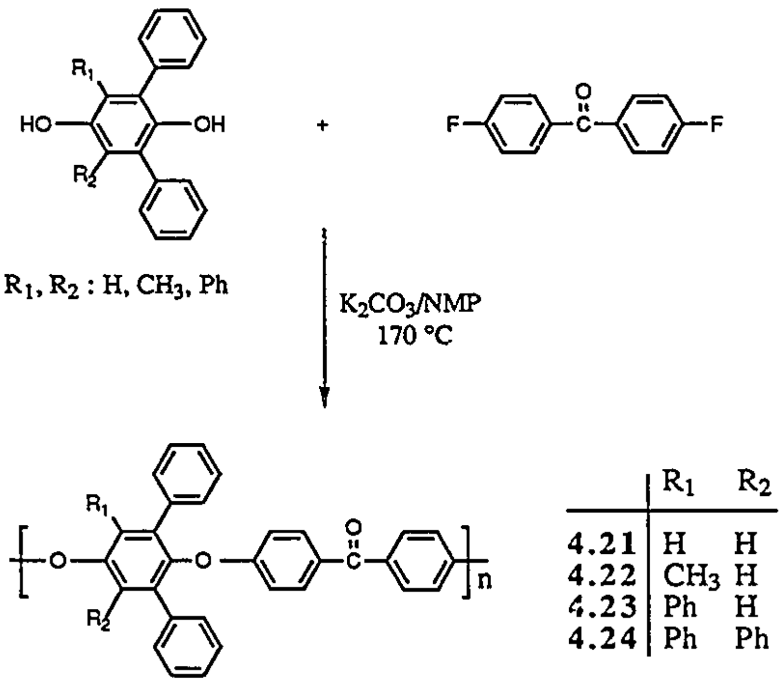
	R_1	R_2
4.15	H	H
4.16	CH_3	CH_3
4.17	Ph	Ph
4.18	Cl	H

prepared from, **2.17a**, **2.17b** with **2.12** (1 : 1 mole ratio) respectively under the same condition as the homopolymers. The polymerization reactions required 2 or 3 days to produce high molecular weight polymers and to obtain high yields (90-95 %).

4.2.2 PREPARATION OF POLY(ETHER KETONE)S FROM HYDROQUINONES

The polymers were prepared as shown in Scheme 4.7 by reaction with 4,4'-difluorobenzophenone in the presence of potassium carbonate in NMP and toluene (1:1 ratio) as solvent. The reactions were heated under reflux until no more water was present in the azeotrope. The toluene was then removed and the temperature maintained at 170 °C for 12 to 40 hours. With these highly hindered monomers the polymerizations required

Scheme 4.7



	R_1	R_2
4.21	H	H
4.22	CH_3	H
4.23	Ph	H
4.24	Ph	Ph

long reaction times to achieve reasonable molecular weight polymers and to obtain high yields (85-90%). Polymers prepared from 2,6- or 2,3,6-substituted hydroquinones **2.22a**, **2.22b**, **2.22c** are completely amorphous. The polymerization reaction with 2,6-diphenyl-3-methylhydroquinone **2.22b** proceeds much faster and this effect was also observed in the preparation of the poly(ether sulfone)s. Our explanation was that the lower acidity imparted to these molecules by the methyl groups increases the rate of reaction [29]. The poly(ether ketone) derived from symmetric monomer 2,3,5,6-tetraphenylhydroquinone **2.22d** is crystalline and precipitated out of solution during the polymerization even in sulfolane as a solvent at 220 °C.

4.3 RESULTS AND DISCUSSION

4.3.1 SOLUBILITY AND PROPERTIES

All of the poly(ether ketone)s which contain substituents in the 2- and/or 2'-positions are amorphous and soluble in solvents such as methylene chloride and chloroform at room temperature due to the increase of free volume. However the polymer derived from 3,3',5,5'-tetraphenybiphenol **2.12** is a semicrystalline polymer and soluble only in high temperature solvents such as benzophenone and diphenylsulfone. As shown by three dimensional models (Fig. 2.1 and 2.2) there is a smaller dihedral angle between the biphenyl rings of tetraphenylbiphenol **2.12** and the carbonyl group of benzophenone which allows a planar structure, presumably through increased resonance, which leads to crystalline polymer.

Poly(ether ketone)s **4.21**, **4.22**, **4.23** derived from the unsymmetric hydroquinones **2.22a**, **2.22b**, **2.22c**, are soluble in polar organic solvents, such as NMP and DMSO, and are readily soluble in chloroform and methylene chloride at room temperature. However, polymer **4.24** obtained from the symmetrically substituted hydroquinone **2.22d** is not soluble in common organic solvents even at high temperature, but is soluble in hot benzophenone and diphenylsulfone. The unsymmetric structures give rise to an increase in free volume of the polymers, while polymer derived from the hindered and symmetrically substituted hydroquinone **2.22d** behaves similarly to PEEK[1] **4.3**, which is soluble only at high temperatures because of the high crystallinity.

Molecular weights of polymers were determined by gel permeation chromatography (GPC) using polystyrene standards. These polymers had molecular weights (Mw) in the range 14,300 to 162,300 and a polydispersity (Mw/Mn) of 1.89 to 2.9 (Table 4.1 and Table 4.2). The polymers have inherent viscosities ranging from 0.31 to 0.98 dL/g. The viscosity of polymers **4.15**, **4.24** could not be measured because of poor solubility.

4.3.2 Tg's AND Tm's OF POLY(ETHER KETONE)S

The thermal behavior (Tg, Tm, and Tc) of the poly(ether ketone)s was investigated by DSC measurements. All DSC results are listed in Table 4.2, Table 4.3, and Figure 4.1. Amorphous poly(ether ketone)s **4.2** and **4.8** could be synthesized from hindered bis or biphenols as shown in Table 4.1 in which polymers contain methyl or phenyl substituents [24, 26, 30]. When compared with polymers without substituents, they are amorphous and their glass transition temperatures increased due to the difficulty of chain rotation and stiffness of backbone. As we expected the prepared polymers show high glass transition temperatures attributed to the phenyl groups in the 3,3'- and 5,5'- positions and rigidity of the backbone. Interestingly for the polymer **4.15**, Tc (351°C) and Tm (400 °C) are similar to those for the polymer derived from 4,4'-dihydroxydiphenyl (Tg 167 °C, Tm 416 °C) which has no substituents [31]. This polymer **4.15** seems to be semicrystalline and the Tg increased 40 °C higher than that of the unsubstituted polymer **4.6** (Tg=167 °C). A possible explanation is that biphenol **2.11** containing hydrogen atoms in 2,2' positions has a smaller dihedral angle in the biphenyl linkage compared to biphenols **2.13**, **2.17a** or **2.17b** containing phenyl, methyl or chloro groups, which allows the polymer **4.15** to crystallize readily.

The poly(ether ketone)s derived from the hydroquinones have a significantly increased glass transition temperature compared to PEEK which has no substitution on the phenyl ring. Polymer **4.21** containing 2, 6-diphenyl substituents on the arylene ring has a Tg of 205 °C, which is 60 °C higher than PEEK **4.3** (Tg=144 °C) [1] and also 50 °C higher than that derived from monophenylhydroquinone **4.4** (see Table 4.1). The glass transition temperatures increase gradually with the addition of substituents, in the order H < methyl < phenyl < diphenyls, in the 5- or 5, 6- positions. This is the same order as in the poly(ether sulfone)s derived from the hydroquinones. In the case of the tetraphenyl substituted polymers the poly(ether ketone) is semicrystalline and DSC scans showed Tg (225 °C), Tc (279 °C), and Tm (383 °C). The Tg's did not increase as much as we expected, perhaps due to the low molecular weight of the polymers.

4.3.3 THERMAL STABILITY

The thermal properties of the polymers prepared are summarized in Table 4.2, Table 4.3, and Figure 4.2. All the polymers show excellent thermo-oxidative stability at high temperatures in both air and nitrogen atmospheres. The polymers **4.16**, **4.19** and **4.22** which contain methyl substituents on the phenyl rings have a lower thermo-oxidative stability with 5% weight loss below 500 °C. The completely phenyl substituted poly(ether ketone)s have a higher thermo-oxidative stability with 5 % weight loss temperatures above 500 °C.

4.3.4 MECHANICAL PROPERTIES

Polymer films which were transparent and tough were cast from chloroform solution (120 mg/5 mL) and they maintained excellent dimensional stability over a wide temperature range from ambient temperature to their glass transition temperatures as shown in the TMA results (Table 4.4 and Figure 4.3). The glass transition temperatures obtained by thermomechanical analysis were in agreement with those obtained from DSC scans. The moduli determined are in the range of 1.5 to 2.8 GPa at room temperature and 1.3 to 2.1 GPa at temperatures 40 °C below the polymer glass transition temperature.

4.4 CONCLUSION

Polymerization of hindered biphenols or hydroquinone with 4,4'-difluorobenzophenone in NMP or sulfolane in the presence of excess anhydrous potassium carbonate afforded high molecular weight polymers. The polymers derived from 2 and/or 2' substituted biphenols and unsymmetrically substituted hydroquinones are amorphous and soluble in solvents such as chloroform and methylene chloride at room temperature, but polymers derived from tetraphenylbiphenol **2.12** and the symmetrically substituted hydroquinone **2.22d** are insoluble semicrystalline materials. The glass transition temperatures are higher than those of the corresponding polymers with no pendent groups on the arylene backbone and the Tg's gradually increased with increasing numbers of substituents. The methyl substituted polymers exhibit lower thermooxidative stability than those of the corresponding polymers with aryl groups which show 5 % weight loss above 500 °C by thermogravimetric analysis.

4.5 EXPERIMENTAL

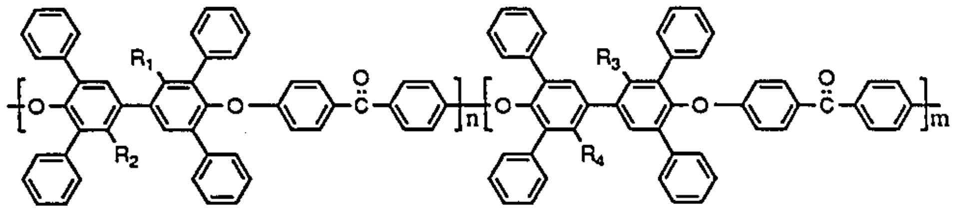
General polymerization: Synthesis of 4.17

In NMP (10 mL) were dissolved 2,6-diphenylhydroquinone (1 g, 3.81 mmol) and 4,4'-difluorobenzophenone (0.97 g, 3.81 mmol), and toluene (7 mL) was added. After the solids dissolved anhydrous potassium carbonate (0.69g, 4.77 mmol) was added. The dark green mixture was vigorously stirred at 150 °C until no further water was collected by azeotropic distillation. The toluene was then removed slowly while the reaction mixture was heated to 170 °C. The reaction temperature was maintained at this temperature for 20 h. After cooling to 100 °C the solution was diluted with additional NMP (7 mL). The mixture was precipitated in methanol/water (200/50 mL) containing a few drops of hydrochloric acid. The precipitate was filtered and dried in vacuum. The resulting polymer was dissolved in chloroform (15 mL), filtered through celite and reprecipitated in methanol (250 mL). The polymer was dried at 140 °C under vacuum for 24 h (89 % yield).

Polymer Characterization

Inherent viscosities were measured in a calibrated Ubbelohde viscometer at a concentration (0.5 g/dL) of polymer in $CHCl_3$ at 25 °C. Molecular weights of polymers were determined relative to polystyrene by gel permeation chromatography (GPC) using $CHCl_3$ as solvent on a Waters 510 HPLC with a set of four µstyragel columns (500, 10^4, 10^5, and 100 Å) in series equipped with a UV detector. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with Seiko 220 DSC at a heating rate of 20 °C/min and Seiko 220 TG/DTA instruments at 10 °C/min under nitrogen and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument at 25 °C to 300 °C with a heating rate of 3 °C/min in static air. The polymer films for the mechanical analyzer were cast from chloroform solution on a glass plate (3 cm diameter) by evaporation of solvent at room temperature for 48 h and dried at 100 °C for 24 h. Film thickness was measured with micrometer.

Table 4.2 Physical and Thermal Properties of Poly(ether ketone)s from Biphenols



Polymers	R_1	R_2	R_3	R_4	Tg[a]/Tg[b] (°C)	Tc(°C)	Tm(°C)	TGA[c](°C) N_2/Air	ηinh[d] (dL/g)	Mw[e]/10^3	Mw/Mn
4.15	H	H	H	H	207	351	400	535/539	-	-	-
4.16	CH_3	CH_3	CH_3	CH_3	282			498/452	0.59	141.4	1.97
4.17	Ph	Ph	Ph	Ph	256			557/558	0.46	162.3	2.04
4.18	Cl	H	H	Cl	211			537/520	0.09	6.8	2.41
4.19	CH_3	CH_3	H	H	248/239			501/495	0.25	56.2	1.39
4.20	Ph	Ph	H	H	228/230			501/493	0.12	14.3	1.89

[a] Tg was determined by DSC at heating rate 20 °C/min under nitrogen (50 mL/min).

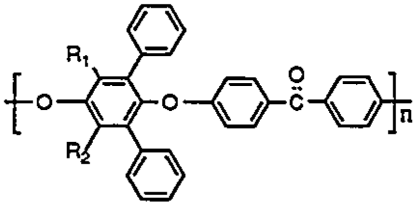
[b] Tg was calculated from the equation $1/Tg^{AB}=w_A/Tg^A + w_B/Tg^B$.

[c] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min).

[d] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

[e] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

Table 4.3 Physical and Thermal Properties of Poly(ether ketone)s from Hydroquinones



Polymers	R_1	R_2	r.t*(h)	Tg^a(°C)	Tc(°C)	Tm(°C)	TGA^c(°C) N_2/Air	ηinh^d (dL/g)	$Mw^e/10^3$	Mw/Mn
4.21	H	H	20	205			504/504	0.62	77.79	2.9
4.22	CH_3	H	12	219			471/483	0.39	64.1	2.3
4.23	Ph	H	40	222			542/504	0.50	54.6	2.4
4.24	Ph	Ph	2	225	279	383	529/504	-	-	-

[a,c,d,e] Footnotes are identical to those in Table 4.2.

* Reaction time.

Table 4.4 Mechanical Properties of Poly(ether ketone)s

Polymers	Y.M[a](GPa)	Tg(°C)[b](DSC)	Tg (°C)[c](TMA)
4.16	2.15	282	283
4.17	2.16	256	250
4.19	2.05	258	253
4.21	1.46	205	198
4.22	1.87	219	208
4.23	2.15	222	213

[a] Young's Modulus measurement was performed by TMA at room temperature.
[b] Temperatures were recorded from DSC results.
[c] Temperatures were recorded where the tan δ curve shows a maximum.

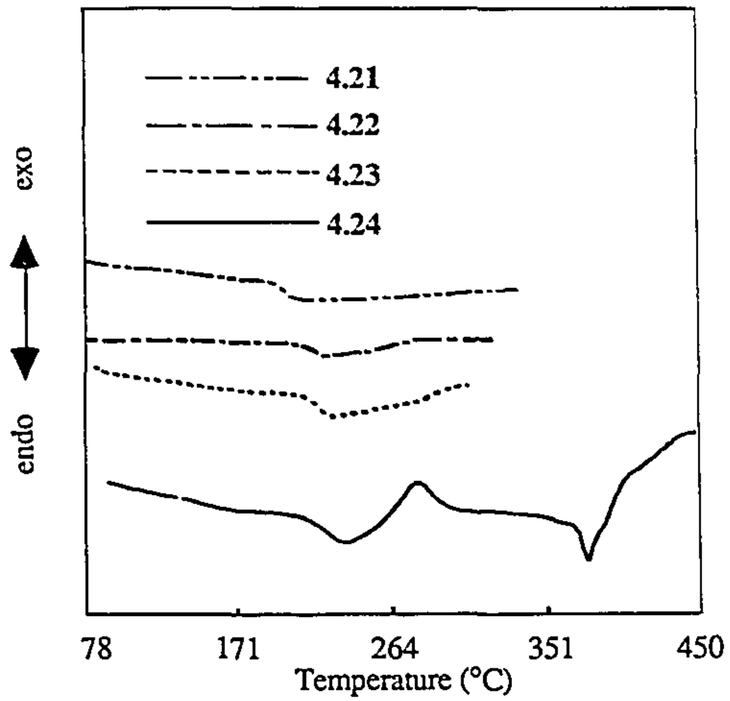


Figure 4.1 DSC analysis of polymers **4.21-4.24** under an atmosphere of nitrogen.

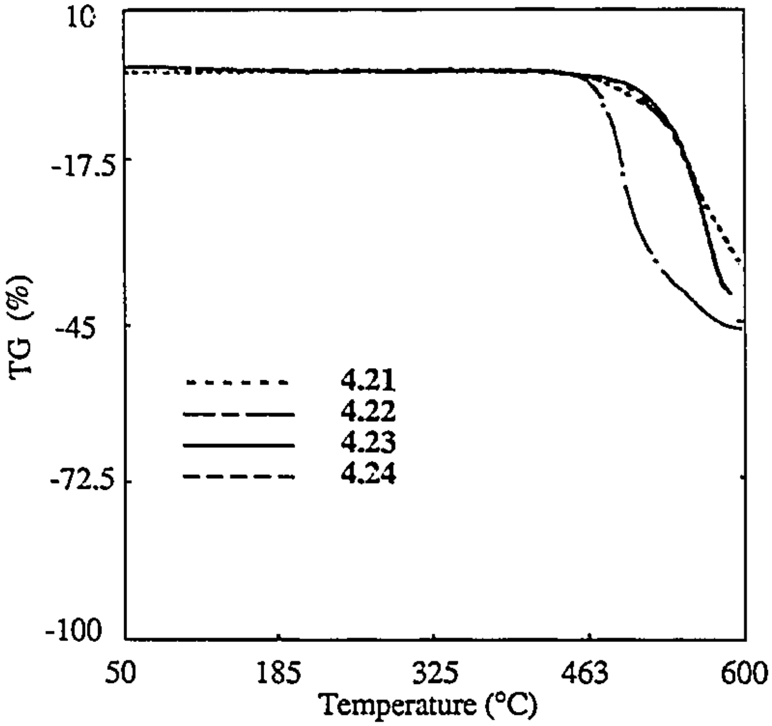


Figure 4.2 TGA thermogram (weight loss vs temperature) for polymers **4.21-4.24** under an atmosphere of nitrogen.

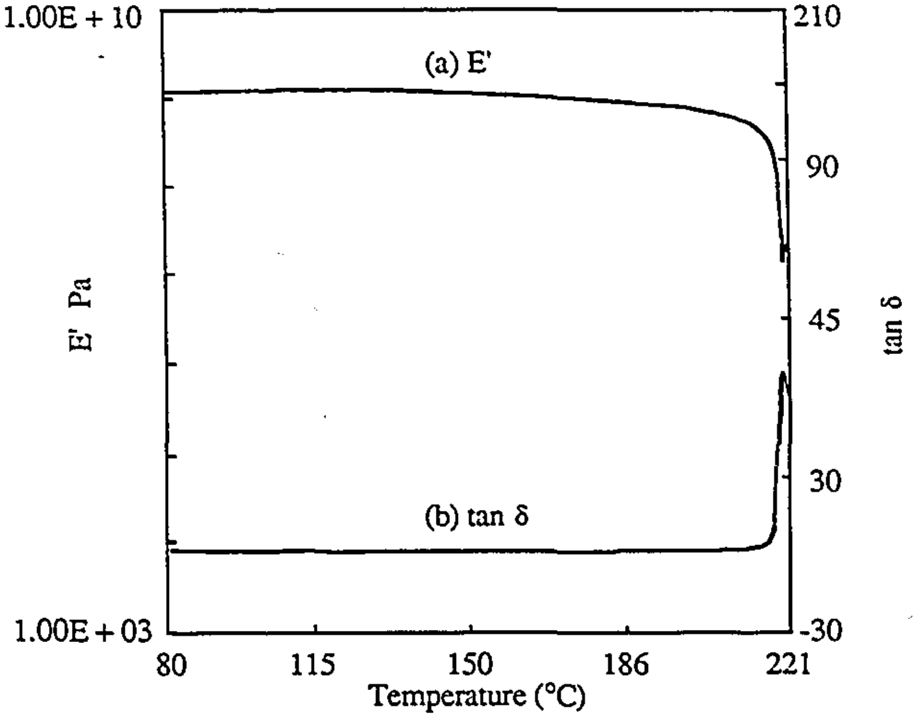


Figure 4.3 Thermomechanical analysis for polymer **4.22**: (a) modulus (E') vs temperature; (b) tan δ vs temperature.

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CHAPTER 5

AROMATIC POLYESTERS

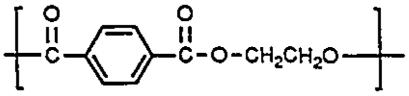
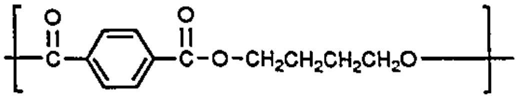
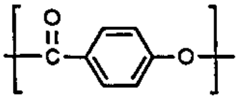
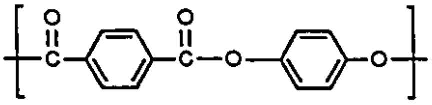
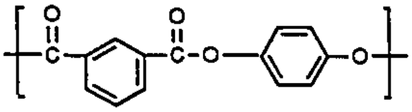
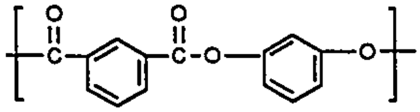
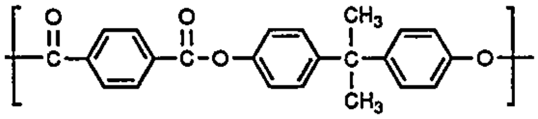
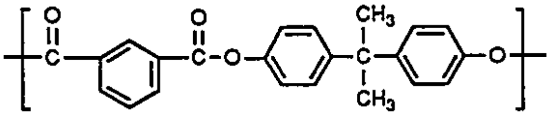
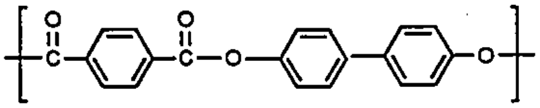
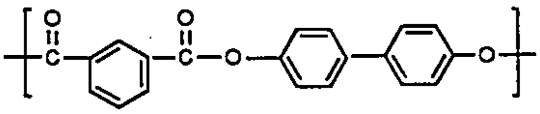
5.1 INTRODUCTION

Polyesters are among the more versatile synthetic polymers in that they find wide commercial use as fibers, plastics, and coatings [1,2]. Aromatic polyesters (commonly called polyarylates) are an emerging class of new engineering polymers which show high impact strength, good flexural recovery, good surface hardness and high dimensional stability. Polyarylates also have good mechanical properties, electrical insulation properties, resistance to degradation by ultraviolet light, and are self-extinguishing [3,4]. Aromatic polyesters are condensation products that are characterized by ester linkages distributed along the polymer backbone. The first of this class to be commercialized was the highly crystalline polymer **5.3** based on p-hydroxybenzoic acid by the Carborundum Company [5]. A few years later amorphous polyarylates **5.7**, **5.8**, made from biphenolate and isophthaloyl dichloride and terephthaloyl dichloride, were made available by the Union Carbide Company [6]. The commercial and related polyesters [7,8,9,10] are listed in Table 5.1.

5.1.1 SYNTHETIC ROUTES TO POLYESTERS

Virtually every known method of esterification has been applied to the synthesis of

Table 5.1 Commercial and Related Polyesters

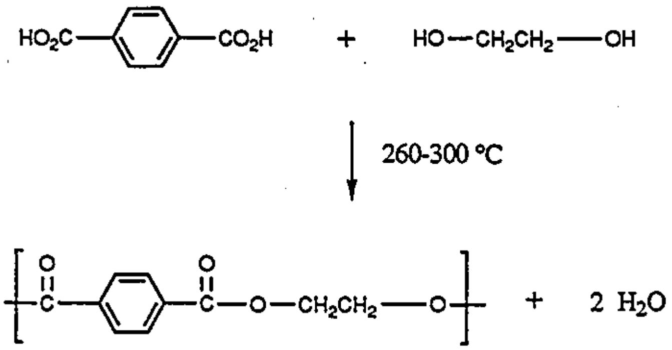
Polymers	Trade name/ Producer	Structure	Tg (°C)	Tm (°C)
5.1	PET/du Pont, ICI		69	265
5.2	Fortrel/ Fiber Industries		80	232
5.3	Carborundum		-	610
5.4			307	467
5.5			160	370
5.6			122	247
5.7	ARDEL/Union Carbide		250	350
5.8	Union Carbide		243	280
5.9			267	487
5.10			207	-

polyesters. In addition, many of these polymers have been made by reactions which are without counterpart in the chemistry of simple esters. The simplest sources of polyesters are the reaction of diols with dicarboxylic acids or the self-esterification of hydroxyacids. The existing polyarylate processes can be subdivided into two categories: polycondensation reactions and ring-opening polymerization. Polyarylates are difficult to prepare by direct polycondensation of biphenols with diacids because the high temperatures necessary for achieving practical molecular weights frequently leads to decarboxylation or carboxyl-catalyzed ether formation. Consequently, polyesters are usually made by transesterification or from the acid chlorides.

5.1.1.1 THE CARBOXYLIC ACID ROUTE

In principle any dibasic acid will condense with any glycol and any hydroxy acid will self-condense to form a linear polyester. The most widely used linear polyester is poly(ethylene terephthalate) **5.1** prepared from terephthalic acid and ethylene glycol [11,12] (Scheme 5.1). The polymer can be prepared in bulk or in solution using an excess of ethylene glycol to increase the esterification rate. This leads initially to low molecular weight hydroxyl-terminated polyester, which is then transesterified with removal of excess glycol to attain high molecular weight. The range of application for this procedure is vast and virtually any stable and reactive diol or diacid may be employed, the exceptions being

Scheme 5.1

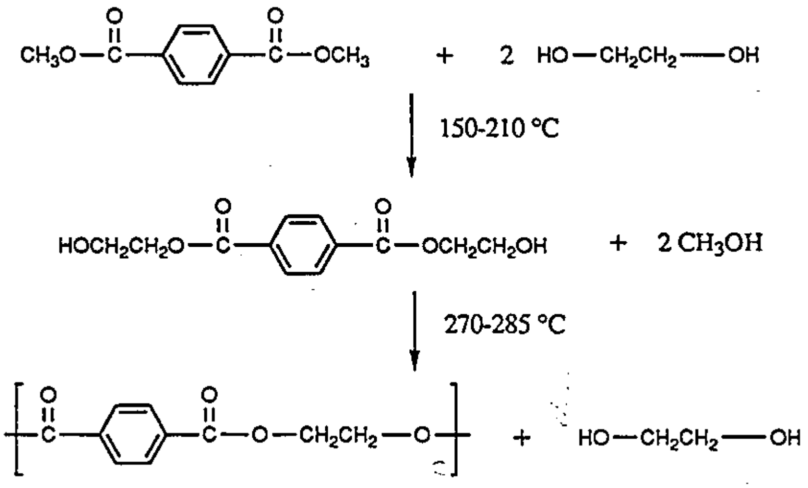


found in acids which are readily decarboxylated, in phenolic hydroxy-acids and dihydric phenols whose esterification is too slow for advantageous use, and in diols having tertiary alcoholic groups which would suffer dehydration at the temperatures necessary for polymerization. Ideally, a high molecular weight linear polyester should result from the completion of the reaction between equimolar amounts of the starting materials. Any imbalance caused by volatilization or side reactions will lead to the formation of a polyester terminated at both ends by either hydroxy or carboxylic acid groups and thus terminate the polymerization at low molecular weight polymer.

5.1.1.2 ESTER EXCHANGE ROUTE

While poly(ethylene terephthalate) **5.1** can also be obtained by the direct esterification of ethylene glycol with terephthalic acid, in practice it was originally almost wholly based on the ester-exchange reaction of glycol with the dimethyl ester of the acid [13,14,15] (Scheme 5.2). The reason for this choice is partly the low melting point of the dimethylester and its solubility in glycol during the early stages of polymerization,

Scheme 5.2



and partly because terephthalic acid itself is difficult to purify to the high standards appropriate for polymerization. The dimethyl ester, on the other hand, can readily be purified by crystallization or distillation. This procedure is generally applied in two stages, the first being the formation of diester, followed by an interchange reaction to form the polymer.

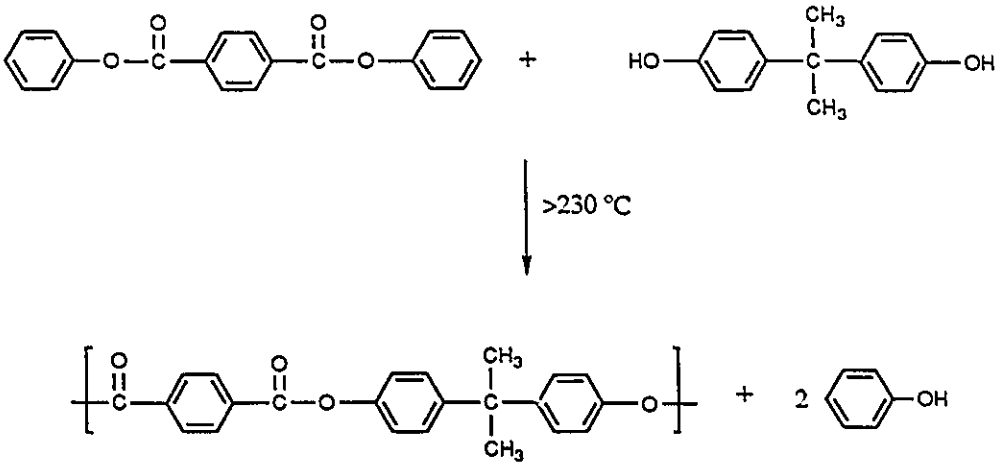
5.1.1.3 DIACETATE ROUTE

The diacetate process involves the reaction of stoichiometric amounts of an aromatic dicarboxylic acid and the diacetate derivatives of an aromatic diphenol at high temperature under an inert atmosphere [16, 17]. Polyesters derived from 4-acetoxy-3-phenylbenzoic acid are synthesized by melt polymerization around 360 °C. The diacetate process is essentiallly a reversible melt process, which requires continuous removal of acetic acid in order to achive high molecular weight polymer. While the chemistry of the process is relatively straightforward, there are a number of variables in the synthesis which must be taken into consideration to assure that the aromatic polyesters exhibit good mechanical properties, low color and good melt stability.

5.1.1.4 BIPHENATE ROUTE

The high temperature reaction between a diaryl ester of an aromatic dicarboxylic acid and an aromatic biphenol results in high molecular weight aromatic polyesters [18,19] (Scheme 5.3). The slight excess of biphenyl ester reportedly ensures high molecular weight polymer by compensating for any stoichiometric imbalance which might occur between the diaryl ester of the aromatic diacid and the biphenol co-reactants as a result of material loss due to sublimation. As the molecular weight increases, any unreacted biphenyl ester can be

Scheme 5.3

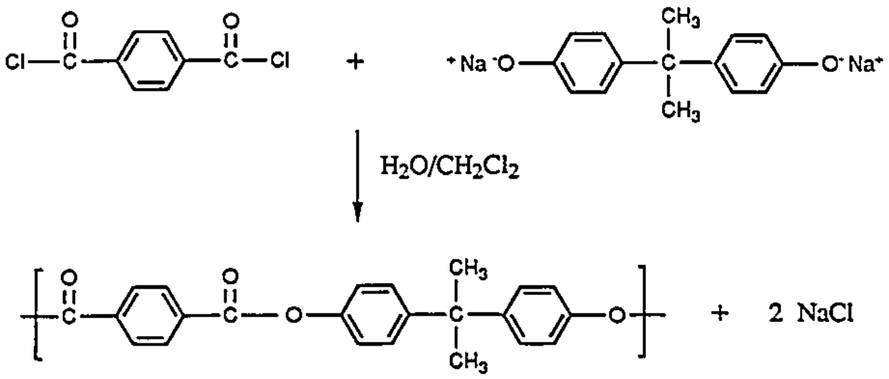


removed downstream in a vented extruder. The reversible nature of the biphenate process requires continuous removal of phenol from the reaction system to ensure obtaining high molecular weight. The biphenate process compares favorably with the diacetate route with respect to product quality. The limiting aspect of this route is the preparation of the diphenyl ester derivatives and in this regard each biphenate case will be unique.

5.1.1.5 INTERFACIAL ROUTE

Interfacial polymerization involves the reaction of an aqueous solution of the dialkali metal salt of a biphenol with a solution of the acid chloride in a water immiscible solvent, such as methylene chloride or chlorobenzene [11,20] (Scheme 5.4). It is advantageous that the polyester formed be soluble in the organic phase. As the two starting immiscible solutions are brought into contact, the polymerization occurs at the interface where a film of the polymer is formed. These reactions are markedly catalyzed by small amounts of quaternary ammonium or sulfonium compounds [21]. The reactions take place at temperatures that are generally within the range of 0 to 35 °C and proceed at very high rates. This

Scheme 5.4



polymerization method has been broadly applied, especially in the preparation of aromatic polyesters derived from a variety of biphenols.

5.1.1.6 LOW AND HIGH TEMPERATURE ROUTES

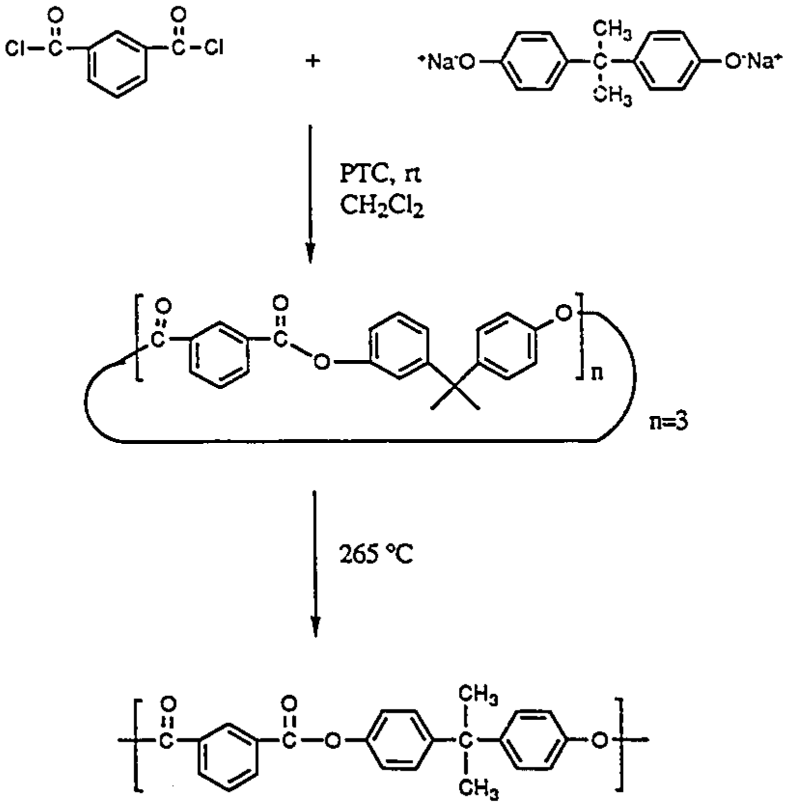
The low and high temperature solution polymerizations of aromatic polyesters have been utilized for the preparation of aromatic polyesters from bisphenols and aromatic diacid chlorides. In the low temperature general procedure [22,23], polymer is produced by reacting essentially equivalent amounts of the diacid chloride and dihydroxy compound in an inert solvent, in the presence of a stoichiometric amount of an acid acceptor. These reactions are generally run in a solvent such as tetrahydrofuran in the presence of pyridine or triethylamine at, or below, room temperature.

The high temperature reaction of diacid chlorides with biphenols in an inert solvent yields polyester and hydrogen chloride as a by-product [1,24,25]. This reaction requires temperatures above 200 °C to give high molecular weight polymer. Thus the polymerizations were performed in a suitable high boiling reaction medium at elevated temperatures such as chlorinated benzenes, chlorinated biphenyls or diphenyl ethers, chlorinated naphthalenes as well as non-chlorinated aromatics such as terphenyl, benzophenone, and dibenzylbenzene. The reaction can be catalyzed with a large number of Lewis acids and bases [26]. The typical catalysts are aluminum, titanium, zinc, and magnesium salts. The high temperature solution polymerization is useful for the preparation of crystalline polyarylates.

5.1.1.7 RING-OPENING POLYMERIZATION ROUTE

Ring-opening polymerization of cyclic esters (lactones) is brought about by cationic, anionic, radical, and complex coordination initiators [27,28]. The extent of the polymerization depends on the size of the ring. In general, 4, 7, and 8 membered ring lactones polymerize without difficulty, but in the 5 and 6 membered cyclic esters, the effects of substituents, of replacing methylene groups in the rings by oxygen, and of other cyclic components of the molecules have an important influence on the reactivity. The mechanism of cationic polymerization appears in most instances to involve an intermediate acylium ion formed in each propagation step proceeding from acyl-oxygen bond cleavage. The anionic polymerization proceeds through two different mechanisms. Nucleophilic addition to the carbonyl group followed by acyl oxygen cleavage leads to propagation through alkoxide ion chain ends. The other anionic mechanism involves nucleophilic attack on the carbon adjacent to the ring oxygen, giving alkyl oxygen cleavage and propagating carboxylate ion chain ends. Polymerization of β–lactones may also be initiated with metalloporphyrin or dibutylzinc-triisobutylaluminium initiators. Ring opening takes place at the alkyl oxygen bond and the result is suitable for forming block copolymers. A more recent method of preparing polyesters is by free radical ring opening polymerization by using an initiator such as peroxide. Recently the development of a simple method for preparing oligocyclic esters provided an opportunity for exploring their utility as a

Scheme 5.5

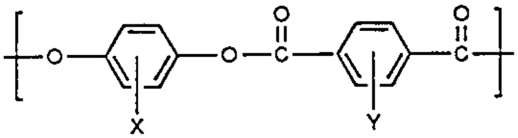


thermoplastic matrix resin in structural composites. Cella and Fukuyama [29] reported a cyclic ester from the reaction of bisphenol A with phthaloyl dichloride. Guggenheim [30] has reported a high yield synthesis of cyclic ester from the reaction of BPA disodium salt and isophthaloyl dichloride or terephthaloyl dichloride in the presence of phase transfer catalyst in methylene chloride and aqueous solution (Scheme 5.5). These cyclic esters undergo polymerization 5.7, 5.8 over a temperature range of 250-300 °C.

5.1.2 STRATEGY AND GOALS

The current interest in aromatic polyesters focuses on the preparation of thermotropic liquid crystalline polymers **5.3** and **5.9** which are synthesized from monomers such as 4,4'-dihydroxybiphenyl, terephthalic acid and *p*-hydrobenzoic acid by condensing the acetate derivatives at elevated temperatures [31,32]. Polyesters of this type are highly crystalline and generally form mesophases when heated before the final homogeneous melt. They are characterized as self-reinforcing materials which have excellent high temperature stability and excellent solvent resistance combined with outstanding strengths and moduli. Since the materials are anisotropic the physical properties vary dramatically with the direction of orientation of the processed parts and this limits their areas of application.

There are several known ways to reduce the crystal melting temperature of rigid-chain polymers, some of which are presumed to leave the chain highly extended. One involves the positional isomerism of a substituent on the aromatic ring. An early patent by Goodman, McIntyre, and Aldred [33] disclosed *p*-phenylene terephthalate polyesters bearing a methyl, methoxy, or halogen substitutent on one or both aromatic rings of the repeating unit. These polymers were reported to have melting temperatures in excess of 350 °C. Substituents having additional degrees of rotational or conformational freedom should provide larger reductions in the melting temperature. Payet [34] reported a polyester which was synthesized from monophenyl hydroquinone and terephthalic acid. Harris [35] reported the substituted polyester derived from hydroquinone and phenylterephthalic acid. Krigbaum *et al* [28] have investigated the effect of substituents upon the transition temperature of poly(*p*-phenylene terephthalate) (Figure 5.1). All the mono and disubstituted polyesters gave a nematic phase upon melting. The polyester bearing a phenyl substituent on each ring is an exception, which is an amorphous glass. The degree of crystallinity is less for disubstituted polymers than those bearing a single substituent.



X, Y=H, Cl, Br, Ph, n-hexyl

Figure 5.1 The repeating unit of a polyester where X and Y are the substituents on the hydroquinone and terephthalic acid moieties

Highly hindered polyesters [36] were prepared from various diacids and 3,3',5,5'-tetramethylbiphenyl-4,4-diol, indicating that methyl or phenyl groups increase the Tg of polymers. Lenz [37] reported liquid crystalline polyesters having 3,3',5,5'-tetraalkylbiphenyl-4,4'-diol units containing halogen substitution in the meta position of the aromatic ring. Becker et al [38] have made the corresponding polyesters from 2-chloro-3,3'5,5'-tetraphenylbiphenyl-4,4-diol. Gaudiana *et al* [39] described the synthesis of copolyesters containing 2,2'-bistrifluoromethyl-1,1'-biphenylene moieties. In these systems the trifluoromethyl groups do not allow the biphenyl rings to be coplanar and the polymer is completely non-crystalline and soluble in a number of solvents despite a high glass transition temperature and a lower mesophase transition temperature.

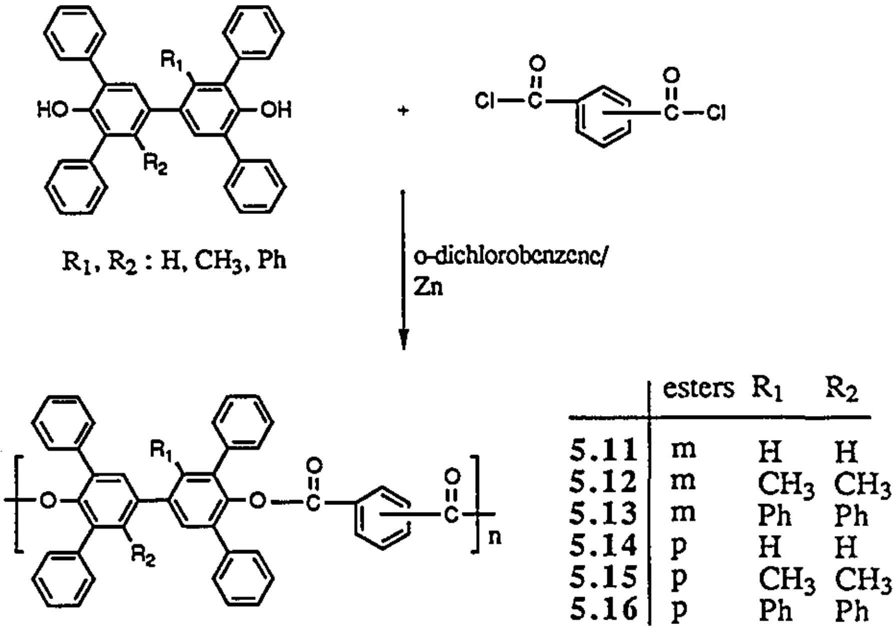
In this section we report the synthesis and characterization of new polyesters which were prepared from modified hindered biphenols (**2.12**, **2.13**, **2.17a** and **2.17b**) and hydroquinones (**2.22a**, **2.22b**, **2.22c** and **2.22d**). We might have expected these polymers to be amorphous and thermotropic liquid crystalline due to the twisted conformation of biphenols and random variation along the chain of the position of the substituents. However, their DSC patterns showed no evidence of thermotropic behavior and high melting points due to stiffness of the backbone and difficulty of rotational or conformational freedom due to these large substituents.

5.2 PREPARATION OF POLYESTERS

5.2.1 PREPARATION OF POLYMERS FROM BIPHENOLS

The polyesters were prepared by the reaction shown in Scheme 5.6 with a series of hindered biphenols **2.12, 2.13, 2.17a, 2.17b**. The highly hindered polyesters are prepared by the reaction at high temperature (200-300 °C) in suitable solvents, such as chlorinated benzene, tetrachloroethane, and chlorinated biphenyls at reflux temperature until no more hydrogen chloride gas was evolved [36]. The series of polyesters were prepared by the reaction of isophthaloyl dichloride or terephthaloyl dichloride with hindered biphenols in the presence of zinc as a catalyst. The hindered biphenols afforded high molecular weight polyesters when the polymerizations were carried out in o-dichlorobenzene at reflux for 6 h and gave yields in excess of 90 %. All the polymers derived from isophthaloyl dichloride with hindered biphenols have better solubility than

Scheme 5.6



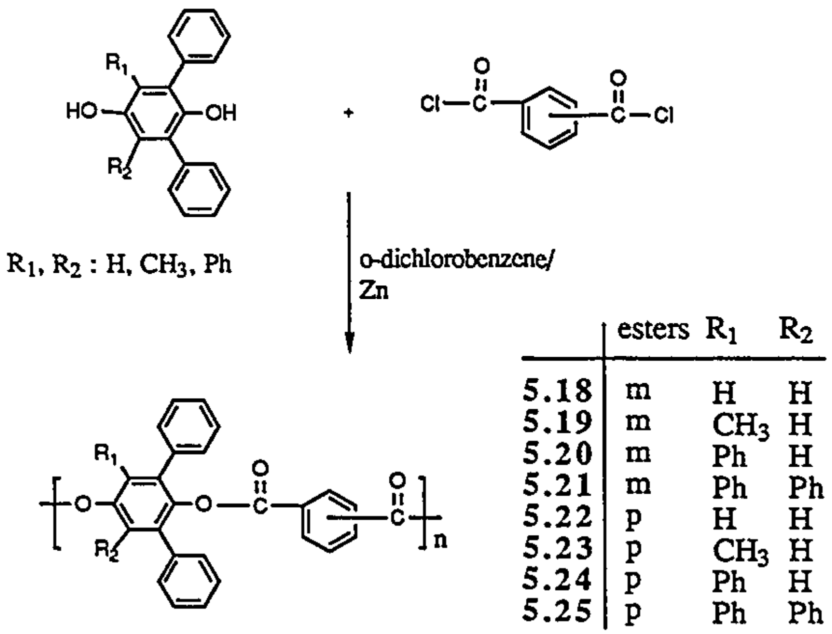
	esters	R_1	R_2
5.11	m	H	H
5.12	m	CH_3	CH_3
5.13	m	Ph	Ph
5.14	p	H	H
5.15	p	CH_3	CH_3
5.16	p	Ph	Ph

the corresponding polymers derived from terephthaloyl dichloride as expected. These latter polymers came out of solution during the polymerization because of their high crystallinity.

5.2.2 PREPARATION OF POLYESTERS FROM HYDROQUINONES

The polymerization and structures of these polymers are outlined in Scheme 5.7. The solution polymerization of hindered hydroquinones, except for **2.22d**, with isophthaloyl dichloride and terephthaloyl dichloride were conducted in *o*-dichlorobenzene at reflux temperature. The highly hindered and symmetric hydroquinone polymers **5.21**, **5.25** were obtained from the reaction in trichlorobenzene at reflux because of solubility limitations. This solvent makes it possible to conduct the reaction at higher temperature. Notwithstanding, the products precipitate from solution. The polymers were obtained in yields over 90 %.

Scheme 5.7



	esters	R_1	R_2
5.18	m	H	H
5.19	m	CH_3	H
5.20	m	Ph	H
5.21	m	Ph	Ph
5.22	p	H	H
5.23	p	CH_3	H
5.24	p	Ph	H
5.25	p	Ph	Ph

5.3 RESULTS AND DISCUSSION

5.3.1 SOLUBILITY OF AROMATIC POLYESTERS

5.3.1.1 SOLUBILITY OF POLYESTERS FROM BIPHENOLS

Table 5.2 summarizes the solubility behavior of polyesters derived from biphenols. The polyester with methyl substitution at the 2,2'-positions **5.12** has good solubility compared to the corresponding phenyl or hydrogen substituted polyesters. Polymer **5.12** is very soluble in chloroform and common organic solvents at room temperature. The polymer **5.11** is swell in polar solvents, such as, NMP, DMAc and DMSO. In contrast polymer **5.13** shows poor solubility. A possible explanation for different solubilities according to the substituents in 2, 2' positions is that introduction of the substituents on the 2, 2' positions of the biphenyl moiety provides for non-coplanarity, which reduces their crystallinity and increases solubility. Presumably the size of substituents on 2, 2' position also could significantly affect the solubility in terms of different geometric structure of the polymers. Polymers **5.14, 5.15** and **5.16** had extremely poor solubility as did polymer **5.9** because of stiffness induced by the terephthaloyl units. The copolymer **5.17** had relatively good solubility and is soluble in aprotic polar organic solvents, possibly because the repeat unit made of three monomers should give lower crystallinity [40, 41].

5.3.1.2 SOLUBILITY OF POLYESTERS FROM HYDROQUINONES

The solubility behavior of polyesters derived from hindered hydroquinones is outlined in Table 5.3. Polymers **5.18, 5.19** derived from isophthloyl dichloride had good solubility in a variety of organic solvents, such as, methylene dichloride, chloroform, NMP, and DMSO. However, polymer **5.20** prepared from 2,3,5-triphenylhydroquinone **2.22c** and isophthaloyl dichloride had somewhat limited solubility in polar solvents. The solubility behavior may be attributed to the additional hindered phenyl group in the 3 position of the arylene ring. In addition, the corresponding polymer **5.21** had extremely poor solubility because of the stiffness of the polymer backbone and the symmetrical molecular structure provided by additional phenyl groups in the 3, 5 positions. The head and tail structural irregularity of substituted hydroquinone polyesters seems to be the major solubility contributing factor along with the *m*- structure of the diacid moiety. In contrast the polymers **5.22**, **5.23**, **5.24**, **5.25** obtained from terephthaloyl dichloride belong to a different solubility category. The most interesting result is that of polymer **5.22** prepared from 2,6-diphenylhydroquinone, which is readily soluble in chloroform, methylene chloride and NMP at room temperature. Polymer **5.23** has limited solubility due to the additional substituent in the 3 position of the arylene ring. The polymer **5.23** is only soluble in polar organic solvents, such as, DMSO and TCE. Polymers **5.24** and **5.25** are not soluble in common organic solvents. The copolymer **5.26** had good solubility. The polymers obtained from hindered hydoquinones had better solubility compared to the corresponding polymers of hindered biphenols. It is possible that in the polymerization of the hydroquinones the unhindered phenolic hydroxy reacts faster with phthaloyl dichloride than the hindered one. This probably leads to the spacing unit shown in Figure 5.2, which may contribute to the solubility. Polymer **5.23** has limited solubility due to the additional

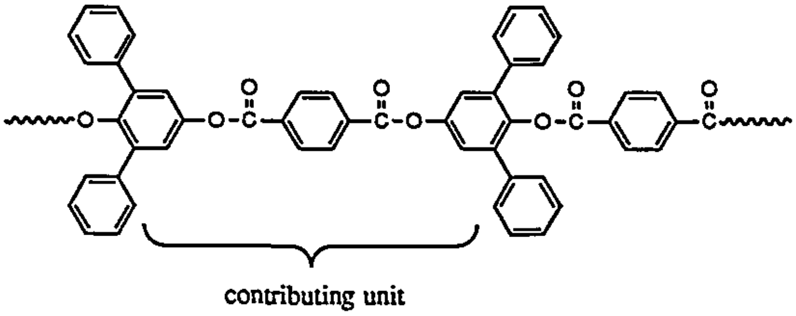


Figure 5.2 The possible unit contributing solubility in polymers derived from hydroquinones

Table 5.2 Solubility* of Polyesters Derived from Biphenols

Polymers	NMP	DMAc	DMSO	TCE	$CHCl_3$	Acetone
5.11	+	+	+	+	-	-
5.12	++	++	++	++	++	-
5.13	-	-	+	-	-	-
5.14	-	-	-	-	-	-
5.15	+	-	-	+	-	-
5.16	-	-	-	-	-	-
5.17	+	+	+	+	+	-

* Solubility : ++, soluble at room temperature; +, soluble at high temperature or swelling; -, insoluble.
NMP: N-methyl-2-pyrrolidinone; DMAc: N,N-dimethylacetamide; DMSO: dimethylsulfoxide; TCE: sym-tetrachloroethane.

Table 5.3 Solubility* of Polyesters Derived from Hydroquinones

Polymers	NMP	DMAc	DMSO	TCE	$CHCl_3$	Acetone
5.18	++	++	++	++	++	-
5.19	++	++	++	++	++	-
5.20	+	+	+	++	+	-
5.21	-	-	-	-	-	-
5.22	++	+	++	++	++	-
5.23	+	+	++	++	+	-
5.24	-	-	-	-	+	-
5.25	-	-	-	-	-	-
5.26	++	++	++	++	++	-

The symbols and solvents are identical to Table 5.2

substituent in the 3 position of the arylene ring. The polymer **5.23** is only soluble in polar organic solvents, such as, DMSO and TCE. Polymers **5.24** and **5.25** are not soluble in common organic solvents. The copolymer **5.26** had good solubility. The polymers obtained from hindered hydoquinones had better solubility compared to the corresponding polymers of hindered biphenols. It is possible that in the polymerization of the hydroquinones the unhindered phenolic hydroxy reacts faster with phthaloyl dichloride than the hindered one. This probably leads to the spacing unit shown in Figure 5.2, which may contribute to the solubility.

5.3.2 Tg AND Tm OF POLYMERS

5.3.2.1 Tg AND Tm OF POLYESTERS FROM BIPHENOLS

Table 5.4 summarizes the results of inherent viscosity, weight average molecular weight and polydispersity (Mw/Mn) obtained by viscometry and GPC. Most soluble polymers derived from these biphenols have inherent viscosities of 0.29-0.30 dL/g in NMP solution at 60 °C. The GPC data indicated that the Mw of polymer **5.12** was 16,500 compared to polystyrene standards, and a polydipersity (Mw/Mn) of 2.4. The glass transition temperature and crystalline melting temperature were determined by DSC. These Tg's and Tm's are summarized in Table 5.4. A comparison between polymers containing *p*- and *m*-units shows that the former had higher crystallinity. The polymer **5.12** and copolymer **5.17** are amorphous, while the polymers **5.11**, **5.13** are crystalline and shown high melting peaks. The Tg's of polymers, **5.11** and **5.12**, are 50 °C higher than the unsubstituted polymer **5.10** (Tg 207 °C). The polymers **5.13**, **5.14**, **5.15**, and **5.16** are highly crystalline. Their structures are sufficiently symmetrical to be considered as smooth stiff cylindrical rods. DSC study of these polymers indicated that, because of high crystallinity, their Tg's were not observed and the polymers decomposed before Tm's were observed. The tendency to crystallize increases as the substituents on the backbone become more symmetrical. The Tg's of the polymers ranged from 233 to 257 °C and they have high Tm's compared to unsubstituted polyesters **5.9**, **5.10**. The methyl substituted polymer **5.12** had the highest Tg (257 °C). Unfortunately no thermotropic behavior was detected in these materials by DSC studies on either heating or cooling. It has been reported [27] that nonlinear biphenol spacers containing large or bulky central substituents between the two phenolic rings are more effective in destroying the liquid crystal properties of the resulting copolyesters than those with smaller substituents. Hence, it was concluded that the geometric and steric effects imparted to the polymer chain backbones by the comonomers were the most important factor affecting the crystallinity of the aromatic polyesters.

5.3.2.1 Tg AND Tm OF POLYESTERS FROM HYDROQUINONES

Table 5.5 summarizes the results of inherent viscosity and GPC data. The inherent viscosity values are in the range of 0.23 to 0.71 dL/g in NMP at 60 °C. Polymer **5.19**, which was prepared by reacting 2,6-diphenyl-3-methylhydroquinone **2.22b** with terephthaloyl dichloride, had the highest viscosity of 0.71 dL/g and molecular weight of 57,900. The weight average molecular weights (Mw) ranged from 17,700 to 57,900 compared to polystyrene standards with polydispersities (Mw/Mn) in the range of 3.1 to 4.4. DSC measurements were conducted by raising the temperature at a rate of 20 °C/min under nitrogen and air atmosphere. The Tg's of the polymers ranged from 203 to 248 °C, depending upon the monomer structures (Figure 5.3). Polymers **5.18**, **5.19**, and **5.22** are amorphous. Polymers **5.20**, **5.21**, **5.23**, **5.24**, and **5.25** are crystalline and show melting peaks in the DSC curves. Polymer **5.18** obtained from 2,6-diphenylhydroquinone **2.22a** and isophthaloyl dichloride had a significantly greater glass transition temperature (55 °C) compared to the polymer **5.5** (Tg 160 °C, Tm 370 °C) derived from hydroquinone and isophthaloyl dichloride [42]. In contrast most polymers prepared from terephthaloyl dichloride are highly crystalline except for polymer **5.22**. This polymer was amorphous and had high glass transition temperature (Tg 222 °C) compared to the monophenyl substituted polyester (Tg 146 °C, Tm 342°C) [43] but lower than the unsubstituted polymer **5.4** [10] (Tg 307 °C, Tm 467 °C) which is completely crystalline. The polymer **5.25** has a chain rigid polymer backbone due to the additional phenyl groups on 3,5 positions and a Tg was not detected in DSC. We concluded that the polyesters which are multi-substituted on one phenyl ring, despite their awkward structure, may crystallize readily due to their rigid backbones however they show no detectable thermotropic behavior in DSC studies. This is much like poly(*p*-phenylene terephthalate) which shows only a high crystalline melting temperature.

5.3.3 EFFECTS OF SUBSTITUENTS ON Tm

We may explain why polymers we have prepared show high crystalline melting points as follows. According to Goodman and Cachia [44], the substituent effect is due to a steric impediment to rotation on the backbone, present as a result of molecular geometry in the higher-melting families. The ester group cannot rotate around the phenyl-COO axis

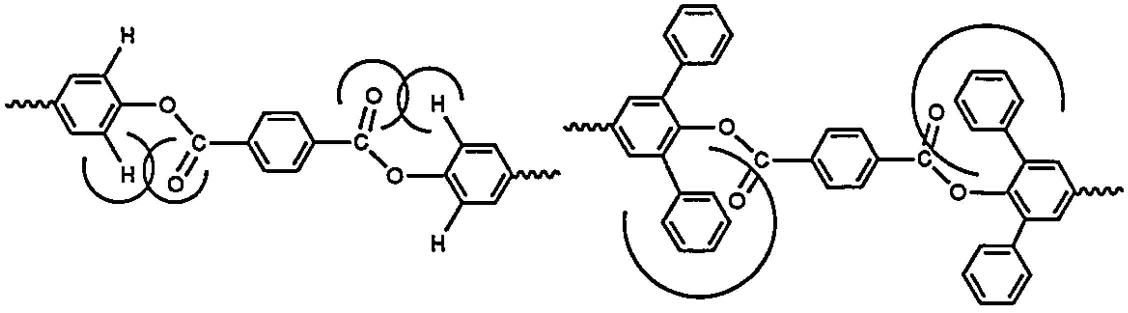


Figure 5.4 Structural conformations due to steric effect on the ortho position

because of interference from substituents, which is probably the reason why ortho-substituted polyesters have somewhat higher melting points. This can explain why the prepared polyesters are highly crystalline with high melting points because of their molecular geometry. As shown in Figure 5.4, the bulky phenyl substituents, in the ortho positions, sterically hinder the carboxyl group and their orbitals are overlapped compared to the unsubstituted one. This impediment represents a further mode of influencing the entropy of fusion of polyesters and increases the melting point.

5.3.4 THERMAL STABILITY

5.3.4.1 MECHANISM OF THERMAL DEGRADATION OF POLYESTERS

In general, polyesters tend to break down thermally as a result of two or more concurrent competitive routes. The pyrolysis of simple model compounds related to poly(ethylene terephthalate) has been reported by Gooding and Ritchie [45]. When this polymer is maintained in a molten state under nitrogen at 300 °C, it slowly decomposes into a number of compounds. Mass spectrometry analysis indicates that the gaseous products are mainly CO, CO_2, and CH_2CHO. Straus and Wall [46] assume that, on the basis of these results, initiation of thermal degradation consists in homolytic scission at C-O linkages in the chain, rather than at C-C bonds, since the C-O bond has a lower strength than the C-C bond. This is illustrated in the structural formula of the ester, where the weaker bonds are indicated by dotted lines (Figure 5.5).

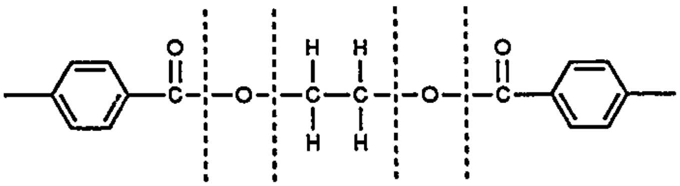


Figure 5.5 Illustration of weaker bonds is indicated by dotted lines

5.3.4.2 THERMAL STABILITY OF POLYESTERS

In general, polyarylates are engineering thermoplastics which show properties such as high softening point, good dielectric constant, high stability to chemical corrosion and thermal stability. The thermal behavior of polymers prepared was measured by TG/DTA. Table 5.4 and 5.5 summarizes typical thermal properties of the polyesters under nitrogen and air. The 5% weight loss temperature of these polymers ranged from 452 °C in air to 476 °C in nitrogen (Figure 5.6). These polymers have thermostability comparable to known polyarylates. The thermal stability of these polyesters was lower than that of the corresponding polysulfones and poly(ether ketone)s because we assume that the bond strength of the ester group in the polyaryates is weaker than the polysulfones and poly(ether ketone)s which have resonance structures to affect stability.

5.3.5 MECHANICAL PROPERTIES

A film of the polymer **5.22** obtained from a solution cast in chloroform is transparent and tough. It maintained dimensional integrity from room temperature to close to its Tg (Figure 5.7). The glass transition temperature as determined by TMA agreed with the Tg determined by DSC. The Young's moduli from TMA/SS were in the range 1.78 to 0.70 GPa between 25 °C - 200 °C.

5.4 CONCLUSIONS

A new series of polyesters was prepared and characterized. Most terephthalate ester polymers were crystalline and exhibited very poor solubility. However the polymer **5.22** is amorphous and readily soluble in common organic solvents. In contrast isophthalate ester polymers belong to a different category. Their solubilities, by modification of the geometry of the hydroquinone or biphenol, are markedly different from the conventional polymers. In the case of polymers from hindered biphenols substituted by hydrogen or phenyl in the 2,2'- positions, they have poor solubility, but polymers containing methyl moieties in the same positions have good solubility. The polymers prepared from hydroquinones had a limited solubility which increased with the degree of substitution in the 3 or 3,5 positions on the arylene ring. Most modified polyesters showed increased glass transition temperatures and maintained good thermal stability.

5.5 EXPERIMENTAL

Materials

All monomers used are reported in Chapter 2. Terephthaloyl and isophthaloyl dichlorides were purchased from Aldrich Chemical Co. They were sublimed and kept in a nitrogen atmosphere. Zinc (Aldrich) was activated with 5% hydrochloric acid, washed with water, methanol, ether, and dried. *o*-Dichlorobenzene was distilled and dried with 3 Å molecular sieves.

Polymer Characterization

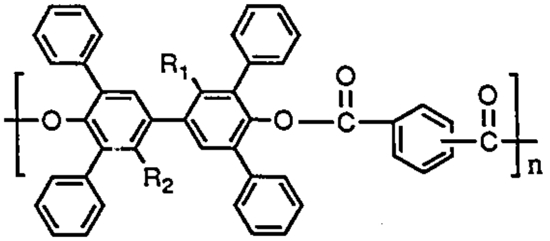
DSC and TG/DTA measurements were conducted with Seiko 220 DSC at heating rate of 20 °C/min, and Seiko 220 TG/DTA instruments respectively. Aluminum pans were used with a heating rate of 10 °C/min under nitrogen and air atmosphere. Inherent viscosities were measured in a calibrated Ubbelohde viscometer at a concentration 0.5g/dL of polymer in NMP at 60 °C. Molecular weight of polymers were determined relative to polystyrene by gel permeation chromatography (GPC) in chloroform as solvent on a Waters 510 HPLC with a set of four μstyragel columns (500, 10^4, 10^5, and 100 Å) in series and a UV detector. Mechanical properties were measured on a Seiko TMA/SS 120 instrument at 25

°C with a heating rate of 3 °C/min in static air. The polymer film for mechanical analysis was cast from 0.1 wt % chloroform solution on a glass plate (3 cm diameter) at room temperature over 48 h, and then was dried at 100 °C for 10 h.

General polymerization (5.12).

In *o*-dichlorobenzene (8 mL) was dissolved 2,2'-dimethyl-3,3',5,5'-tetraphenyl-[1,1'-biphenyl]-4,4'-diol **2.17b** (1 g, 2 mmol) , isophthaloyl dichloride (0.4 g, 2 mmol) and a small amount of zinc dust as a catalyst and the reaction was conducted under a nitrogen atmosphere. The reaction was heated to reflux temperature and kept at that temperature for 6 h. The solution became viscous and was diluted with additional dichlorobenzene (3 mL), allowed to cool and precipitated in methanol. The resulting polyester was filtered and dried under vacuum. The polymer was dissolved in chloroform and filtered through celite (1 cm). The polyester was reprecipitated in methanol and dried in vacuum at 100 °C for 24 h.

Table 5.4 Physical and Thermal Properties of Polyesters from Biphenols



Polymers	R_1	R_2	esters	$Tg^a/Tm(°C)$	$TGA^b(°C)$ N_2/Air	ηinh^c	$Mw^d/10^3$	Mw/Mn
5.11	H	H	m	255/409	474/452	0.30	-	-
5.12	CH_3	CH_3	m	257/ -	466/453	0.29	16.5	2.4
5.13	Ph	Ph	m	- /367	482/464	-	-	-
5.14	H	H	p	- -	444/476	-	-	-
5.15	CH_3	CH_3	p	- -	442/464	-	-	-
5.16	Ph	Ph	p	- -	474/464	-	-	-
5.17[e]	Ph	Ph	m+p	250/ -	482/467	0.30	-	-

[a] DSC were determined at heating rate 20 °C/min under nitrogen (flow rate 50 mL/min).

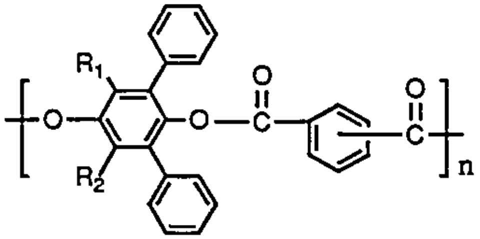
[b] Temperature at which 5% weight loss were determined by TGA at heating rate 10 °C under air and nitrogen (flow rate 200 mL/min).

[c] Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 60 °C.

[d] Molecular weights were determined by GPC in chloroform based on polystyrene standards.

[e] Polymerization was carried out in 50:50 % of tere and isophthaloyl dichlorides.

Table 5.5 Physical and Thermal Properties of Polyesters from Hydroquinones



Polymers	R_1	R_2	esters	Tg^a/Tm(°C)	TGA^b(°C) N_2/Air	ηinh^c	$Mw^d/10^3$	Mw/Mn
5.18	H	H	m	210/ -	443/432	0.30	19.2	3.5
5.19	CH_3	H	m	193/ -	427/428	0.28	17.7	4.4
5.20	Ph	H	m	209/343	473/448	0.23	-	-
5.21	Ph	Ph	m	246/323	435/418	-	-	-
5.22	H	H	p	222/ -	443/436	0.71	57.9	3.1
5.23	CH_3	H	p	202/ 354	447/424	0.29	-	-
5.24	Ph	H	p	248/ -	469/434	-	-	-
5.25	Ph	Ph	p	- / -	458/408	-	-	-
5.26[c]	Ph	H	m+p	203/ -	418/405	0.20	-	-

[a,b,c,d,c] were performed as in Table 5.4

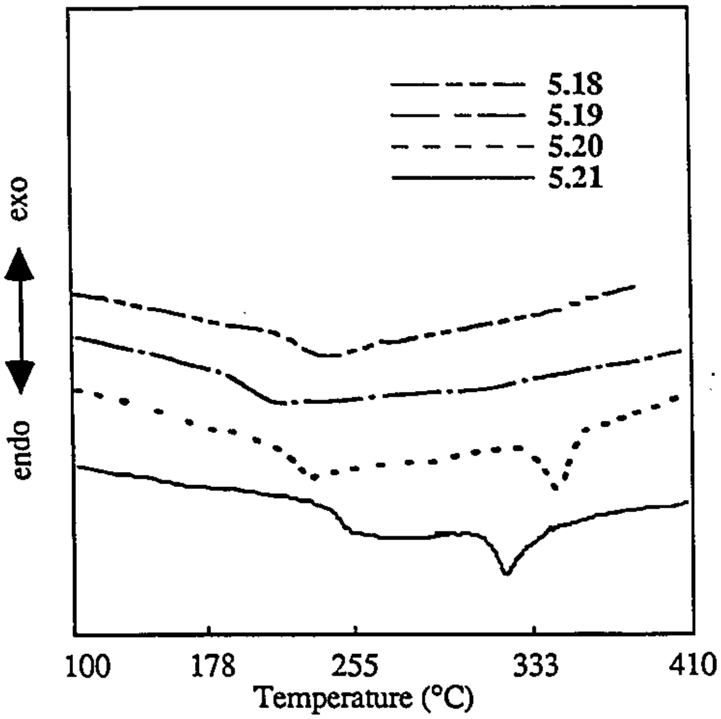


Figure 5.3 DSC analysis of polymers **5.18-5.21** under an atmosphere of nitrogen.

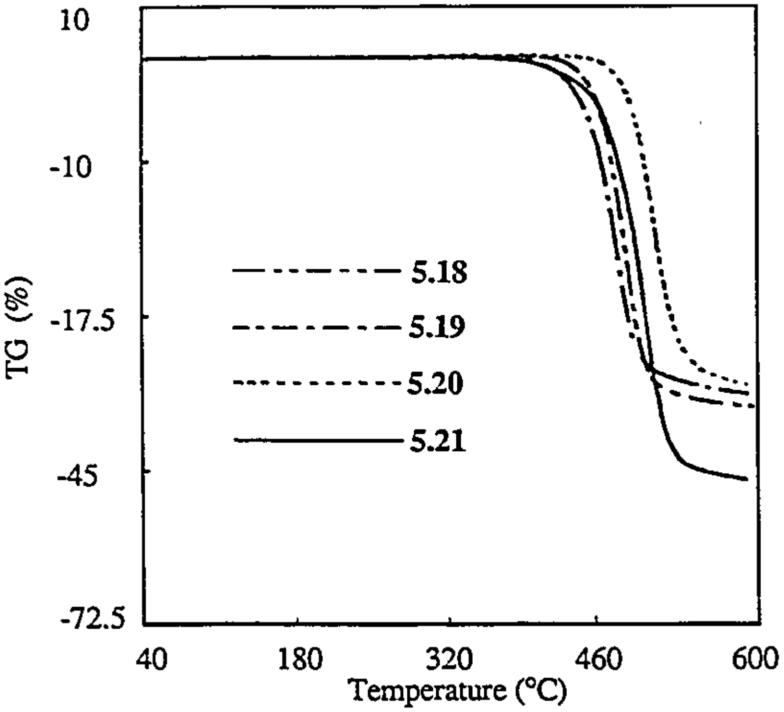


Figure 5.6 TGA thermogram (weight loss vs temperature) for polymers **5.18-5.21** under an atmosphere of nitrogen.

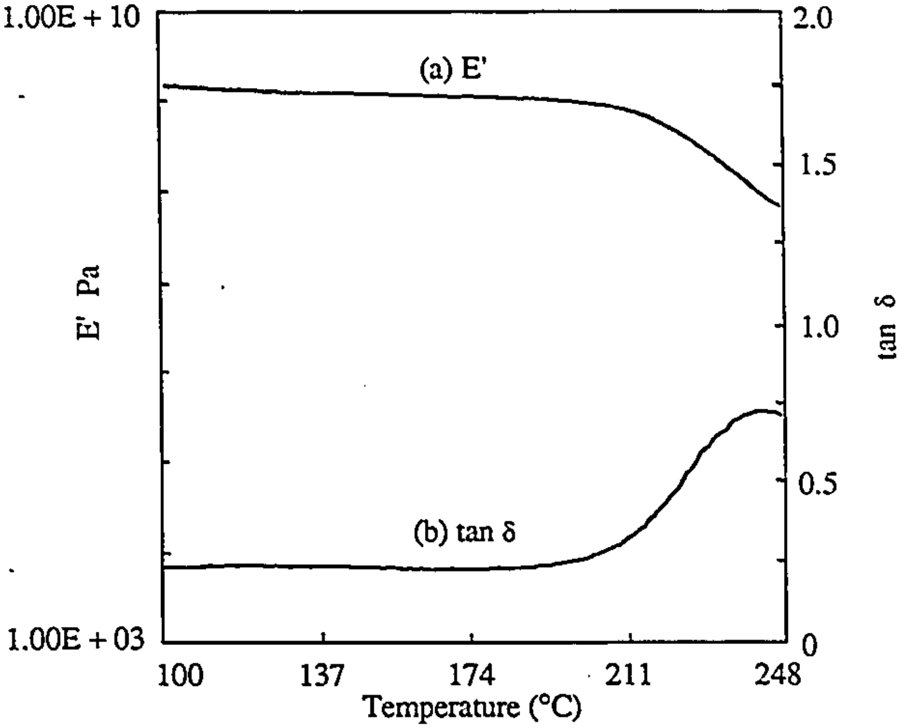


Figure 5.7 Thermomechanical analysis for polymer **5.22**:

(a) modulus (E') vs temperature; (b) tan δ vs temperature.

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CHAPTER 6

POLYIMIDES

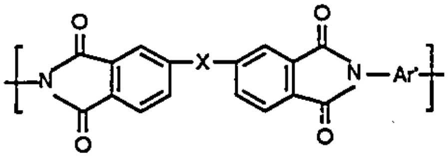
6.1 INTRODUCTION

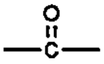
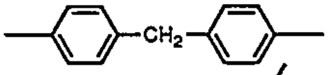
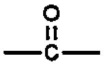
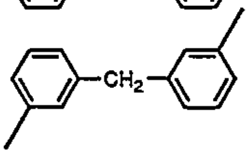
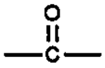
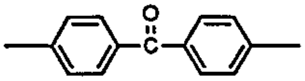
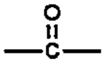
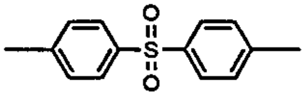
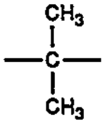
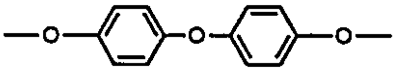
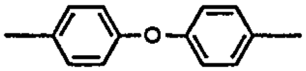
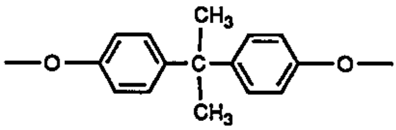
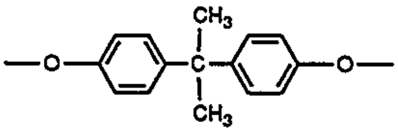
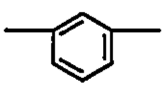
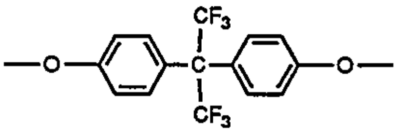
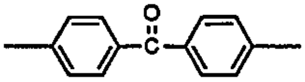
Polymers containing heterocyclic rings in the main chain are becoming increasingly important industrially, due to the attractive combination of properties conferred by the presence of heterocyclic units. In particular, aromatic, heterocyclic polyimides exhibit excellent properties, outstanding mechanical properties and oxidative stability, and are of major commercial and industrial importance [1,2]. These materials are widely used in place of metals and glass in high performance applications throughout the electronics, automotive, aerospace, and packaging industries [3]. Most of the commercial polyimides (Kapton , Pyre-ML, Vespel) [4] are based on *p,p* '-diaminodiphenylether and pyromellitic dianhydride and were developed by duPont. ULTEM [5], developed by General Electric Company, is derived from bisphenol A dianhydride and *m* -phenylenediamine. Thermoplastic soluble polyimides [6,7,8] are listed in Table 6.1.

6.1.1 SYNTHETIC ROUTES TO POLYIMIDES

The first synthesis of polyimides was carried out by Bogert and Renshaw [9], who observed that when 4-aminophthalic anhydride or dimethyl-4-aminophthalate is heated, water or alcohol is evolved and a polyimide is formed. However, particular interest in the

Table 6.1 Thermoplastic Soluble Polyimides



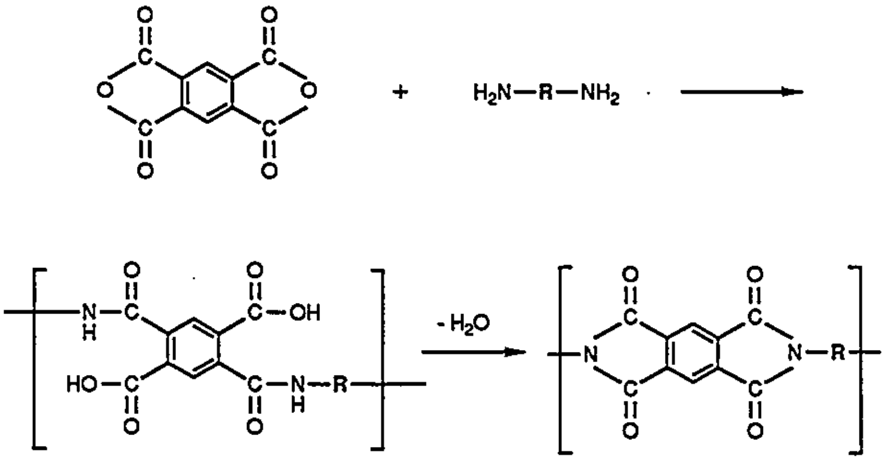
Polymers	X	Ar'	Tg(°C)
6.1	 $-\mathrm{C}(=\mathrm{O})-$		290
6.2	 $-\mathrm{C}(=\mathrm{O})-$		232
6.3	 $-\mathrm{C}(=\mathrm{O})-$		267
6.4	 $-\mathrm{C}(=\mathrm{O})-$		273
6.5	 $-\mathrm{C}(\mathrm{CH_3})_2-$		352
6.6			255
6.7			215
6.8			227
6.9			217
6.10			248

synthesis of polyimides arose during the last 20 years, when it was found that many polymers of this class had extremely valuable properties. Wholly aromatic polyimides are derived from aromatic dianhydrides and aromatic diamines, or from aromatic compounds containing both an amine and anhydride group, by polycondensation, displacement reaction, and Diels-Alder reaction.

6.1.1.1 TWO-STEP POLYMERIZATION

Aromatic polyimides are synthesized [10,11,12] by the reaction of dianhydrides with diamines as illustrated in Scheme 6.1. The direct production of high molecular weight aromatic polyimides in a one stage polymerization cannot be accomplished because the polyimides are insoluble and infusible. The polymer chains precipitate from the reaction media before high molecular weights are obtained or if the reaction is carried out in the melt the reaction mixture becomes intractable. Polyimides are, therefore, generally synthesized by a two-step polycondensation method which has found very widespread use, where

Scheme 6.1



6.11

soluble polyamic acids are obtained in the first stage of reaction. This first stage consists in the acylation of a diamine by a dianhydride of a tetracarboxylic acid in a polar solvent such as NMP, DMSO, DMAc, and DMF, with the formation of the polyamic acid. The second stage of the reaction, imidization, is carried out thermally or chemically. The thermal cyclization [13] of polyamic acid to the polyimide is performed in the solid state by heating at temperatures above 150 °C or by heating a cast solution of a polyamic acid, with a low solid content (15-25 %) in vacuum or inert atmosphere. Generally, the solvent is removed at a temperature between 100°C and 150 °C and the polymer is then heated to 300 °C or 350 °C. Polyamic acids also can be dehydrated by a chemical process using an aliphatic anhydride in the presence of a tertiary amine [14]. Common reagents are acetic anhydride with triethylamine or pyridine.

A modified two-step polymerization to polyimide involves the reaction of the dianhydride with silylated diamines which are obtained by the reaction of trimethylchlorosilane and the diamine [15]. The reaction gives a poly(amide trimethylsilyl ester) in a solvent such as tetrahydrofuran at room temperature, by transfer of the silyl group to the carboxylic group, which is subsequently cyclized to polyimide, with elimination of trimethylsilanol, by heating at 150 °C.

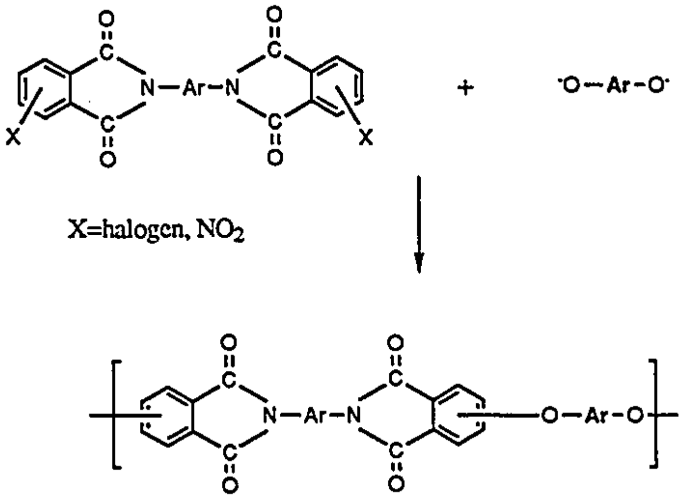
6.1.1.2 ONE-STEP POLYMERIZATION

Sterically hindered monomers, or those with inappropriate acid/base relationships which react sluggishly in the two-step procedure, can be successfully polymerized in a one-step reaction. Polymerization is carried out by heating the diamine and the dianhydride in phenolic solvents, such as phenol, *p*-chlorophenol, *m*-, *p*-cresol, and 2,4-dichlorophenol, and then casting the polyimide/phenolic solvent system to form films. Harris [16] has shown that a sterically hindered dianhydride and a set of diamines of varying basicity can be reacted together in a one-step polymerization at high temperature in m-cresol to yield high molecular weight polyimides. An alternative one-step route to polyimides is the reaction of dianhydrides with diisocyanates [17,18]. The reaction is catalyzed by water or a metallic alkoxide with carbon dioxide as a by-product. The mechanism is complex and the catalytic effect of water is interpreted as arising from a partial hydrolysis of isocyanate, followed by reaction of the aromatic amine with the anhydride through the intercession of an unstable seven-membered ring intermediate [19].

6.1.1.3 MODIFIED ROUTE (Nucleophilic Nitro Displacement Reaction)

Another synthetic route [20,21] to polyimides is the aromatic nucleophilic substitution reaction of activated nitroaromatics by phenoxide dianions (Scheme 6.2). The reaction takes place in anhydrous DMSO or DMF after the formation of the bisphenolate. In general, nitro displacement polymerization leads to high molecular weight poly(ether

Scheme 6.2



imide)s for bisphenols such as bisphenol A and 4,4'-dihydroxydiphenyl ether in which each hydroxy group is attached to separate benzene rings. However, low molecular weight polymers were obtained for mononuclear difunctional phenols such as hydroquinone and resorcinol. The imide ring activates the nitro group sufficiently to allow facile nucleophilic substitution. Poly(ether imide)s such as ULTEM were synthesized by the classical route [22]. Although the polymer-forming step is the reaction of diamine and dianhydride by a conventional two step method, the key step is the aromatic nucleophilic substitution reaction leading ultimately to the dianhydride. An increasingly wide range of bisphenols is available commercially, greatly increasing the applicability of these synthetic routes

6.1.2 THE GOALS AND STRATEGY

Aromatic polyimides have developed rapidly in recent years due to their outstanding properties [1,2,23] However their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents. The direct linkage between aromatic and heterocyclic nuclei makes the chain very rigid and ensures high glass transition temperatures or crystalline melting points, leading to good mechanical properties at high temperatures. However, their high Tg or Tm and very poor solubility are important drawbacks to their use, therefore the synthetic strategy used will depend strongly on structure of monomers and on the final application for which the polymers are intended. Modified structures (see Table 6.1) with flexible linkages between aromatic rings in the diamine and dianhydride provide good solubility. Several soluble polyimides systems have been described. Kurita [24] demonstrated that the introduction of bipyridyl units into the polymer chain enhanced the solubility of the polymer. Takekoshi *et al* [21,22] have synthesized bisphthalic dianhydrides by the condensation of BPA and 4-nitro-N-methyl phthalimide followed by conversion to the dianhydride, which is polymerized with meta phenylenediamine to give ULTEM® **6.9** which showed excellent solubility. Harris [25] reported soluble polyimides through the introduction of trifluoromethyl substituents in the 2,2' positions on biphenyl, which forces the aromatic rings into a noncoplanar conformation providing good solubility.

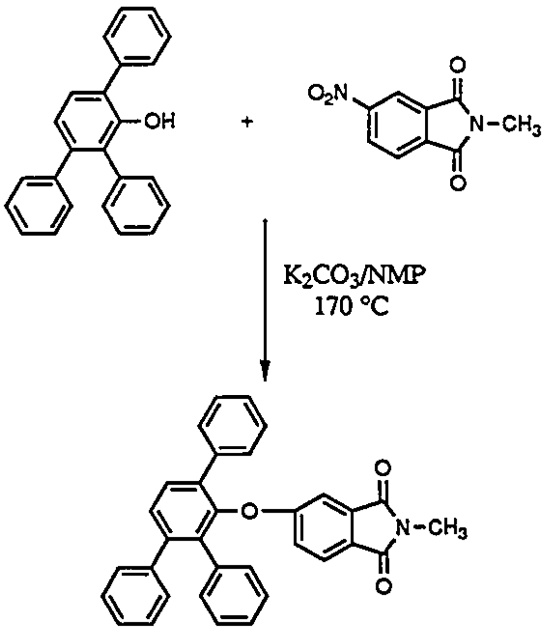
In this section we describe the synthesis of modified monomers which incorporate both flexible ether linkages and rigid biphenyl-containing bulky phenyl substituents in order to obtain processable polymers. We describe the successful synthesis of a series of dianhydrides containing hindered biphenyl ether linkages and novel soluble aromatic polyetherimides prepared by the condensation of these monomers with phenylenediamines through the two-step polymerization. These aromatic polyetherimides are all amorphous and are readily soluble in organic solvents at room temperature. They have excellent thermal-oxidative stability with high glass transition temperatures

6.2 PREPARATION OF MONOMERS AND POLYMERS

6.2.1 MONOMER SYNTHESIS

Recently there has been a considerable effort directed at the nitro displacement reaction by Takekoshi *et al* [20,21,22]. They found that nitro displacement of N-phenyl-3 or 4-nitrophthalimide and various bisphenol salts proceeded readily in polar aprotic solvents to form bisetherimides in high yields. During the displacement reaction, the negative charge of the expected Meisenheimer type transition state is well-delocalized by resonance effects. This effect significantly lowers the activation energy of the displacement reaction. In particular, nitroimides are one order of magnitude more reactive than the corresponding

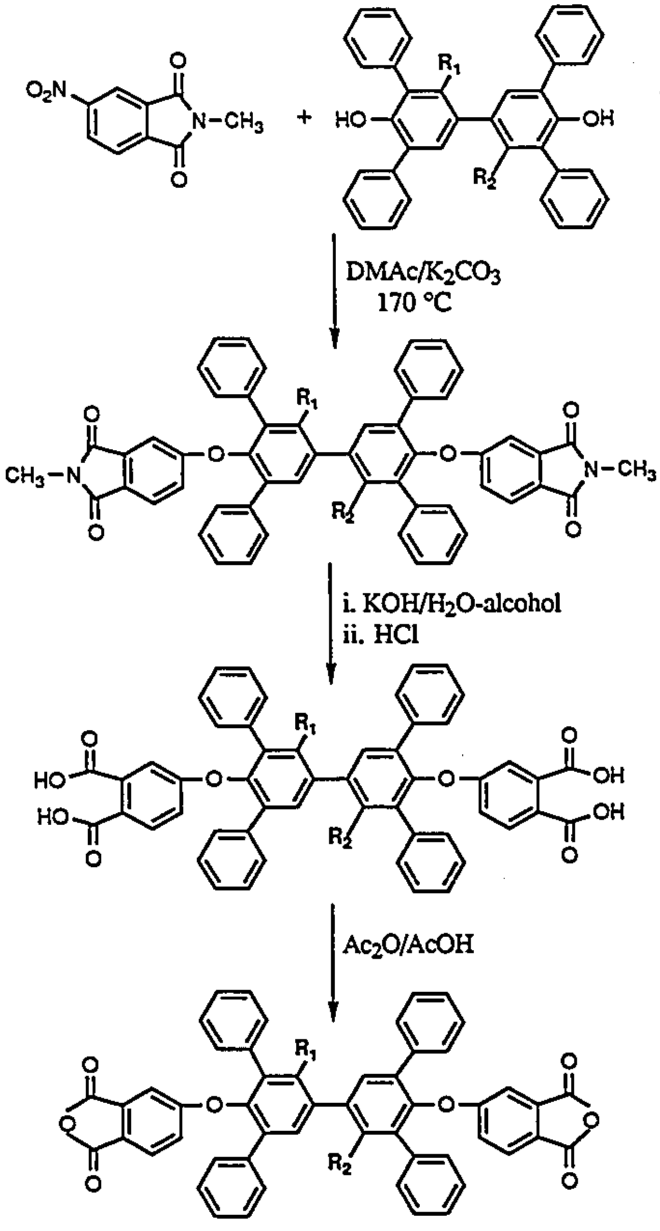
Scheme 6.3



6.12

fluoro derivatives [26]. We wished to investigate the nitro displacement reaction of N-methyl-4-nitrophthalimide with the sterically hindered biphenols, **2.12**, **2.13**, **2.17a** and **2.17b**. In the model study (Scheme 6.3) the displacement reaction between N-methyl-4-nitrophthalimide and 2,3,6-triphenylphenol was successfully achieved in NMP using potassium carbonate as a base at 170 °C. The displacement reactions had to be carried out under anhydrous conditions with a weak base because the imide rings of nitrophthalimides are sensitive to a base-catalyzed hydrolytic ring-opening reaction which produces carboxylic acids. For this reason the weak base, potassium carbonate, should minimize the ring opening reactions. Moreover the displacement reactions with these biphenols are slower than BPA because of the phenyl substituents in the 2,6 positions which provide steric hindrance. These kinds of reactions must be performed necessarily under mild condition in order to minimize ring opening during the long reaction. We attempted the nitro displacement reactions with hindered biphenols containing methyl, phenyl or chloro

Scheme 6.4



a : R_1=H, R_2=H
b : R_1=CH_3, R_2=CH_3
c : R_1=Ph, R_2=Ph
d : R_1=Cl, R_2=H

6.13a, b, c, d

6.14a, b, c, d

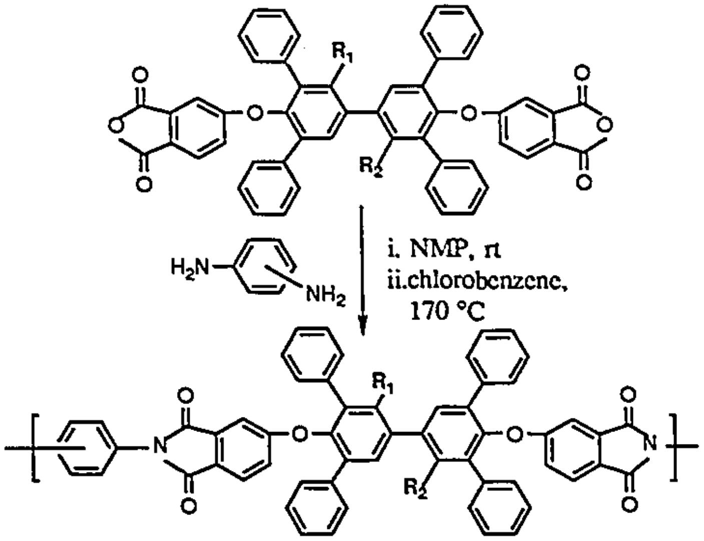
6.15a,b, c, d

substituents and N-methyl-4-nitrophthalimide in the presence of potassium carbonate and found that these reactions could be successfully performed and isolated in high yields ranging from 68 to 88 %. The results are displayed in Table 6.2. The displacement reaction of 2-chloro-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol **2.13** showed that the first displacement reaction proceeds as rapidly as other biphenols, but the second reaction was much slower and this effect can be explained in part by the higher acidity influencing the rate [27]. The chlorine in the 2-position would increase the acidity of the phenol and hence decrease the nucleophilicity of the anion relative to a hydrogen substituent, which would decrease the rate of the displacement reaction. Hydrolysis of N-methylphthalimide, whether acid or base catalyzed, is usually very slow. The bis(ether imide)s **6.13(a,b,c** and **d)** were hydrolyzed in a conventional manner in an aqueous potassium hydroxide solution containing alcohol to the corresponding tetracarboxylic acids for 3-5 hours at reflux temperature in quantitative yield. The anhydrides were formed via a ring closing reaction of the dicarboxylic acid in the presence of a dehydrating agent such as an acetic anhydride or trifluoroacetic acid. All of the bis(ether)tetracarboxylic acids **6.14(a,b,c** and **d)** were cyclized to bisanhydrides **6.15(a,b,c** and **d)** in high yield using acetic anhydride and acetic acid. The bisanhydrides synthesized are listed in Table 6.2.

6.2.2 POLYMERIZATION OF DIANHYDRIDES WITH DIAMINES

Aromatic polyimides are usually insoluble and infusible so that the polymer either precipitates out of solution, or solidifies during the reaction. Therefore, most polyimides are preferably formed in two discrete steps with isolation of the intermediate polyamic acid, followed by heating to cyclize at high temperature. However modified monomers containing flexible linkages and twisted conformations can be polymerized without isolation of the polyamic acid. We were able to successfully polymerize the

Scheme 6.5

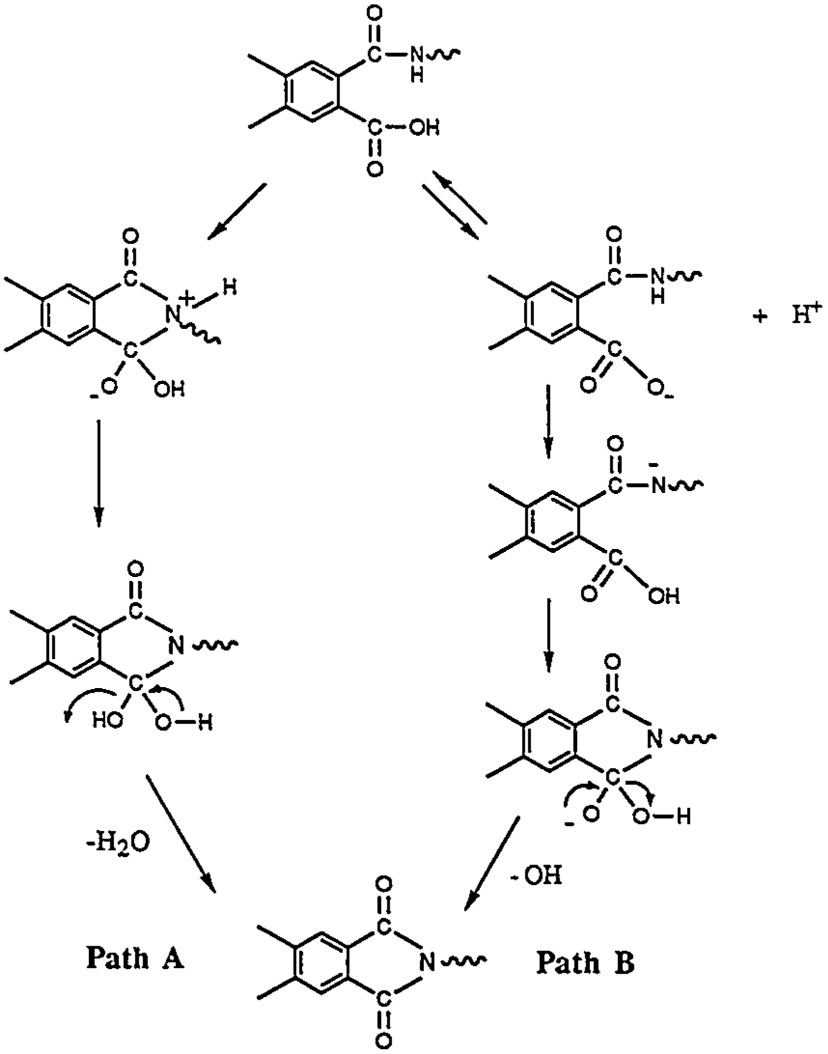


bis(etherphthalic anhydride)s obtained with either meta or para phenylenediamine in NMP to polyamic acids. The polyamic acids were converted to the corresponding poly(etherimide)s by dehydration. The liberated water was removed by azeotropic distillation with chlorobenzene. The reaction was maintained at 170 °C for 5 h. We had difficulty in making high molecular weight polymers in very small scale reactions because of problems in controlling the stoichiometry between the two monomers, dianhydride **6.15c** and phenylene diamine (8.6:1 weight ratio). We also attempted copolymerizations of BPA-dianhydride with our dianhydrides and phenylenediamines under similar conditions.

6.2.3 MECHANISM OF POLYMERIZATION

The proposed reaction pathways [28] for cyclization of polyamic acids are shown in Scheme 6.6. The first point to note is that the time at which the hydrogen attached to the nitrogen is lost is different in the two pathways. In Path A, the free polyamic acid is cyclized and the amide proton is transferred to oxygen. However, in Path B, cyclization is

Scheme 6.6



through the ionization of the polyamic acid and involves the ionized form of the polyamic acid as the preferred precursor to the activated complex. Since the conjugate base of the amide is a considerably stronger nucleophile than the amide, ring cyclization should occur considerably faster in Path B. Imidization is known to proceed faster in the presence of amide solvents [29]. The primary rationale for this phenomenon is that solvent molecules allow the reacting species to attain favorable conformations for cyclization. It seems quite probable that they also assist in the loss of the carboxyl proton. The amide solvents are known to form strongly hydrogen bonded complexes with the carboxyl groups. Thus, the transfer of a proton to the basic solvent under the imidization conditions would seem quite likely [29]. In fact, the solvent molecule probably functions as a proton sink, accepting the proton from the carboxyl group and then donating it back after the ring closure. Of course, many of the steps may take place simultaneously, and free ions may not be formed. In the absence of solvent, ring closure may proceed via the attack of neutral amide on the undissociated acid.

6.3 RESULTS AND DISCUSSION

The polymer properties were evaluated by DSC, TGA/DTA, viscometry, TMA and GPC. The results are summarized in Table 6.3, 6.4 and described in the following text.

6.3.1 SOLUBILITY AND PROPERTIES

Aromatic polyimides as a class are generally insoluble in common solvents. They can be rendered soluble with many of the structural modifications noted previously in this thesis for reduction of Tm, or enhancement of amorphous character and reduction of Tg. Poly(etherimide)s prepared from the bulky dianhydrides that we have synthesized and *p*-, *m*-phenylene diamines were amorphous and soluble in common organic solvents such as, N-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide, chloroform and methylene chloride at room temperature. The bulky substituents, such as the phenyl groups in 2,2' positions, force noncoplanarity between the phenylene rings of the biphenyl moiety which then take up more spatial volume and hence increase the solubility. The molecular weights of the resulting polymers were determined by gel permeation chromatography (GPC) using polystyrene standards. These polymers had molecular weights (Mw) in the range 14,200-

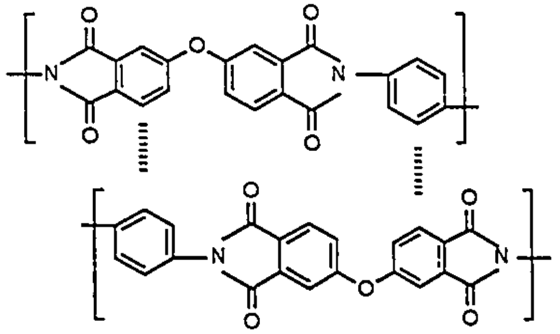
41,100 and polydispersities (Mw/Mn) of 1.63-2.63. Inherent viscosities (ηinh=0.13-0.32) of polymers were measured at room temperature in chloroform.

6.3.2 Tg OF POLYIMIDES

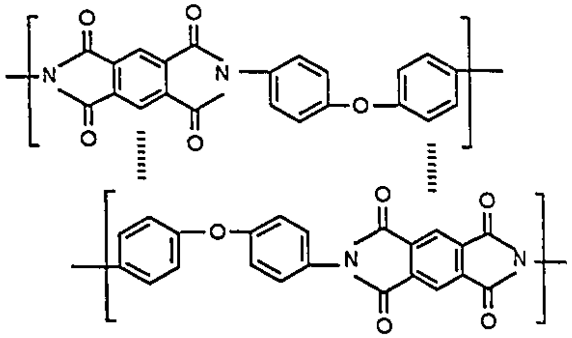
The glass transition temperatures (Tg's) of the polymers listed in Table 6.3 and 6.4 were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C / min under air or nitrogen atmosphere. The resulting polymers showed Tg' in the range of 240-317 °C (see Table 6.3 and 6.4). As we expected the Tg's were enhanced due to the rigid biphenyl units. The Tg of the polymer (286 °C) derived from dianhydride (**6.14b**) and meta-phenylenediamine was 70 °C higher than the Tg (217 °C) of the polymer **6.8** derived from BPA-dianhydride and meta-phenylenediamine [30]. The Tg's of copolymers appeared at the mid point between those of the corresponding homo polymers which is in agreement with theoretical values (see Table 6.4).

6.3.3 Tg AND STRUCTURE-PROPERTY RELATIONSHIPS OF POLYIMIDES

The Tg of polyimides is strongly influenced by both intramolecular (chain mobility) and intermolecular (charge-transfer-complex and preferred layer packing) factors [31,32] (Figure 6.1). The trend of Tg cannot be explained only by intramolecular factors (*i.e.* the more flexible the lower the Tg). The ortho-containing polymers contradict this explanation of backbone flexibility with their Tg's being considerably higher than expected. Highly dipolar bridging groups such as carbonyl and sulfonyl impart higher Tg than do groups such as oxy or methylene, which can be explained by using intermolecular factors. The existence of charge transfer complex (CTC) formation between dianhydride and imide groups in poly(pyromellitic dimide)s was first proposed by Kotov et al [31]. Fryd

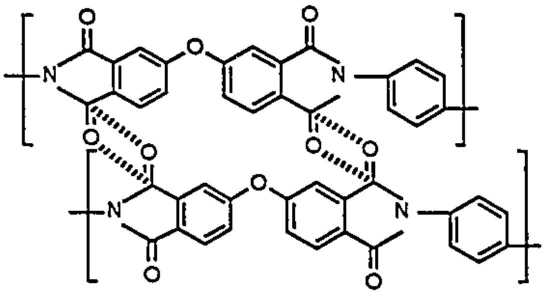


6.32 Tg=342 °C

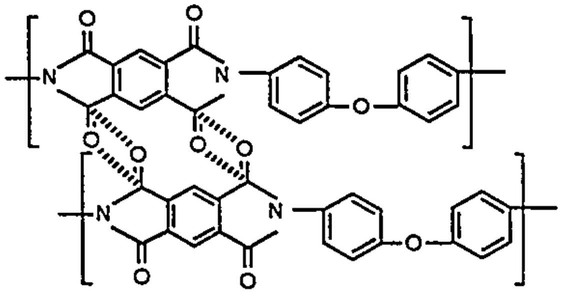


6.33 Tg=399 °C

Charge-Transfer-Complex (CTC) model for polyimide in the solid state

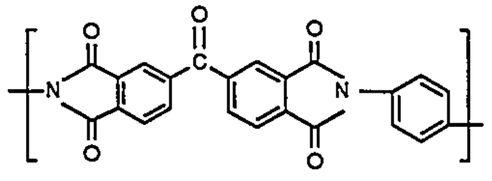


6.34

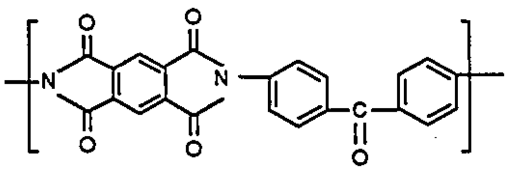


6.35

Preferred Layer Packing (PLP) of diimides for polyimides in the solid state



6.36 Tg=333 °C



6.37 Tg=412 °C

Figure 6.1 The prime factors contributing to interchain attraction forces in polyimides.

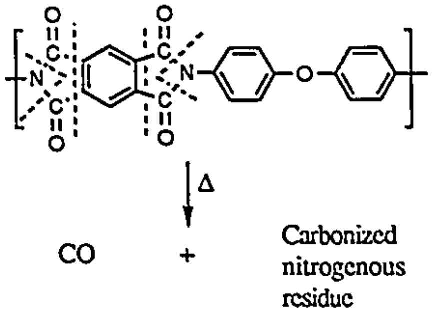
suggested that CTC formation between dianhydride and imide groups increases interchain interaction forces [33], and further proposed CTC formation as a main cause for the high Tg's of polyimides. He observed that the presence of a bridging group within dianhydride repeating units affects Tg's more profoundly than its presence within diimide repeating units. For instance, Tg's of polyimides **6.33** and **6.37** are significantly higher than that of polyimides **6.32** and **6.36**, respectively. The presence of bridging groups such as O and CO between dianhydride groups, therefore reduces the interchain attraction forces of the CTC present in the solid state polyimides **6.32** and **6.36**. Some recent studies have revealed new evidence against the validity of the CTC model. Zubkov [32,34] employed an X-ray method and observed a preferred layer packing (PLP) of diamines in crystalline regions of polyimides. The PLP can also qualitatively account for the observed predominating effects on Tg's by bridging groups within dianhydride monomers. Due to the presence of bridging groups within dianhydride monomers **6.35**, carbonyl-carbonyl or dipolar attractions in the PLP of diimide groups will be largely disrupted. In contrast, the presence of bridging groups within diamine monomers exerts only a dilution of the packing density of the PLP of diimido groups **6.34** and therefore provides less influence on the Tg's of polyimides. Presumably the prepared poly(ether imide)s might have very weak charge transfer complex interactions and preferred layer packing interactions because the hindered biphenyl units make it difficult to pack together, thus diluting the packing density. The polymers contain bulky bridging groups within the dianhydride and the ether units reducing the electron affinity of the dianhydride groups. Thus there may exist very weak interchain attraction forces from a charge transfer complexes and preferred layer packing interaction.

6.3.4 THERMAL STABILITY OF POLYIMIDES

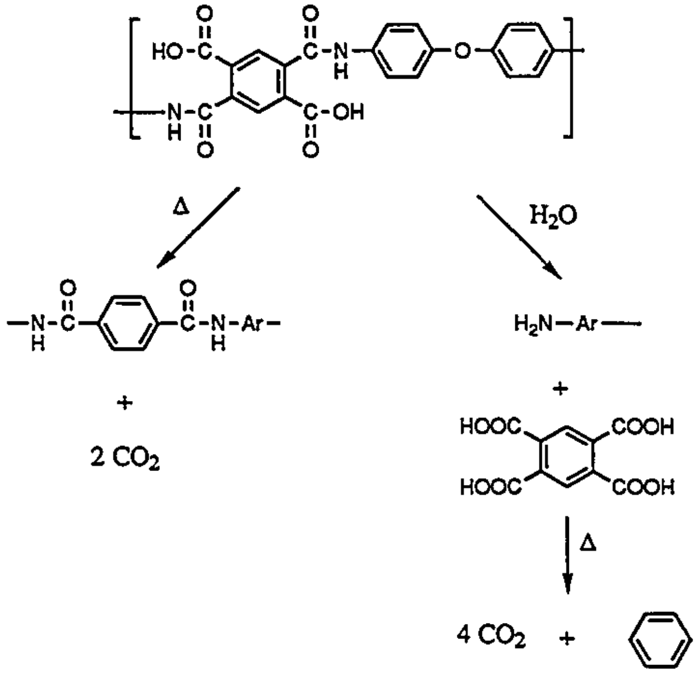
6.3.4.1 MECHANISM OF THERMAL DEGRADATION

The main thermal degradation mechanism of the polyimide chain has not been exactly identified. However, some evidence for the main degradation path may be gained from the

Scheme 6.7



Proposed mechanism A



Proposed mechanism B

elemental analyses and infrared spectrum. Bruck [35] has studied the thermal degradation of aromatic polypyromellitimide in air and vacuum. The major degradation products were carbon monoxide and carbon dioxide. It is assumed that the carbon monoxide originates from the imide groups by thermal free radical degradation (Scheme 6.7, mechanism A). Pyrolysis of polyimide takes place in two distinct phases: one at 580-625 °C, where a large weight loss occurs, and the second at 700-950 °C, where only a 4.5 % weight loss occurs [36] The former results from C-N and C-O bond cleavage and the latter is caused by loss of CO with concurrent formation of nitrene and benzyne moieties. IR and mass spectrometric data suggest the participation of polyamic acid impurities in the degradation process by thermal cleavage of its carbonyl bonds and hydrolytic scission of its amide groups. The polyamic acid units are expected to decarboxylate at elevated temperatures and undergo free radical as well as hydrolytic scissions. The hydrolytic scission of the polyamic acid could arise from catalytic amounts of absorbed water molecules held by hydrogen bonding (mechanism B) [35].

6.3.4.2 THERMAL STABILITY OF POLYIMIDES

The poly(ether imide)s showed excellent thermoxidative stability by thermogravimetric analysis, with 5% weight losses above 500 °C under atmospheres of air and nitrogen (Figure 6.3). The resulting polymers containing aromatic substituents demonstrated high oxidative stability compared to the corresponding polymer containing aliphatic substituents [37].

6.3.5 MECHANICAL PROPERTIES

We were able to cast the films of polymers (**6.26, 6.28, 6.30**) from chloroform solution (100 mg/5 mL). The Young's moduli of thin films (5 mm x 2.05 mm x 0.08 mm) of these polymers are 1.70-2.46 GPa respectively at room temperature. These films maintained good mechanical properties over a wide temperature range from ambient temperature to their glass transition temperatures as shown by the TMA results (Figure 6.4).

6.3.6 POLYIMIDE COLOR

The films obtained from our poly(ether imide)s are yellow in colour. Aromatic polyimides have been recognized from the earliest days of their invention as highly colored polymers with colors ranging from yellow to deep red [38]. Polyimides derived from highly purified monomers have been prepared and range in color from bright yellow to nearly colorless, depending on the structure [39]. St. Clair investigated the relationship of polyimide structure and solubility. He reported that polyimides with an interruption of structural symmetry could have reduced color [40]. Achievement of reduced color requires first rigorous purification of the starting materials, but beyond monomer purification, there are significant structural considerations related to color reduction and elimination. There are the inclusion of bulky electron-withdrawing groups such as SO_2 or $C(CF_3)_2$, in the diamine and electron-donating groups in the dianhydride and groups such as oxygen or sulfur, which function as separator groups and which also enhance chain mobility. In addition, interruption of symmetry will reduce color, interruption can be assisted by utilizing *m,m* ' or *o, p* '-diamines in the main chain. The electron-withdrawing units in the diamine and electron-donating units in the dianhydride decrease their Lewis-base and Lewis-acid characters, respectively. The most effective approach for lowering color has been to use diamines or dianhydrides that contain alkyl groups that not only eliminate electronic interactions that may cause color, but also tend to break up extended conjugation along the chain which can result in color [41]. The prepared polyimides have structurally inhibited chain-chain packing due to the bulky units and ether kinks, and therefore allow less interchain interaction to occur via this increased entropy mechanism. The 2,2'-

diphenyl groups in bisanhydride units separate the chromophoric centers and cut down the electronic conjugations. However they have a yellow color, which presumably results from impurities of monomers and small amounts of isoimide that form during either a chemical or a thermal cyclodehydration [42].

6.4 MISCIBILITY OF POLY(ETHER IMIDE)S WITH POLYCARBONATE

By definition, any physical mixture of two or more different polymers or copolymers that are not linked by covalent bonds is a polymer blend, or polyblend [43]. There has been a resurgence of interest in polyblends arising primarily from the demand for engineering plastics. Polymer systems studied range from poly(vinyl chloride) [44], which contains a poly(ethylene-co-vinyl acetate), to Noryl [45] based on the miscible blend of polystyrene and poly[oxy-2,6-dimethyl-1,4-phenylene)]. Development of new polymer blends to meet a specific need is based on economic reasons. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious pecuniary advantage. Our aim here was to study the miscibility of the prepared polyimides/polycarbonate blend by measurement of glass transition temperatures

6.4.1 BLEND SAMPLE PREPARATION

The two polymers, poly(ether imide)s and polycarbonate, were first dissolved together in chloroform (3-4 %) at room temperature. After filtering through cotton, the solution was poured into a large amount of methanol, and the precipitate was filtered and dried under vacuum at 85 °C for 24 h. The dried blends were compression-molded at 1 kbar pressure under vacuum at room temperature into white circular pellets 9-11 mg in weight. All samples were treated by annealing at 330 °C for 5 min and cooling to room temperature.

6.4.2 DSC STUDIES

Characterization of glass transition behavior by differential scanning calorimetry (DSC) is the usual means to assess the extent of morphological homogeneity in polymer blends. The popularity of this approach is due primarily to its convenience. The basis for utilizing Tg is the expectation that a single Tg, intermediate between the glass transition temperatures of the pure components, can be taken as evidence of thermodynamic miscibility. As the DSC measured glass transition temperatures in polymer blends are very broad, in order to enhance the deflection, it requires relatively fast heating rates on the sample (30 °C/min).

The glass transition data in this investigation cover a wide range of homopolyetherimides, copolyetherimides and blends (Table 6.5). The theoretical Tg of the blends are calculated according to the Fox equation [46].

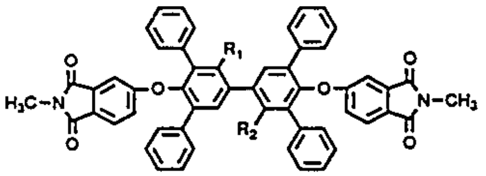
$$1/Tg = W_1/Tg_1 + W_2/Tg_2 \qquad (6.1)$$

W_1 : the weight fraction of homopolymer, Tg_1 : Tg of poly(ether imide)s, W_2 : weight fraction of polycarbonate, Tg_2 : Tg of polycarbonate. All the Tg's of blends measured by DSC satisfactorily agreed with the Tg calculated on the basis of eq 6.1 (Table 6.5 and Table 6.6). The blends prepared from homo and co-poly(ether imide)s containing a meta linkage (from *m*-phenylene diamine) remained miscible at 50 : 50 weight ratio. In contrast the blends **B6.18** and **B6.20** derived from homo-poly(ether imide)s containing a para linkage (from *p*-phenylene diamine) **6.18** and **6.20** with polycarbonate were not miscible, showing the two glass transition temperatures of the pure polymers (Figure 6.5). All blends **B6.24, B6.26, B6.28** and **B6.30** from "para-oriented" co-poly(ether imide)s were not miscible and showed two separate glass transition temperatures of similar sharpness. Figure 6.6 shows the series of thermograms obtained with samples of this blend containing various proportions of polymer **6.21**. The single glass transition region occurs at progressively higher temperatures as the composition shifts from pure polycarbonate towards pure polyetherimide. However the blend (75 %) **B6.35** does not show a large increase in the Tg which was approximately the same as the Tg of the 50 % blend. There is substantial evidence to suggest that significant amounts of both component molecules may intermix in an interfacial regions between the dispersed phase and the matrix. It is possible that this interfacial mixing may involve the lower molecular weight molecules of both components for which the thermodynamic driving force for compatibility is the greatest. There is also substantial evidence indicating that the size of the interfacial area is different for different polymer pairs and may be a relative indication of an approach to compatibility in these systems [47]. The glass transition region is noticeably broader when the two components are present in comparable amounts. This phenomenon, which occurs with many other comparable blends, was noticed also by other workers [48]. It has been interpreted [49] that the connectivity in one dimension along the chain provides the main reason for an inhomogeneity in concentrations sufficient to cause a glass transition broadening, and is also probably due to the existence of concentration fluctuations in the interaction of a chain segment with its nearest neighbors. We attempted to produce blends of our poly(ether imide)s with Udel , with Ultem, and with the prepared poly(ether ketone)s and polysulfones. The blends showed phase separation in the DSC studies and gave two Tg's equivalent to the Tg's of the homopolymers.

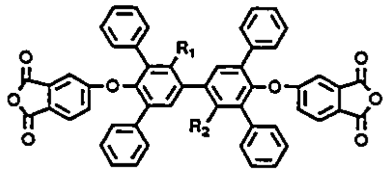
6.5 CONCLUSION

We have successfully synthesized a series of modified dianhydrides containing hindered biphenyl units. Polymerizations with *m*- and *p*- phenylenediamine in NMP did not give high molecular weight polymers probably because of a stoichiometric imbalance. Because of the pendent phenyl groups on the rigid backbone which can not pack, the resulting polymers are amorphous and show high glass transition temperatures along with exceptional solubility. The polyimides containing *m*-phenylene diamine show better miscibility with polycarbonate than polyimides derived from *p*-phenylene diamine. The resulting polymers had 5% weight losses above 500 °C by themogravimetric analysis, indicating high thermooxidative stability.

Table 6.2 Characterization Data for Bisphthalimides and Dianhydrides



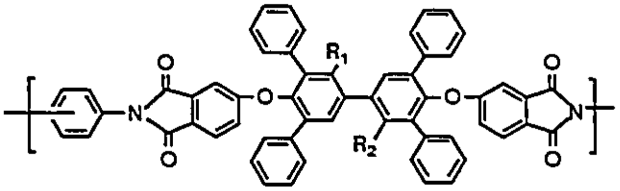
6.13a,b,c,d



6.15a,b,c,d

	R_1	R_2	mp, °C	yield, %	Analysis, % calcd [found]				NMR(^{1}H)
					C	H	N	Cl	
6.13a	H	H	254-255	86	80.18[79.16]	4.49[4.50]	3.46[3.55]		3.50 (s, 6 H), 6.85-7.77 (m, 30 H)
6.13b	CH_3	CH_3	234-236	87	80.37[80.71]	4.82[4.94]	3.55[3.54]		2.00 (s, 6 H), 3.08 (s, 6 H), 6.75-7.65 (m, 28 H)
6.13c	Ph	Ph	267-270	88	82.48[82.44]	4.61[4.74]	2.91[2.73]		3.06 (s, 6 H), 6.60-7.45 (m, 38 H)
6.13d	H	Cl	215-217	68	76.91[77.18]	4.18[4.06]	3.32[3.22]	4.20[4.76]	3.11 (s, 6 H), 6.88-7.87 (m, 29 H)
6.15a	H	H	276-279	85	79.79	3.86			7.05-7.79 (m, 30 H)
6.15b	CH_3	CH_3	275-278	93	79.99[80.17]	4.23[4.17]			2.01 (s, 6 H), 6.60-7.67 (m, 28 H)
6.15c	Ph	Ph	305-307	97	82.21[82.28]	4.10[4.15]			6.60-7.45 (m, 38 H)
6.15d	H	Cl	232-236	95	76.42[75.90]	3.58[3.61]		4.34[4.08]	6.77-7.55 (m, ArH).

Table 6.3 Physical and Thermal Properties of Homopolyetherimides



Polymers	R_1	R_2	diamine	Tg[a]	TGA[b] Air/N_2	ηinh[c]	Mw[d]x10^{-3}	Mw/Mn
6.16	H	H	p	305	522/568	0.22	22.7	2.56
6.17	H	H	m	279	520/563	0.13	26.7	2.35
6.18	CH_3	CH_3	p	312	513/527	0.27	39.4	1.63
6.19	CH_3	CH_3	m	286	517/521	0.26	37.1	1.57
6.20	Ph	Ph	p	317	533/558	0.16	25.5	2.00
6.21	Ph	Ph	m	284	554/566	0.14	25.0	1.85
6.22	H	Cl	p	300	519/541	0.28	37.5	2.26
6.23	H	Cl	m	285	526/537	0.20	24.6	1.98

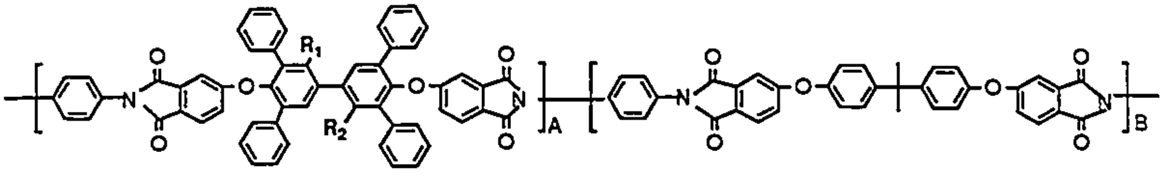
[a] Tg was determined by DSC at heating rate 20 °C/min under nitrogen (50 mL/min).

[b] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min).

[c] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

[d] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

Table 6.4 Physical and Thermal Properties of Copolyetherimides



Polymers	R_1	R_2	diamine	Tg^a(°C)	TGA^b(°C) Air/N_2	ηinh^c	Mw^{d}x10^{-3}	Mw/Mn	Y.M^e(GPa)
6.24	H	H	p	253	512/545	0.21	25.5	2.20	
6.25	H	H	m	247	527/538	0.19	30.3	1.90	
6.26	CH_3	CH_3	p	283	508/508	0.31	36.2	2.57	2.46
6.27	CH_3	CH_3	m	240	501/519	0.18	14.2	2.33	
6.28	Ph	Ph	p	284	526/535	0.32	37.5	2.48	1.70
6.29	Ph	Ph	m	246	533/548	0.18	26.5	2.63	
6.30	H	Cl	p	265	526/531	0.31	41.1	1.98	2.24
6.31	H	Cl	m	244	518/516	0.20	23.4	2.38	

[a,b,c,d] Footnotes are identical to those in Table 6.3.

[e] Young's Modulus was performed by TMA at room temperature.

Table 6.5 Tg of Polymer Blends made from Polycarbonate and Poly(ether imide)s[a]

Blends[a]	Polyimides	Tg[b](°C)	Tg[c](°C)	Tg[d](°C)
B6.16	**6.16**	305	208	203
B6.17	**6.17**	279	200	197
B6.18	**6.18**	312	171, 280	204
B6.19	**6.19**	286	205	199
B6.20	**6.20**	317	151, 298	205
B6.21	**6.21**	284	202	198
B6.22	**6.22**	300	207	202
B6.23	**6.23**	285	202	198
B6.24	**6.24**	253	161, 241	190
B6.25	**6.25**	247	193	188
B6.26	**6.26**	283	155, 271	198
B6.27	**6.27**	240	192	186
B6.28	**6.28**	284	152, 270	198
B6.29	**6.29**	246	190	188
B6.30	**6.30**	265	152, 261	193
B6.31	**6.31**	244	196	187

[a] The sample is a mixture of polycarbonate and polyetherimide (weight ratio 1 : 1).

[b] Tg of polyetherimide.

[c] Tg of blend determined by DSC.

[d] Tg was calculated from the equation $1/Tg^{AB}=w_A/Tg^A + w_B/Tg^B$ (polycarbonate Tg^B= 152 °C).

Table 6.6 Tg's of Polymer Blends made from Polycarbonate and Polyetherimide **6.21**

Blends[a]	Polycarbonate : Polymer **6.21** (%)[b]	Tg[c](°C)	Tg[d](°C)
B6.32	100 : 0	152	152
B6.33	75 : 25	175	172
B6.34	50 : 50	202	198
B6.35	25 : 75	232	202
B6.36	0 : 100	284	284

[b] The designation of the sample is polycarbonate to polyetherimide ratio.
[a,c,d] Footnotes are identical to those in Table 6.5.

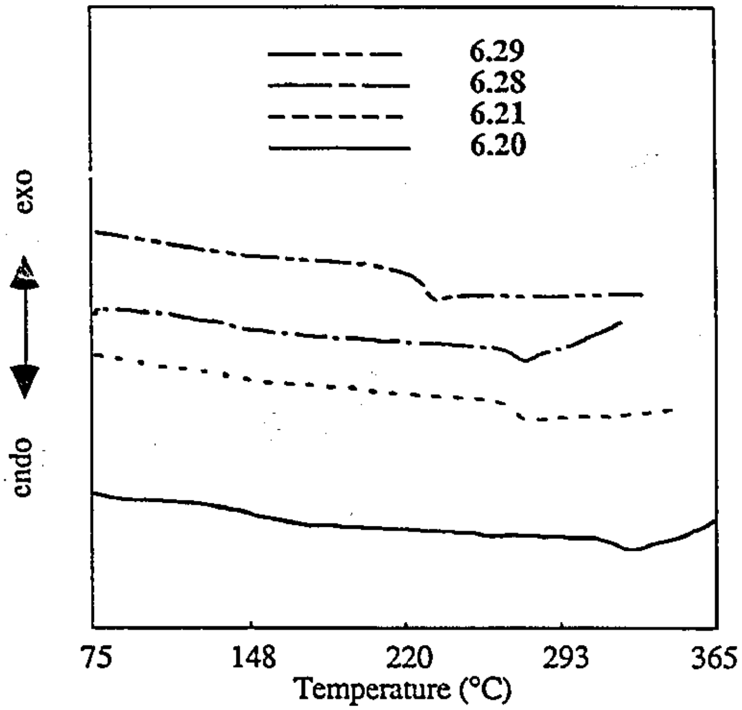


Figure 6.2 DSC Analysis of polymers **6.20**, **6.21**, **6.28** and **6.29** under an atmosphere of nitrogen.

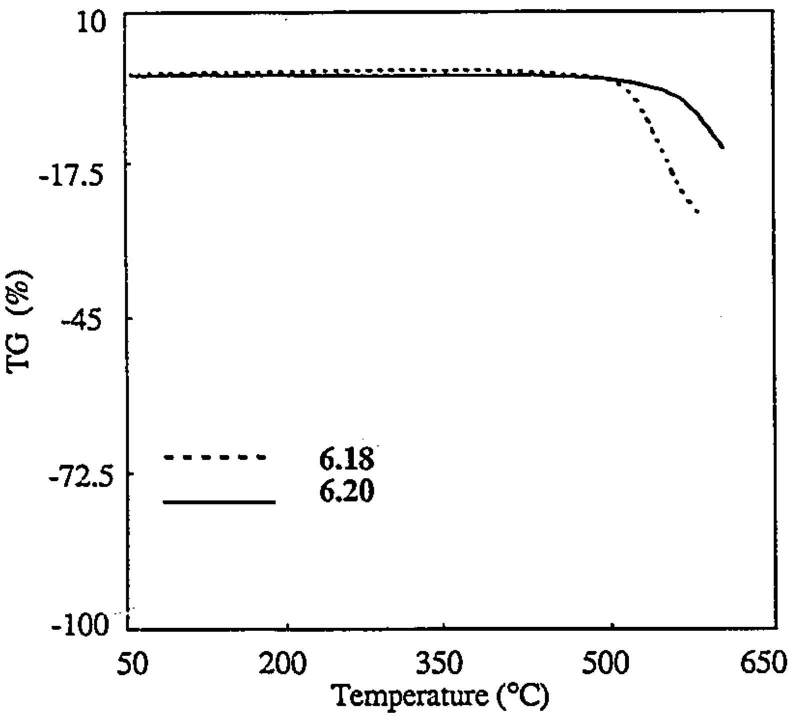


Figure 6.3 TGA thermogram (weight loss vs temperature) for polymers **6.18** and **6.20** under an atmosphere of nitrogen.

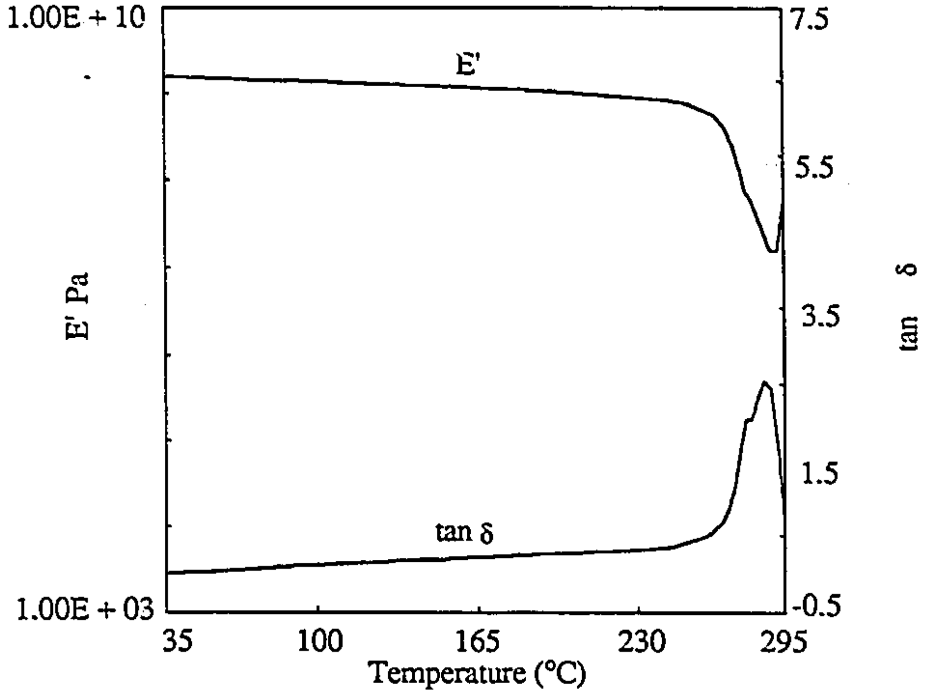


Figure 6.4 Thermomechanical analysis for polymer **6.28**:

(a) modulus (E') vs temperature; (b) tan δ vs temperature.

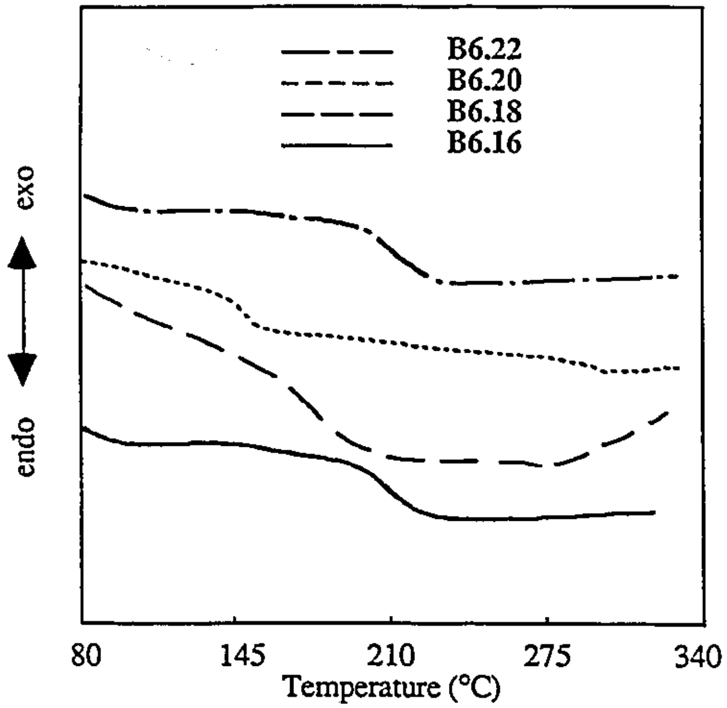


Figure 6.5 DSC Analysis of blends **B6.16**, **B6.18**, **B6.20** and **B6.22** under an atmosphere of nitrogen.

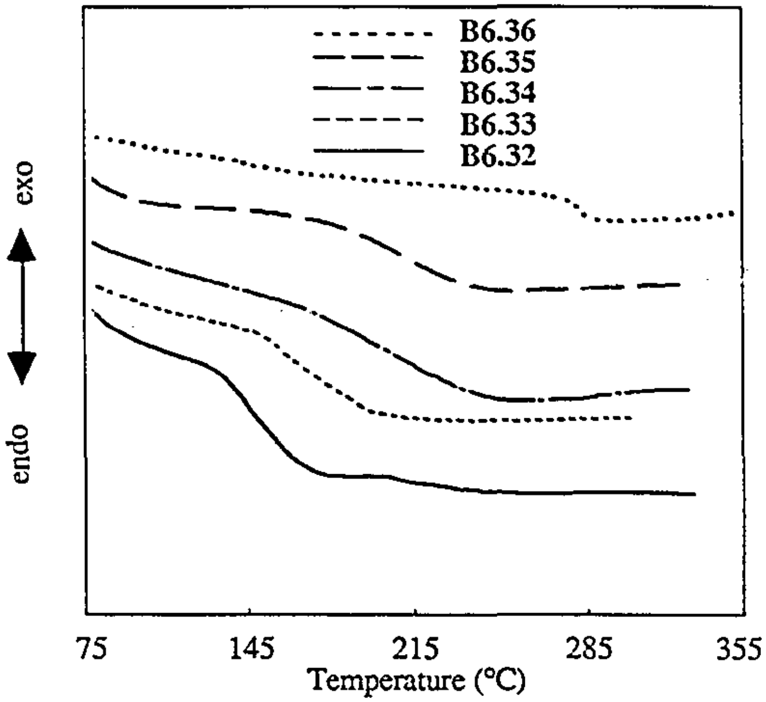


Figure 6.6 DSC Analysis of blends **6.32**- **6.36** under an atmosphere of nitrogen.

6.6 EXPERIMENTAL

General Methods

^{1}H NMR spectra were taken in $CDCl_3$ solution on a Varian XL-200 instrument, chemical shifts are given in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a VG ZAB-HS spectrometer, ion source 240 °C and 70 eV electron impact, direct inlet: *m/z* (assignment). Melting points were determined on a Fischer-Johns melting point apparatus. Elemental analyses were performed by Galbraith Laboratories Inc. IR spectra were performed on a Analet AQS-60 FTIR spectrophotometer. In experiments requiring dry solvent, DMAc, NMP were dried by shaking with 3 Å molecular sieves, and dried over calcium hydride and then distilled under vacuum. Phenylenediamines were purified by distillation or sublimation. Pure 4-nitro-N-methylphthalimide and BPA-dianhydride were supplied by the General Electric Company. Common reagents, e.g. potassium carbonate, potassium hydroxide (50 %) and acetic anhydride were used without further purification.

Model reaction

1-(N-Methylphthalimid-4-oxy)-2,3,6-triphenylbenzene (6.12)

The 2,3,6-triphenylphenol (1 g, 3.10 mmol) and 4-nitro-N-methylphthalimide (0.83 g, 4.03 mmol) were dissolved in NMP (10 mL) and toluene (7 mL) added under nitrogen atmosphere. After a homogenous solution was obtained potassium carbonate (0.56g, 4.03 mmol) was added. The mixture was heated to reflux until no further water appeared as an azeotropic mixture with toluene. The toluene was then removed by distillation. The reaction was maintained for 10 h at 170 °C. The mixture was extracted with $CHCl_3$ and water. The organic layer was evaporated and the recovered solid was recrystallized from $CHCl_3$ and methanol; mp 198-201 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 3.08 (s, 3 H, CH_3), 6.96-7.94 (m, 20 H ArH).

MS (EI) *m/z* 481 (M^+).

Preparation of Monomers

4,4'-Bis(N-methylphthalimid-4-oxy)-3,3',5,5'-tetraphenylbiphenyl (6.13a)

A mixture of 3,3',5,5'-tetraphenylbiphenyl-4,4'-diol **2.12** (7.5 g, 15.2 mmol), 4-nitro-N-methyl phthalimide (9.4 g, 45.6 mmol), potassium carbonate (6.7 g, 48.48 mmol), DMAc (50 mL) and toluene (25 mL) was stirred under a nitrogen atmosphere at reflux in a three necked flask equipped with a Dean-Stark trap for 3 h. During this time water and toluene were azeotropically removed. The reaction was kept at 165 °C for 10 hours. The solution was precipitated in a mixture of water (50 mL) and methanol (150 mL). A crude product (10.6 g, 86 % yield) was isolated by filtration and washed with hot methanol and recrystallized from ethyl acetate and then dried in vacuum (98 % purity by HPLC); mp 254-255 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 3.05 (s,6 H, CH_3), 6.85-7.77 (m, 30 H, ArH).

MS (EI) *m/z* 808 (M^+).

Elemental analysis (%). Calculated for $C_{54}H_{36}O_6N_2$: C, 80.18; H, 4.49; N,3.46. Found : C, 79.76 ; H, 4.50; N,3.55.

4,4'-Bis-(3,4-dicarboxyphenoxy)-3,3',4,4'-tetraphenylbiphenyl (6.14a)

A mixture 4,4'-bis-(N-methylphthalimid-4-oxy)-3,3',5,5'-tetraphenylbiphenyl (**6.13a**) (7.5 g, 9.3 mmol), methanol (100 mL), water (50 mL) and 50 % sodium hydroxide (20 g) was stirred at reflux for 7 h. Acidification of the solution with concentrated hydrochloric acid gave 7.5 g (98 % yield) of product. mp 173-176 °C.

^{1}H NMR (200 MHz, CD_3OD), δ 6.81-8.08 (m, ArH);

IR 3300 cm^{-1} (OH stretch of -COOH).

4,4'-Bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetraphenylbiphenyldianhydride (6.15a)

A mixture of 4,4'-bis-(3,4-dicarboxyphenoxy)-3.3',4,4'-tetraphenylbiphenyl **6.14a** (7.0 g, 8.5 mmol), acetic acid (60 mL) and acetic anhydride (6 mL) was stirred at reflux for 5 h. The solution was cooled and filtered (5.7 g, 85 %). mp 276-279 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 7.05-7.79 (m, ArH).

MS (EI) *m/z* Calculated for $C_{52}H_{30}O_8$ 782.8054, Found 782 (M^+).

4,4'-Bis(N-methylphthalimid-4-oxy)-2,2'-dimethyl-3,3',5,5'-tetraphenyl biphenyl (6.13b)

To a 50 mL three-necked round bottom flask equipped with a Dean-Stark trap and condenser were added, 2,2'-dimethyl-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol **2.17b** (8 g,15.4 mmol), 4-nitro-N-methylphthalimide (7.9 g, 38.3 mmol), DMAc (45 mL), and toluene (20 mL) under nitrogen atmosphere. The reaction mixture was stirred and potassium carbonate (6.8 g 49.2 mmol) was added. The reaction mixture was heated to reflux (150 °C) for 3 h until the water of reaction was removed. Toluene was removed from the Dean Stark trap until the temperature rose to about 160 °C and the reaction was maintained at this temperature for 10 h. The reaction mixture was precipitated in a mixture of methanol (150 mL) and water (50 mL), isolated by filtration and dried. There was obtained crude product (9.8 g, 87% purity in HPLC, 85 % yield). Recrystaliization from isopropyl alcohol gave fine white crystals (98 % purity by HPLC, 82 % yield); mp 234-236 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 2.00 (s, 6 H, CH_3), 3.08 (s, 6 H, N-CH_3), 6.75-7.65 (m, 28 H).

MS (EI) *m/z* 836 (M^+).

Elemental analysis (%). Calculated for $C_{56}H_{40}O_6N_2$: C, 80.37; H, 4.82; N,3.46. Found: C, 80.71 ; H, 4.94; N,3.54.

4,4'-Bis(3,4-dicarboxyphenoxy)-2,2'-dimethyl-3,3',5,5'-tetraphenyl biphenyl (6.14b)

A mixture of 4,4'-bis(N-methylphthalimid-4-oxy)-2,2'-dimethyl-3,3',5,5'-tetraphenyl biphenyl (**6.13b**) (9.0 g, 10.8 mmol) , isopropyl alcohol (60 mL), water (20 mL) and 50 % sodium hydroxide (20 g) was stirred at reflux for 5 h, and then water (20 mL) was added. Acidification of the hot solution with hydrochloric acid was carried out over 2 h and the reaction was then cooled down. The product was isolated by filtration and washed with hot water and dried The product was obtained as a white solid (8.9 g, 97 % yield). mp 167-169 °C.

^{1}H NMR (200 MHz, CD_3OD), δ 6.60-7.67 (m, ArH).

IR 3300 cm^{-1} (OH stretch of -COOH).

4,4'-Bis(3,4-dicarboxyphenoxy)-2,2'-dimethyl-3,3',5,5'-tetraphenyl-biphenyldianhydride (6.15b)

A mixture of 4,4'-bis(3,4-dicarboxyphenoxy)-2,2'-dimethyl-3,3',5,5'-tetraphenyl-biphenyl **6.14b** (9.0 g, 10.6 mmol), glacial acetic acid (60 mL) and acetic anhydride (6 mL) were stirred at reflux for 5 h until a white solid precipitated. The product (7.8 g, 90 %) was purified by recrystallization from toluene/acetic acid; mp 275-278 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 2.01(s, 6 H, CH_3), 6.90-7.63 (m, 28 H, ArH).

MS (EI) *m/z* 810 (M^+).

Elemental analysis (%). Calculated for $C_{54}H_{34}O_8$: C, 79.99; H, 4.23. Found : C, 80.17 ; H, 4.17.

4,4'-Bis(N-methylphthalimid-4-oxy)-2,2',3,3',5,5'-hexaphenylbiphenyl (6.13c)

A mixture 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol **2.17a** (8 g, 12.4 mmol) and 4-nitro-N-methylphthalimide (6.2 g, 30.1 mmol) was placed in a 100 mL three-neck flask equipped with a Dean-Stark trap and a stirrer. The mixture was stirred and heated under nitrogen for 3 h during which time the water was azeotropically removed and then the reaction was maintained at 160 °C for 10 h. After cooling, the solution was poured into a mixture of water (50 mL)/methanol (150 mL) and then the crude white precipitate was collected by filtration. The product was thoroughly washed with water and hot methanol and dried under vacuum. The product was recrystallized from acetonitrile and chloroform (10.5 g, 88 %); mp 268-270 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 3.06 (s, 6 H, CH_3), 6.60-7.45(m, 38 H, ArH).

MS (EI) *m/z* 960 (M^+).

Elemental analysis (%). Calculated for $C_{66}H_{44}O_6N_2$: C, 82.48; H, 4.61; N,2.91. Found : C, 82.44 ; H, 4.74; N, 2.73.

4,4'-Bis(3,4-dicarboxyphenoxy)-2,2',3,3',5,5'-hexaphenylbiphenyl (6.14c)

A mixture of 4,4'-bis(N-methylphthalimid-4-oxy)-2,2',3,3',5,5'-hexaphenylbiphenyl **6.13c** (9.0 g, 9.4 mmol), isopropyl alcohol (40 mL), methanol (20 mL), water (15 mL) and 50% sodium hydroxide (15 g) was stirred at reflux for 3 h. Water (50 mL) was added and the resulting mixture was acidified with hydrochloric acid. The white precipitate was filtered and washed with hot water and then dried under vacuum (8.8 g, 96 %); mp 169-172 °C. ^{1}H NMR (200 MHz, CD_3OD), δ 6.78-8.03 (m, ArH).

IR 3300 cm^{-1} (OH stretch of -COOH).

4,4'-Bis(3,4-dicarboxyphenoxy)-2,2',3,3',5,5'-hexaphenylbiphenyl dianhydride (6.15c)

A mixture of 4,4'-bis(3,4-dicarboxyphenoxy)-2,2',3,3',5,5'-hexaphenylbiphenyl **6.14c** (12 g), glacial acetic acid (50 mL) and acetic anhydride (5 mL) was stirred at reflux during which time a white solid precipitated. The solid was removed by filtration. It was washed twice with acetic acid and water and then dried under vacuum (7.1g, 93% yield); mp 305-307 °C.

^{1}H NMR (200 MHz, CDCl$_3$), δ 6.77-7.55 (m, ArH).

MS (EI) *m/z* 934 (M$^+$).

Elemental analysis (%). Calculated for $C_{64}H_{38}O_8$: C, 82.21; H, 4.10, Found : C, 82.28 ; H, 4.15.

4,4'-Bis(N-methylphthalimid-4-oxy)-2-chloro-3,3',5,5'-tetraphenyl biphenyl (6.13d)

A 100 mL three-necked flask was equipped with a condenser, Dean-Stark trap and thermometer inlet, and charged with 2-chloro-3,3',5,5'-tetraphenylbiphenyl-4,4-diol **2.13** (8 g, 16.34 mmol), 4-nitro-N-methylphthalimide (10.12 g, 49.02 mmol), potassium carbonate (2.93 g, 21.24 mmol), DMAc (60 mL) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was heated to reflux until no water appeared at azeotropic temperature, and then maintained at 170 °C for 15 h after toluene removed. The mixture was cooled and precipitated in mixture solution of water (200 mL) / methanol (50 mL). The resulting product was recrystallized in ethanol and chloroform (68 %); mp 215-217 °C.

^{1}H NMR (200 MHz, CDCl$_3$), δ 3.11 (s, 6 H, CH$_3$), 6.88-7.87 (m, ArH).

MS (EI) *m/z* 842 (M$^+$).

Elemental analysis (%). Calculated for $C_{54}H_{35}O_6N_2Cl$: C, 76.91; H, 4.18; N, 3.32; Cl, 4.20. Found : C, 77.18 ; H, 4.06; N,3.22; Cl, 4.76.

4,4'-Bis(3,4-dicarboxyphenoxy)-2-chloro-3,3',5,5'-tetraphenylbiphenyl (6.14d)

A mixture of 4,4'-bis(N-methylphthalimid-4-oxy)-2-chloro-3,3',5,5'-tetraphenylbiphenyl **6.13d** (9.0 g, 10.67 mmol), isopropyl alcohol (60 mL), methanol (20 mL), water (15 mL) and 50% sodium hydroxide (17 g) was stirred at reflux for 7 h. Water (50 mL) was added and the resulting mixture was acidified with hydrochloric acid. The white solid was filtered and washed with hot water and then dried under vacuum (8.5 g, 95 %); mp 175-177 °C.

^{1}H NMR (200 MHz, CD_3OD), δ 6.78-8.03 (m, ArH).

IR 3300 cm^{-1} (OH stretch of -COOH).

4,4'-Bis(3,4-dicarboxyphenoxy)-2-chloro-3,3',5,5'-tetraphenylbiphenyl dianhydride (6.15d)

A mixture of 4,4'-bis(3,4-dicarboxyphenoxy)-2-chloro-3,3',5,5'-tetraphenylbiphenyl **6.14d** (8 g), glacial acetic acid (50 mL) and acetic anhydride (5 mL) was stirred at reflux for 10 h. The solvent was evaporated and the recovered product recrystallized from acetic acid and chloroform (7.4g, 95% yield); mp 232-236 °C.

^{1}H NMR (200 MHz, $CDCl_3$), δ 6.77-7.55 (m, ArH).

MS (EI) *m/z* 818 (M$^+$).

Elemental analysis (%). Calculated for $C_{52}H_{29}O_8Cl$: C, 76.42; H, 3.58, Cl, 4.34 Found : C, 75.90 ; H, 3.61, Cl, 4.08.

Polymerization

The synthesis of poly(ether imide)s is given below as a general procedure. To a 50 mL round bottom flask was added 4,4' -bis(3,4-dicarboxyphenoxy)-2,2-dimethyl-3,3',5,5'-tetraphenylbiphenyl dianhydride (1 g, 1.23 mmol), *m*-phenylenediamine (0.133 g (1.23 mmol), and distilled NMP (8 mL). The flask was purged with nitrogen and the solution was stirred for 3 h under a nitrogen atmosphere at room temperature. The solution became viscous as the polyamic acid formed. Then 4 mL of chlorobenzene was added. The reaction system was heated to reflux with stirring for 3 h while chlorobenzene was distilled off and the water removed by azeotropic distillation. The reaction mixture was cooled and precipitated into a large excess of methanol. The polymer was dissolved in chloroform and filtered through celite. The filtrate was reprecipitated in methanol. The poly(ether imide)s were separated by filtration and dried in a vacuum oven at 80 °C for 24 h.

Copolymerization

The same reaction as above was performed for 3 h using 4,4'-bis(3,4-dicarboxyphenoxy)-2,2'-dimethyl-3,3',5,5'-tetraphenylbiphenyl dianhydride (0.5 g, 0.616 mmol) and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (0.31 g 0.616 mmol) and p-phenylenediamine (0.129 g, 1.23 mmol) and NMP (7 mL). The reaction mixture was treated in the same manner as above.

Polymer characterization

Inherent viscosities were measured in a calibrated Ubbelohde viscometer at a concentration of 0.5g/dL in $CHCl_3$ at 25 °C. Polymer molecular weights were determined relative to polystyrene by gel permeation chromatography (GPC) in $CHCl_3$ as solvent on a Waters 510 HPLC with a set of four µstyragel columns (500, 10^4, 10^5, and 100 Å) in series and a UV detector. Differential scanning calorimetry (DSC) and themogravimetric analyses (TG) were performed with Seiko 220 DSC at heating rate of 20 °C/min with 50 mL/min gas flow and Seiko 220 TG/DTA instruments respectively at a heating rate of 10 °C/min with 200 mL/min gas flow rate under nitrogen and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument from 25 °C to 350 °C with a heating rate of 3 °C/min in static air. The polymer films for the mechanical analyzer were cast from chloroform solution (100 mg/5 mL) on a glass plate (3 cm diameter) by evaporation of solvent at room temperature for 48 h and dried at 100 °C for 24 h. Film thickness was measured with micrometer.

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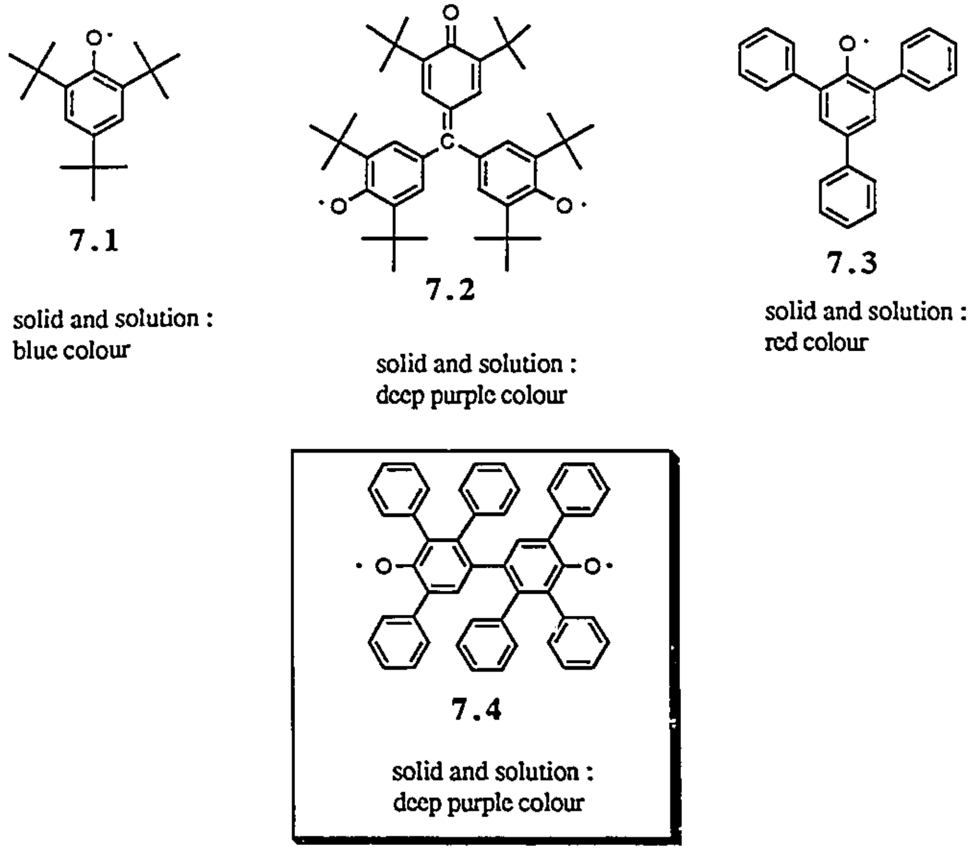
CHAPTER 7

CHEMISTRY OF 2,2',3,3',5,5'-HEXAPHENYLBIPHENYL-4,4'-DIOL

7.1 INTRODUCTION

The chemistry of hindered phenols [1,2] *i.e.*, phenols carrying bulky ortho substituents, has been investigated intensively during the last 30 years. Many of these phenols form relatively stable free radicals and both the phenols and phenoxy radicals are important in inhibition of autooxidation reactions of organic substances [3]. Phenoxy radicals are also electron acceptors having high polymer compatibility and they exhibit excellent electron mobility in molecularly dispersed polymeric films [4].

The most widely used agents for the generation of phenoxy radicals from phenols are oxidizing agents, such as Ag_2O, MnO_2, HgO, $K_3Fe(CN)_6$, and others [5,6] which are capable of one electron abstraction. These phenoxy radicals form either by homolytic cleavage of the O-H bond in phenol with loss of the hydrogen atom or by loss of one electron from the corresponding phenoxide anion [5,7]. The stability and reactivity of phenoxy radicals depend on the structure and position of the substituents on the phenols [8]. Groups which are effective in inhibiting dimerization or further reactions are *tert*-butyl, phenyl, carbonyl and nitrile. Radical stability increases when methyl is replaced by



7.1

solid and solution :
blue colour

7.2

solid and solution :
deep purple colour

7.3

solid and solution :
red colour

7.4

solid and solution :
deep purple colour

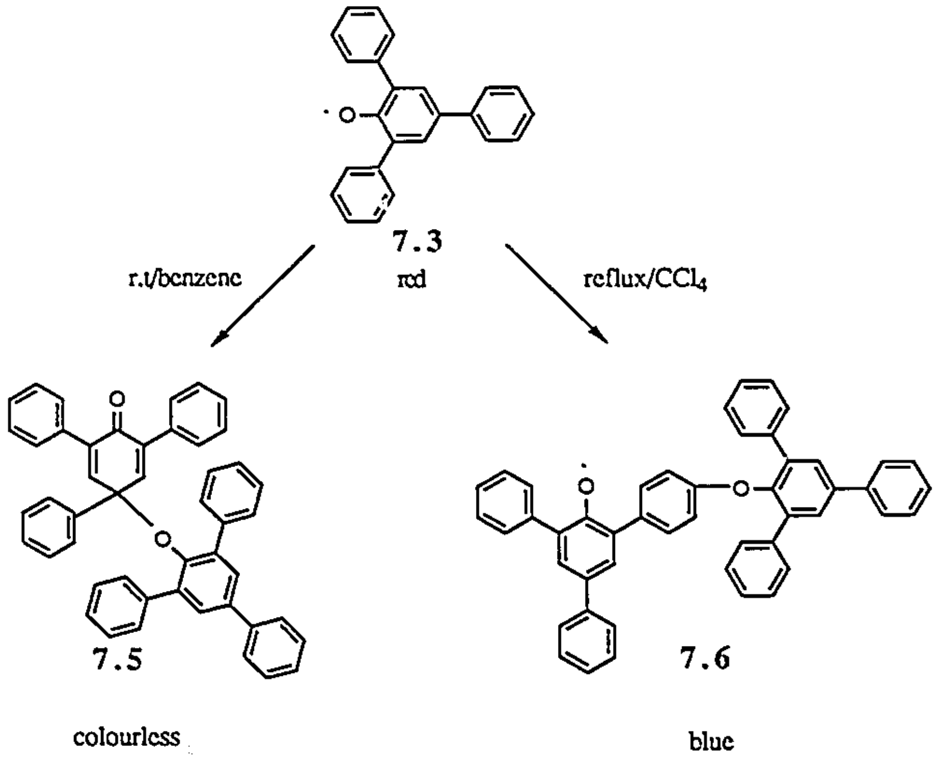
Figure 7.1 Stable phenoxy radicals which are highly colored

larger alkyl groups with ortho position [9]. The phenoxy radicals **7.1**, **7.2** and **7.3** survive for a sufficient time to be used as substrates for other experiments. They exist in solution over periods of hours or even days because of the shielding effect of the bulky groups in the ortho and para positions (Figure 7.1). The 2,4,6-trisubstitution usually retards or prevents further reaction (*i.e.* addition or substitution) and the absence of α-CH groups in the substituents prohibits formation of quinone methides [10]. We felt that 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-dioxyl **7.4** would be an ideal structure for applications such as an antioxidant and as an oxidizing agent. This biphenoxy radical is stable and possible side reaction are minimized for two reasons: (a) the unpaired electrons are stable because delocalization in the π bond system of the phenoxy radical is not possible due to the noncoplanality between the central phenyl rings so that the diphenoquinone cannot form and (b) steric hindrance effectively reduces the free interaction of the unpaired electrons. Another advantage of the biphenoxy radical is the excellent solubility in common organic solvents. The chemistry of these hindered biphenols such as their stability, oxidation potentials and use as oxidizing agents will be discussed in this chapter.

7.2 THERMOLYSIS OF 2,2',3,3',5,5'-HEXAPHENYL BIPHENYL-4,4'-DIOXYL

Hindered phenols containing bulky ortho and para substituents, such as *tert*-butyl or phenyl groups, have been reported [1,2] to form radicals that are quite stable in the presence of air and moisture. Dimroth [1] reported the chemistry of 2,4,6-triphenylphenoxy radical **7.3** which has a structure similar to 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-dioxyl 7.4. Interestingly the red 2,4,6-triphenylphenoxy radicals are in equilibrium with the corresponding quinol ether **7.5** in benzene solution at room temperature. However when the triphenylphenoxy radical **7.3** was heated in CCl_4 solution, the solution turned blue to give the parent phenol and 2-(*p*-2,4,6-triphenylphenoxyl)-2,4,6-triphenylphenoxy **7.6** (Scheme 7.1) [11,12] via a C-O coupling reaction through the pendent phenyl group. The 2,4,6-tri-t-butylphenoxy radical decomposed upon heating to give the parent phenol, isobutylene and high molecular weight products [13]. Oxidation of some bisphenols yields phenoxy radicals which undergo intramolecular ring closure producing spiro compounds [14]. Hay [15] has reported the thermolysis of 3,3',5,5'-tetraphenyldiphenoquinone. The reaction was performed at 300 °C which is above the melting point. The resulting products are the parent biphenol and two dibenzofuran derivatives resulting from intramolecular ring closure reactions.

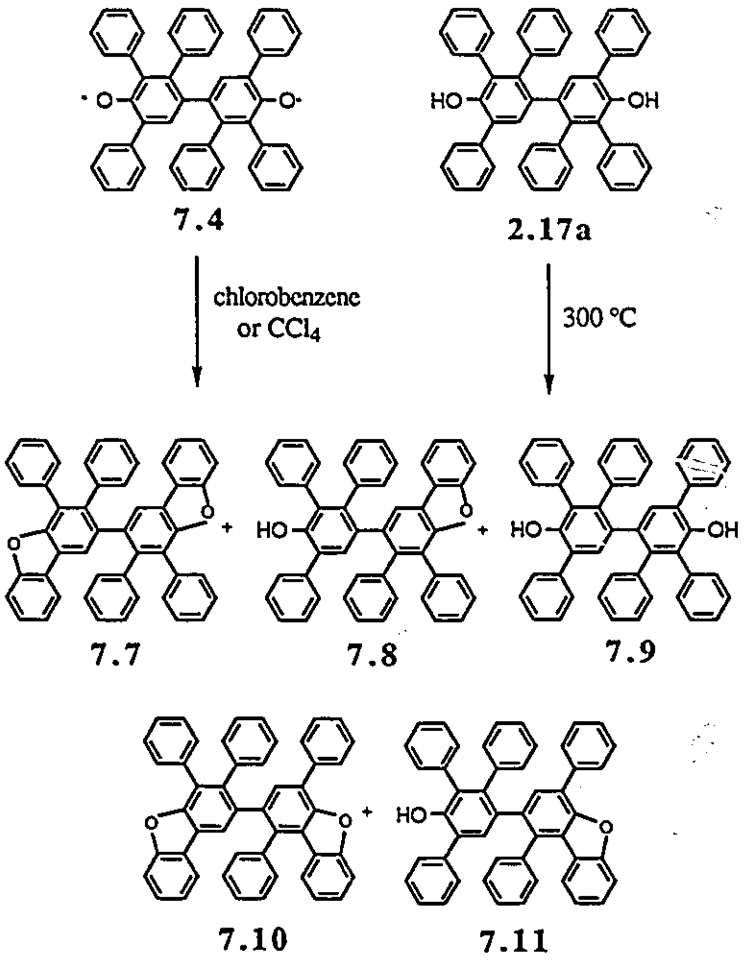
Scheme 7.1



We investigated the thermolysis reaction of the biphenoxy radical from 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol. The hindered biphenol **2.17a** was oxidized to biphenoxy radical **7.4** with silver oxide in chlorobenzene. When the solution of biphenoxy radical **7.4** was heated to reflux, the mixture which initially is a dark-violet color gradually fades and becomes light yellow. The thermolysis products are similar to those from tetraphenyldiphenoquinone [15]. We performed the reaction in two different solvents, CCl_4 and chlorobenzene (Scheme 7.2). In CCl_4 solution monodibenzofuran **7.8** and biphenol **7.9** were produced. In chlorobenzene solution the resulting products were bisdibenzofuran **7.7**, monodibenzofuran **7.8** and the parent biphenol **7.9** which were separated by flash chromatography using ethylacetate-hexane (5:95) as eluent. The difference in these results can be explained by the higher reaction temperature in chlorobenzene. We also studied the reaction of 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-

diol at 300 °C under an air atmosphere. The biphenol melted and gave a violet solution and the progress of the reaction was monitored by HPLC and thin layer chromatography. The resulting products were biphenol, monodibenzofuran and bisdibenzofuran. The reaction was slow and the main products isolated are unreacted biphenol and monocyclized phenol and a minor amount of dicyclized phenol. All three compounds exhibited two melting points. The reasons, probably, lie in the fact that these

Scheme 7.2



structures are chiral on the biphenylene axis (see Chap. 2). Similar behavior has been reported for 1,1'-binaphthyl which exhibits two or more crystalline forms and shows two melting points derived from the racemic compound (mp 145 °C) and the eutectic mixture (mp 158 °C) of enantiomorphic crystals [16]. Another possible explanation is that two different isomers **7.10** and **7.11** are formed which would give two melting points.

7.3 OXIDATION POTENTIALS OF BIPHENOLS

The oxidation potential of phenols, *i.e.*, the oxidizing power of phenoxy radicals, decreases with increasing steric crowding in the 2- and 6- positions. Although steric hindrance decreases the oxidation potential of phenoxy radical, their stability increases. The effect of substituents on phenolic rings has been the subject of several studies [17,18]. For example, in the case of the 2,4,6-triphenylphenoxy radical and the 2,4,6-tri-t-butylphenoxy radical, the equilibrium is shifted to the right, since the triphenylphenoxy radical is a stronger oxidizing agent than tri-t-butylphenoxy radical due to the electron withdrawing of phenyl groups. The influence of steric and polar effects of substituents in the 2-, 4- and 6- positions on the relative oxidation potentials of phenols is usually pronounced. Since oxidation potentials refer to the oxidizing power of phenoxy radicals, they do reflect to a certain extent the relative stability and reactivity of aryloxy radicals, particularly of those which carry substituent groups in the 2-, 4-, and 6- positions.

Oxidation potentials of a series of biphenols have been determined using in this laboratory technique of differential pulse voltammetry method [19]. All potentials referred to herein are experimental room temperature (25 °C) values referenced to Ag/Ag+. Scan speeds were

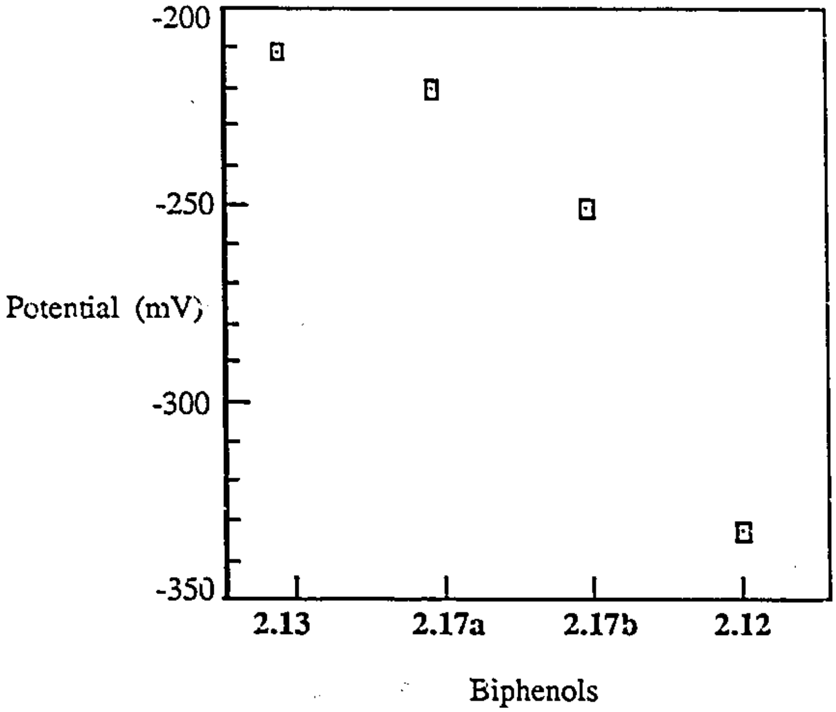
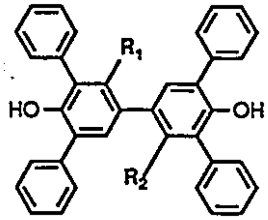


Figure 7.2 The oxidation potential of a series of biphenols **2.12**, **2.13**, **2.17a** and **2.17b** by differential pulse voltammetry method. (determined by G. Barbiero)



Biphenols	R_1	R_2
2.12	H	H
2.13	CH_3	CH_3
2.17a	Ph	Ph
2.17b	Cl	H

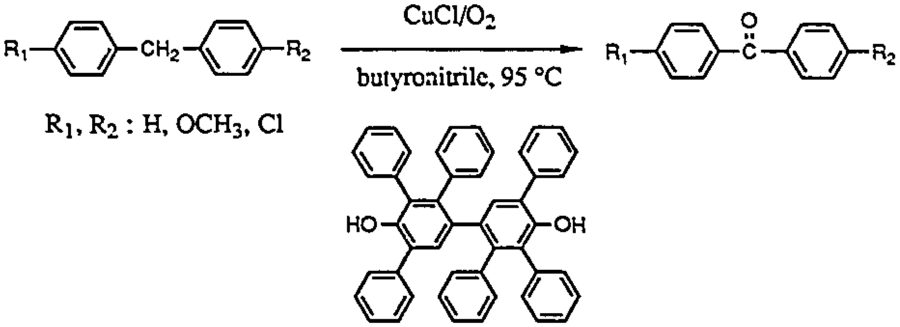
20 mV/sec unless otherwise mentioned. The oxidation potentials of these hindered biphenols are illustrated in Figure 7.2. The chloro substituted biphenol **2.13** has the highest oxidation potential (-208 mV) because of the electron withdrawing group (chloro) and biphenol **2.12** shows the lowest potential (-334 mV) probably because the unpaired electrons can be delocalized into the phenyl rings. The biphenol **2.17a** has the second highest potential (-220 mV), followed by the biphenol **2.17b** (-253 mV). This can be explained by the fact that the phenyl groups and the methyl groups force the pendant phenyls to be perpendicular to the biphenyl rings. Therefore, there is a counter effect; the phenyls which act as electron withdrawing groups and the methyls which behave as electron donating groups.

7.4 A NEW OXIDATION OF DIPHENYLMETHANES

A number of studies have been reported in which diarylmethanes have been oxidized to benzophenones by molecular oxygen in a strongly basic medium [20] or under phase transfer-catalysis conditions [21,22]. However, they require extremely severe conditions (e.g. high pressure) in aqueous media, or strong basic systems in anhydrous solvents with accompanying decomposition of catalysts which limits the reaction temperature [23]. The oxidation of diphenylmethanes was carried out with 2,2',3,3',5,5'-hexaphenybiphenyl-4,4'-diol as a catalyst as described below. An outstanding advantage of this technique is that the reaction can be carried out in a neutral medium which considerably extends the scope and effectiveness of the reaction (Scheme 7.3).

The 2,2',3,3',5,5'-hexapheny-[1,1-biphenyl]-4,4'-diol was oxidized to 2,2',3,3',5,5'-hexaphenybiphenyl-4,4'-dioxyl by Cu(I)Cl in butyronitrile at 95 °C, under vigorous stirring with oxygen bubbling through the reaction mixture. After 2 h

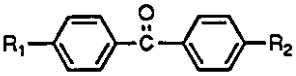
Scheme 7.3



diphenylmethane was added. As shown in Figure 7.3 diphenylmethane was oxidized to give benzophenone in high yields in the presence of a catalytic amount of the biphenoxy radical (10 mole % of substrate) formed *in situ* from the biphenol. In the absence of biphenoxy radical only 30% conversion was observed. Attempts to bring about oxidation of diphenylmethane using 3,3',5,5'-tetraphenyl-4,4'-diphenoquinone as catalyst under similar conditions also resulted only in 30% conversion indicating that it had little if any effect on the course of the reaction. This is an agreement with the fact that the oxidation potential of tetraphenylbiphenol is lower than the hexaphenyl biphenol and therefore it is not a catalyst for the reaction. This adds support to the concept that a radical reaction is involved in the oxidation of diphenylmethane and derivatives.

We have also studied the oxidation of diphenylmethane derivatives, 4,4'-dimethoxydiphenylmethane, 4-chlorodiphenylmethane, 4,4'-dichlorodiphenylmethane, fluorene and 4,4'-bis(N-phthalimido)-1,1'-diphenylmethane. The 4,4-dichlorodiphenylmethane was prepared by Friedel-Crafts alkylation as described in the literature [21] procedure (87 % para and 13 % ortho, distribution as found by HPLC). The 4,4'-dimethoxydiphenylmethane was prepared by methylation of 4,4-dihydroxy-diphenylmethane with dimethylsulfate in dimethylsulfoxide. The 4,4'-bis(N-phthalimido)-diphenylmethane was synthesized by the reaction of 4,4'-diaminodiphenylmethane and

Table 7.1 Oxidation of Diphenylmethanes



R_1	R_2	Conversion (%) [a]	mp (°C)
OMe	OMe	90	133
H	H	97	47-48
Cl	H	95	77
Cl	Cl	95	145
Fluorene		98	84-85

[a] Indicated by HPLC

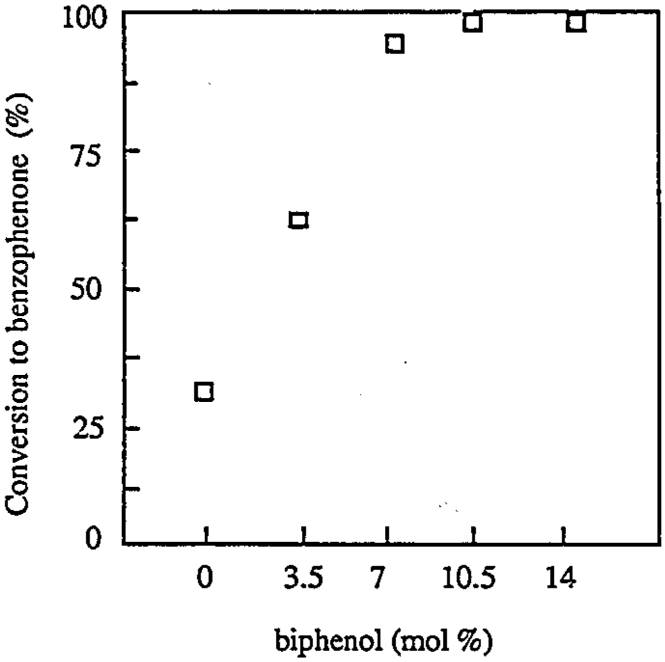
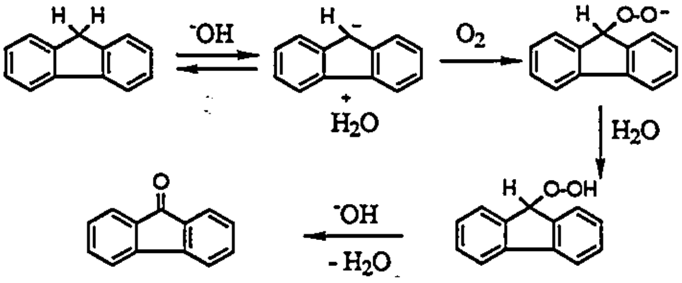


Figure 7.3 Conversion of diphenylmethane to benzophenone with biphenol (**2.17a**) (mol %) catalyst.

phthalic anhydride. Under the conditions described above these substrates, except for 4,4'-bis(N-phthalimido)-diphenylmethane, were readily oxidized to benzophenones in 90-98 % yields as shown in Table 7.1. The oxidation of a mixture of 4,4'-dichloro-diphenylmethane and 2,4'-dichloro-diphenylmethane was carried under similar condition to give the corresponding benzophenone derivatives 4,4'-dichloro-benzophenone and 2,4'-dichloro-benzophenone, respectively. Recrystallization from methanol gave pure 4,4'-dichloro-benzophenone (mp 144 °C, lit.144-146 °C). However 4,4'-bis(N-phthalimido)-diphenylmethane could not be oxidized because of solubility problems and presumably the lower reactivity of the methylene group due to the strong electron withdrawing groups.

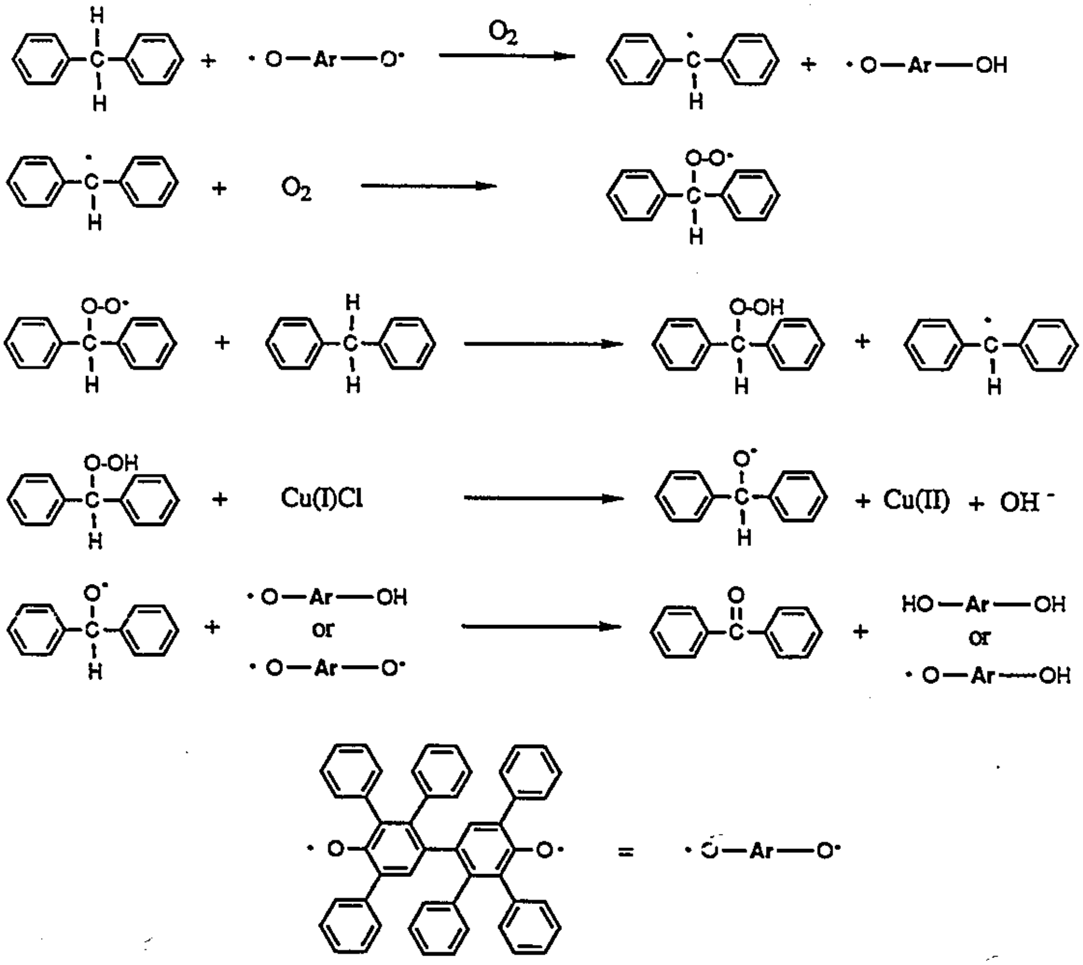
The autooxidation mechanism by which diphenylmethane is converted to benzophenone in basic medium has been studied [24]. This mechanism involves a process where the rate limitation is the rate of ionization of diphenylmethane. The diphenylmethide ion is trapped by oxygen more readily than it is protonated in dimethyl sulfoxide-*tert*-butyl alcohol (4:1) solutions. Sprinzak [25] reported that the oxidation of fluorene in basic media proceeds by direct reaction of the fluorenyl carbanion with oxygen to form initially the hydroperoxide which decomposes to yield 9-fluorenone, as depicted in Scheme 7.4. We propose a

Scheme 7.4



Proposed Mechanism of Oxidation of Fluorene possible mechanism for the oxidation of diphenylmethane derivatives in neutral media. The biphenoxy radical could abstract the hydrogen atom of diphenylmethane and the diphenylmethane radical would then be trapped by oxygen. The peroxy radical could then abstract hydrogen atom from diphenylmethane. Hydroperoxide yields are reduced by presence of metal salts [26] and collapse of this radical produces benzophenone (Scheme 7.5).

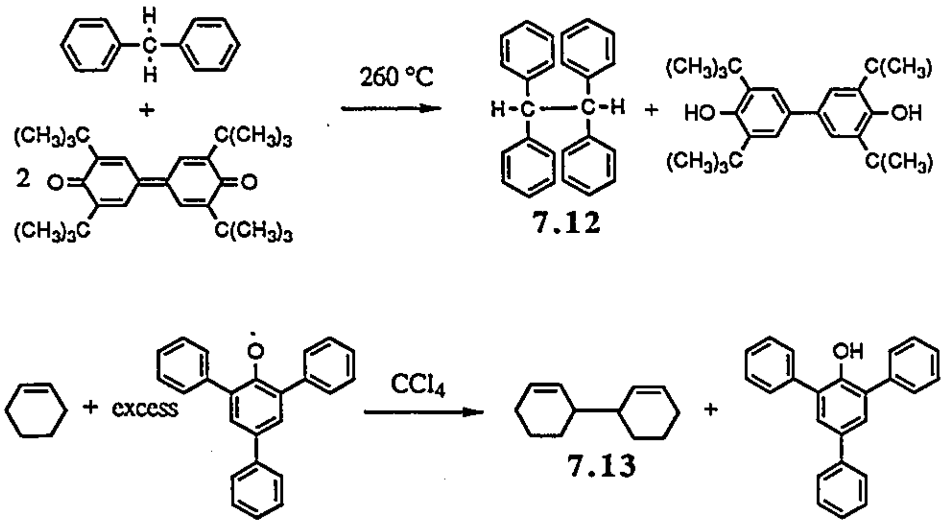
Scheme 7.5



7.5 CARBON-OXYGEN COUPLING OF ACTIVE METHYLENE GROUPS WITH BIPHENOXY RADICALS

Aryloxy radicals have been obtained by ferricyanide oxidation of the corresponding phenols in alkaline solution [27,28]. It has been reported that once formed they usually undergo radical dimerization by way of self-coupling reactions to furnish dimeric, trimeric products and often ill-defined polymeric materials as well. The analogous carbon-carbon dimerizations of phenoxy radicals to dibenzyl and stilbene derivatives takes place very readily when there is a methyl or methylene group in the para position [29]. Diphenylmethane has been converted to 1,1',2,2'-tetraphenylethane **7.12** in the presence of 3,3',5,5'-tetra-tert-butyldiphenoquinone at 260 °C [30] and cyclohexene couples to give 3,3'-bicyclohexenyl **7.13** in the presence of 2,4,6-triphenylphenoxy radical in solution [31]. The results of these reactions can be formally derived from the isomeric benzyl or allylic radicals (Scheme 7.6). The oxidation of cyclohexene in acetic anhydride solution with free radical initiators has been studied by Shine and Snyder [32]. The major product

Scheme 7.6



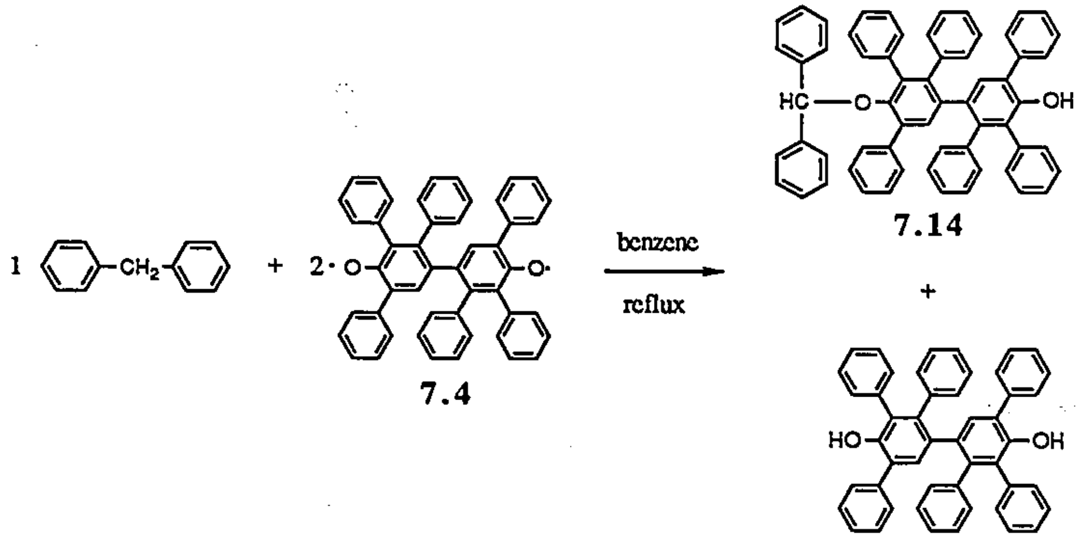
7.12

7.13

formed was 3,3'-bicyclohexenyl **7.13**, and the minor products were 3-cyclohexenyl acetate and cyclohexyl acetate.

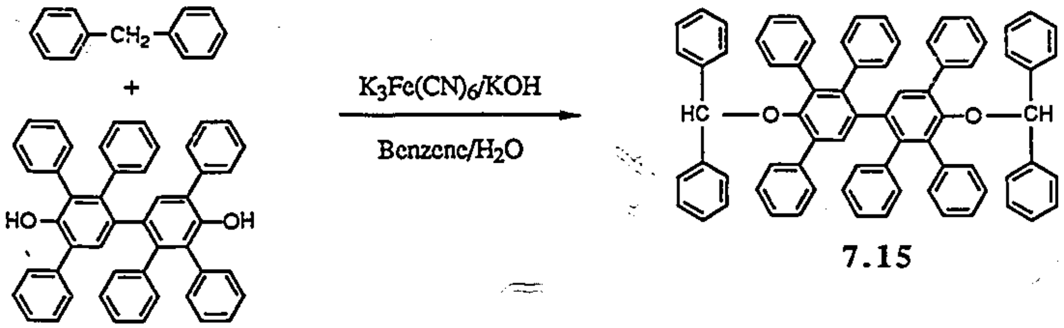
We attempted the reaction of the preformed 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diyloxy radical (2 mmol) and diphenylmethane (1 mmol) in benzene solution in the absence of oxygen. This reaction was performed at reflux temperature until the dark-violet color faded and the solution became almost colorless. The resulting products were the carbon-oxygen coupled monofunctional compound **7.14** and the hexaphenylbiphenol (Scheme 7.7). This was unexpected because we expected that the oxidation of diphenylmethane under these conditions would result in 1,1',2,2'-tetraphenylethane as in the reaction with the tetraphenyldiphenoquinone. This was a novel reaction which we decided to explore further. We also attempted the reaction of diphenylmethane and the biphenoxy radical under basic conditions in the presence of excess $K_3Fe(CN)_6$ and KOH in benzene-water solution in the absence of oxygen. The dark-violet hexaphenylbiphenoxy radical was formed in the solution. The reaction with the diphenylmethane was continued at reflux

Scheme 7.7



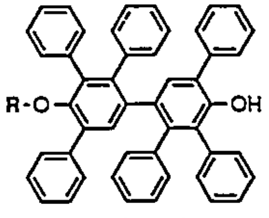
temperature until the dark violet color disappeared (Scheme 7.8). The difunctionally coupled compound **7.15** was obtained in high yield (Figure 7.4 and 7.5). The reaction was followed by thin layer chromatography and HPLC. Following this procedure, a variety of diphenylmethanes and benzyl substituted compounds, such as 4-chlorodiphenylmethane, 4,4'-dichlorodiphenylmethane 4,4'-dimethoxydiphenylmethane, ethylbenzene, benzylphenylether and deoxybenzoin were reacted with hexaphenylbiphenoxy radical. These results are listed in Table 7.2. All of the difunctional compounds are new products which are derived from the carbon-oxygen coupling reaction in high yield. We have also attempted the reaction with allylic analogues, such as cyclohexene, 3,4-dihydro-2H-pyran and allylbenzene, under similar conditions. The resulting products were also mono or difunctionalized compounds which came from carbon-oxygen coupling reactions on the 3-position of the allylic groups. In the case of 3,4-dihydro-2H-pyran, the monofunctional product was insoluble and precipitated out of solution. Allylbenzene gave isomeric products arising from an electron delocalization in the 1 or 3 positions of the allyl group. It was interesting to note that, in the case of cyclohexene, 3,3'-dicyclohexenyl was not produced as in the reaction with triphenylphenoxy radical. Similarly we have reacted 2-chloro-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol with diphenylmethane or ethylbenzene under similar conditions. The products were principally the difunctional

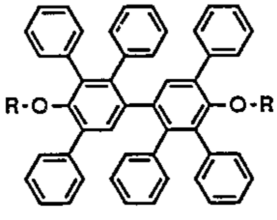
Scheme 7.8

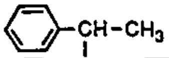
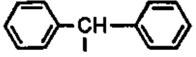
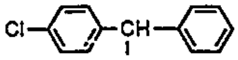
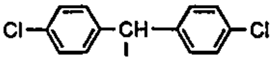
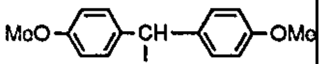
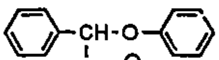
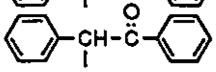
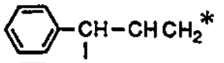
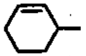
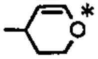
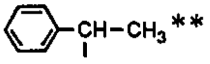
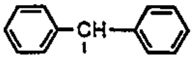


7.15

Table 7.2 Characterization of C-O Coupled Products


monofunctional


bifunctional

R	yields (%)	mp(°C)	products	Analysis, % calc[found]		^{1}Hnmr (methylenic hydrogen, δ)
				C	H	
	92	245-248	bifunctional	90.32[90.05]	5.92[5.94]	4.33(q, 2H)
	95	243-245	bifunctional	91.14[90.77]	5.58[5.33]	5.10(s, 2H)
	87	248-250	bifunctional	85.12[84.86]	5.02[4.99]	5.02, 5.04 (ss, 2H)
	85	282-285	bifunctional	79.86[79.53]	4.53[4.38]	5.01(s, 2H)
	82	275-279	bifunctional	85.53[85.32]	5.71[5.66]	5.02(s, 2H)
	85	242-245	bifunctional	88.24[88.13]	5.40[5.20]	5.45, 5.66(ss, 2H)
	75	295-297	monofunctional	88.52[88.68]	5.28[5.56]	5.02(s, 1H), 5.64(s, 2H)
 *			bifunctional (two products)			
	90	252-253	bifunctional	89.74[89.57]	6.28[6.39]	5.51(m, 2H)
 *	80	176-178	monofunctional	87.82[86.62]	5.56[5.39]	5.02(s, 1H), 6.03(m,1H)
2-chloro-3,3'5,5'-tetraphenyl-[1,1'-biphenyl]-4,4'-dioxy						
 **	76	235-240	bifunctional	[85.17]	5.64[5.80]	4.34(m, 2H)
	88	250-253	bifunctional	86.84[86.91]	5.29[4.78]	5.27, 5.32(ss, 2H)

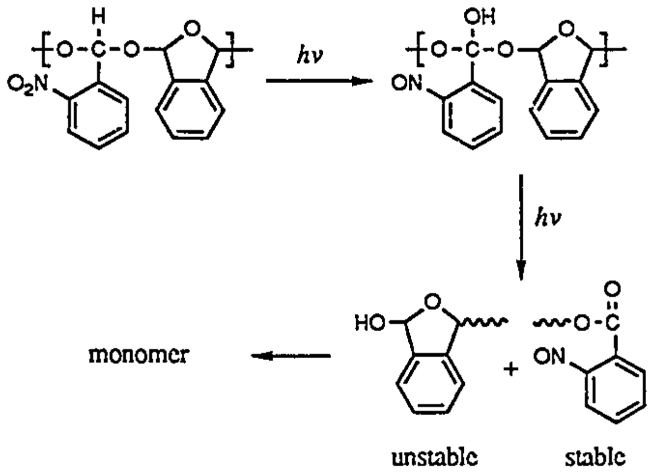
* The products were difficult to separate and purify.

** The products were monofunctional and bifunctional (24:76 in HPLC).

compounds with the monofunctional compounds as minor products because presumably in this case the two phenoxy radicals have different oxidation potentials. The chloro-substituted phenoxy radical has a higher oxidation potential compared to the phenoxy radical because of the electron withdrawing effect of the chloro group. From these results we see that the biphenoxy radicals react with carbon radical of the diphenyl methane derivatives before carbon-carbon radical coupling occurs.

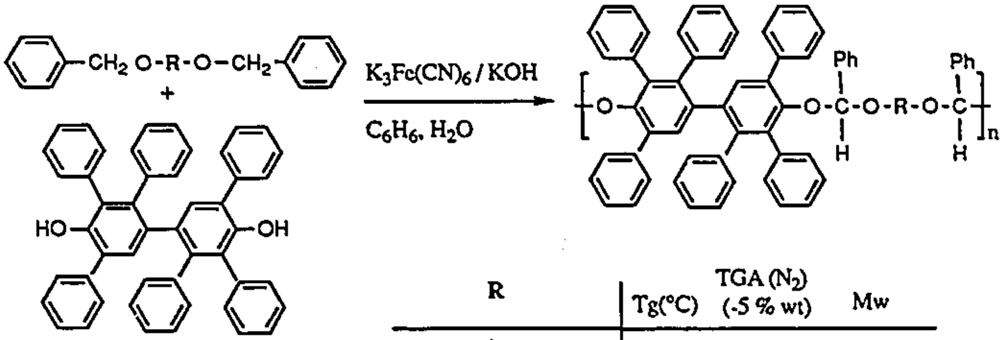
Ito and Wilson [33] have reported that the copolymer of o-nitro-benzaldehyde and phthalaldehyde can be used as a photoresist. On irradiation the backbone of the copolymer undergoes scission by the radiation induced intramolecular oxidation of the C-O-C link (see Scheme 7.9). The exposed areas showed a loss of film thickness of up to 50%. Frechet *et al* [34] found that the hydrolytic scission process of poly(phthalaldehyde) was brought about by photogenerated acid from onium salts such as $Ph_3S^+AsF_6$, $Ph_2I^+AsF_6$ and *p*-$C_6H_{13}OPhN_2^+BF_4^-$ which are the most effective components in acid generation.[35] When the poly(phthalaldehyde) films in the presence of up to 10% by weight of various onium salts were exposed to deep UV or to electrons at room temperature, the irradiated areas simply evaporated.

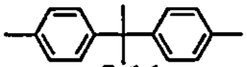
Scheme 7.9



Since the reaction of the hexaphenylbiphenol with diphenylmethane under oxidizing condition is essentially quantitative (Scheme 7.8) we have attempted the polymerization of activated bismethylene compounds with hexaphenyl biphenol under basic conditions in the presence of potassium ferricyanide for 12 h (Scheme 7.10). The polymers obtained, **7.16** and **7.17**, were of low molecular weight, Tg (169 and 195 °C) and showed low thermooxidative stability because of the acetal groups. The reason for making polymers containing acetal derivatives is that materials of this type might find use as positive photoresists.

Scheme 7.10



R	Tg(°C)	TGA (N$_2$) (-5 % wt)	Mw
 **7.16**	167	347	11,300
 **7.17**	195	271	12,100

7.6 NEW OXIDATION OF PRIMARY ALCOHOLS TO ALDEHYDES

Several oxidants for selective conversion of a primary alcohol to an aldehyde, such as nitroxyl radical, pyridinium chlorochromate and dimethylsulfoxide-acetic anhydride (Swern oxidation) have been employed for the oxidation of small molecules and polymers [36,37,38]. The carbon-oxygen coupling reactions between the radical formed from 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol and molecules containing benzylic or allylic methylene groups have been demonstrated in section 7.5. In this section we describe a new method for oxidation of primary alcohols to aldehydes which promises to be of considerable synthetic scope.

Utilizing the previously described reaction conditions, a series of primary alcohols (ethanol, dodecanol, benzyl alcohol, 4-chlorobenzyl alcohol and 3-phenyl-1-propanol) were protected with t-butyl groups by bubbling isobutylene into a benzene solution at room temperature [39]. The tert-butylation reactions are exothermic and must be cooled in a water bath during the reaction. The carbon-oxygen coupling reaction of t-butylethylether and 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol was carried out under similar conditions as described in section 7.5 to produce the difunctional product. All carbon-oxygen coupling reactions between 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol and the t-butyl ethers were slower than the diphenylmethane derivatives probably because of the steric hindrance of t-butyl groups (Scheme 7.11). At the early stages of the reaction mostly monofunctional compounds were produced followed by a very slow second carbon-oxygen coupling reaction. The acetal structure **7.18** rapidly undergoes hydrolysis in contact with water in the presence of acid to give the corresponding aldehyde [40]. These reactions were monitored by ^{1}H NMR which showed the appearance of proton peaks of aldehydes **7.19** at ca 10 ppm (Figure 7.6 and 7.7).

We investigated the thermolysis of ethylacetals in TG/DTA (themogravimetric/differential thermal analysis) at a heating rate 10 °C in the range 30-350 °C. We assume that the carbon-oxygen bonds were broken at 190 - 210 °C, the temperature at which there is a 24.05 % weight loss, which corresponds to the loss of mass of the acetal group (theoretical

Scheme 7.11

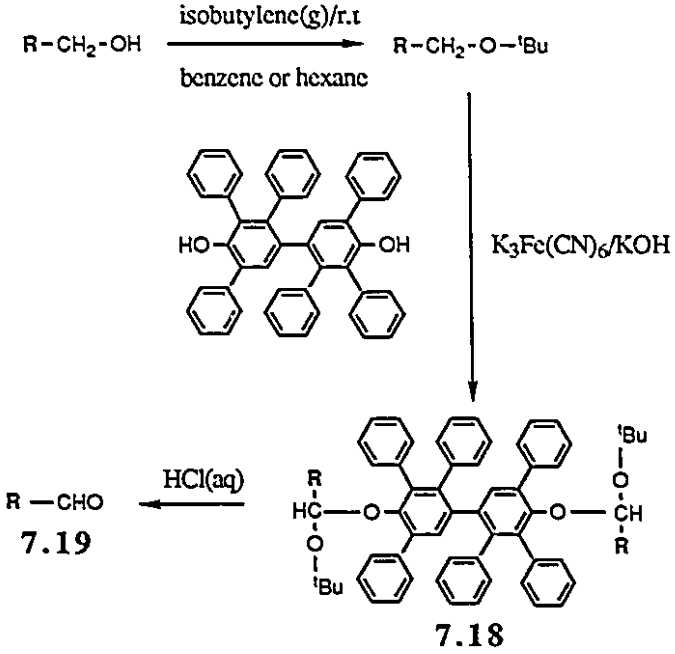
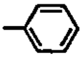
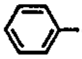


Table 7.3 Characterization of Acetal Products

R	Products (7.18)	Analysis, % calc[found]		NMR (7.18)	NMR (7.19)
		C	H	(methylenic hydrogens, δ)	(aldehydic hydrogen, δ)
CH_3	bifunctional	85.48[85.44]	6.93[7.19]	4.53(m, 2H)	9.78(q, 1H)
$CH_3-(CH_2)_{10}$	bifunctional			4.27(m, 2H)	9.78(t, 1H)
	bifunctional		6.46[6.32]	5.03(d, 2H)	10.08(s, 1H)
Cl– 	bifunctional	81.14[80.87]	5.84[5.60]	5.00(d, 2H)	10.01(s, 1H)
 $-(CH_2)_2$	two monofunctionals				

24.00 %). During the second heating the melting points of 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol at 248 and 258 °C were observable (Figure 7.8).

7.7 CONCLUSIONS

2,2',3,3',5,5'-Hexaphenylbiphenyl-4,4'-dioxyl radical has a high oxidation potential and is stable. Our results indicated that the reaction of diphenylmethane and substituted diphenylmethane with 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-dioxyl proceeds via a radical mechanism. The reactions have been performed under very mild conditions. This new oxidation technique is applicable for a wide range of substrates and results in high yields. Under basic conditions, in the presence of $K_3Fe(CN)_6$/KOH, C-O coupling reactions produced high yields of the diethers or diacetals (from ethers) without any side reactions. The tert-butylated alcohols react with 2,2',3,3',5,5'-hexaphenyl-[1,1-biphenyl]-4,4'-diol in the presence of potassium ferricyanide under basic conditions. The resulting bisacetals can be converted to aldehydes under acidic conditions.

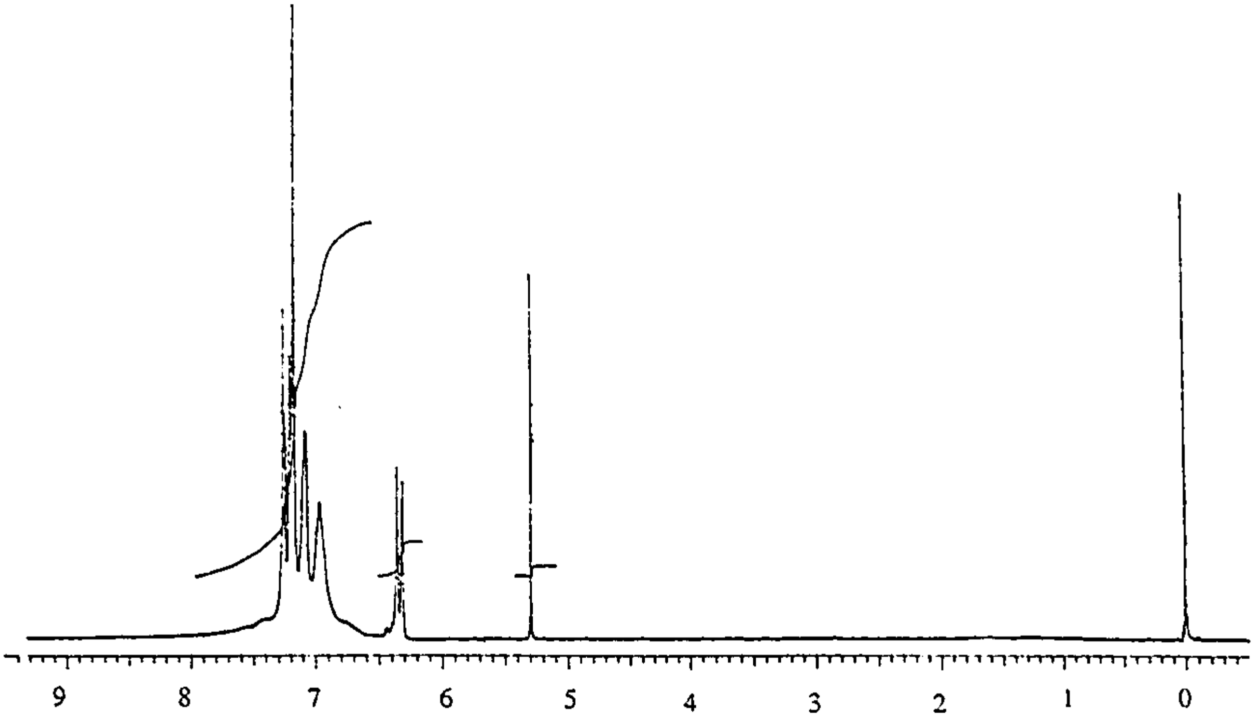


Figure 7.4 Proton nmr spectra of biphenol **2.17a**

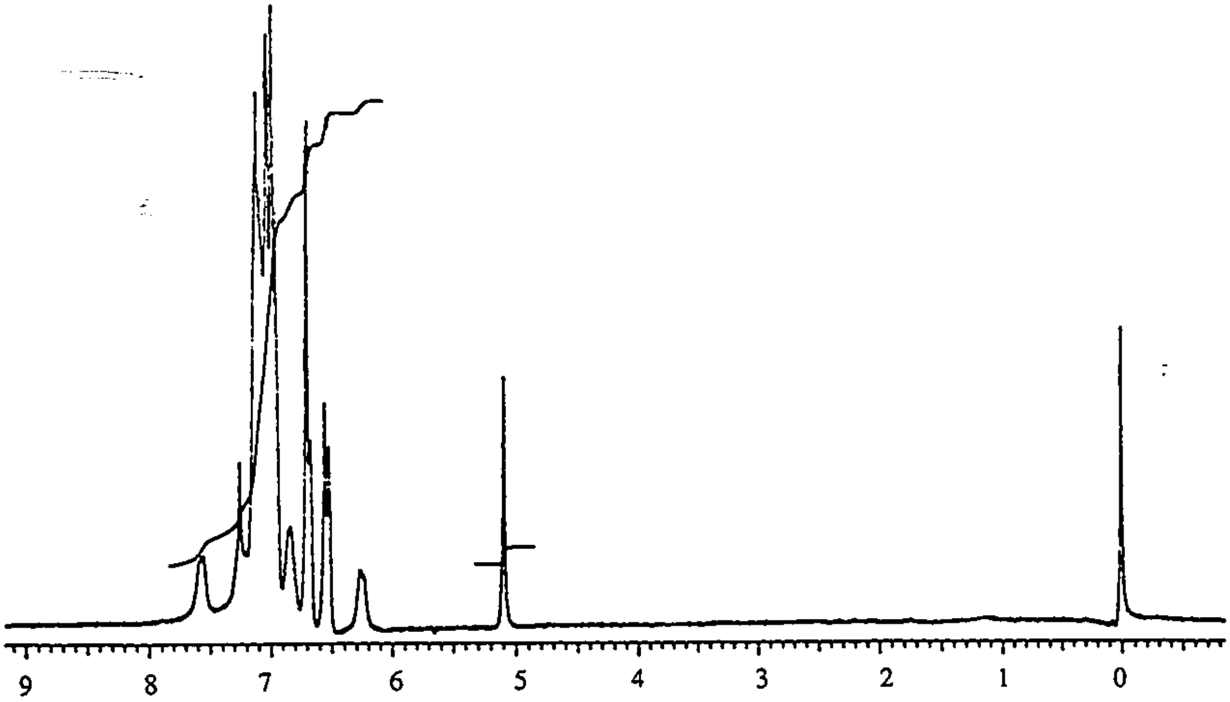


Figure 7.5 Proton nmr spectra of bifuntional product **7.15**

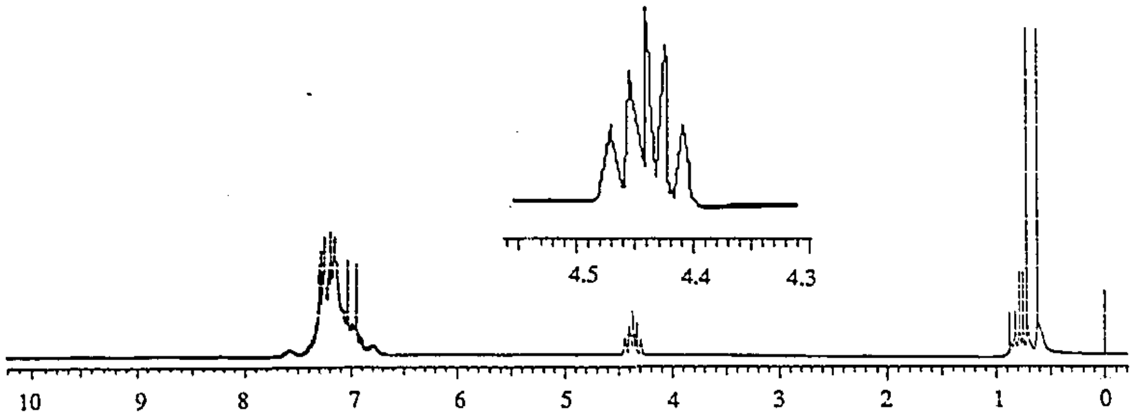


Figure 7.6 Proton nmr spectra of bisethylacetals **7.18**(R=CH_3). Top: methylenic protons

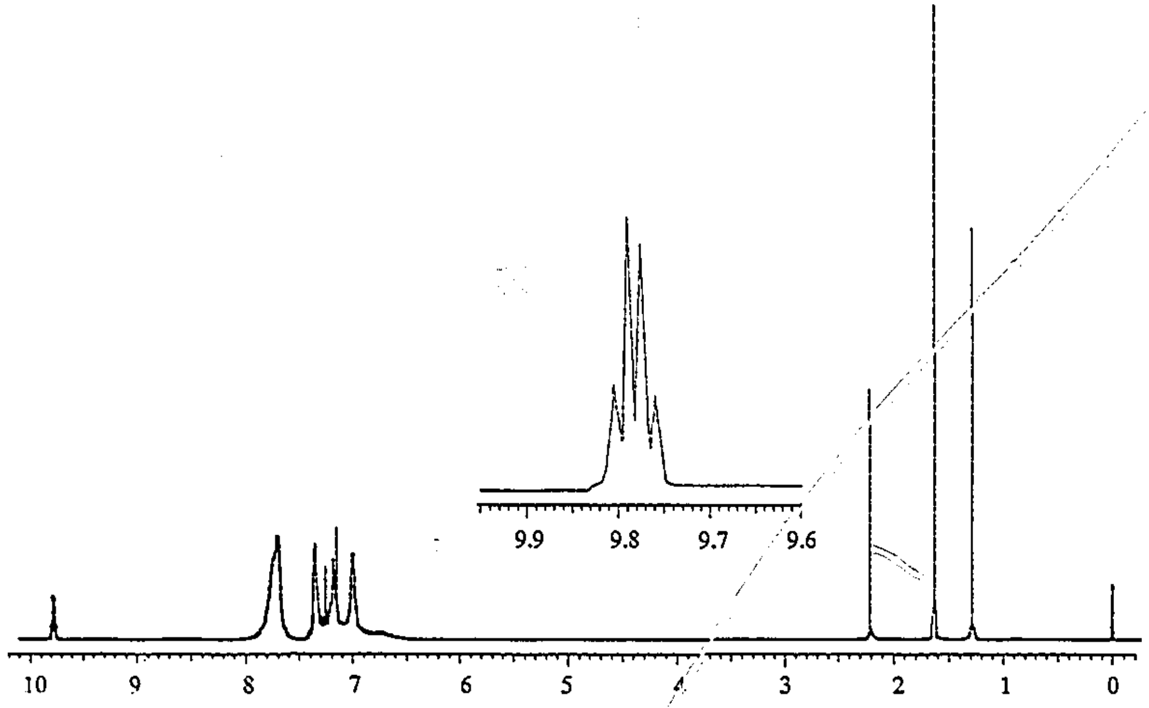


Figure 7.7 Proton nmr spectra of a mixture of aldehyde **7.19** (R=CH_3) and residue (biphenol **2.17a** and isobutylene). Top: aldehyde protons.

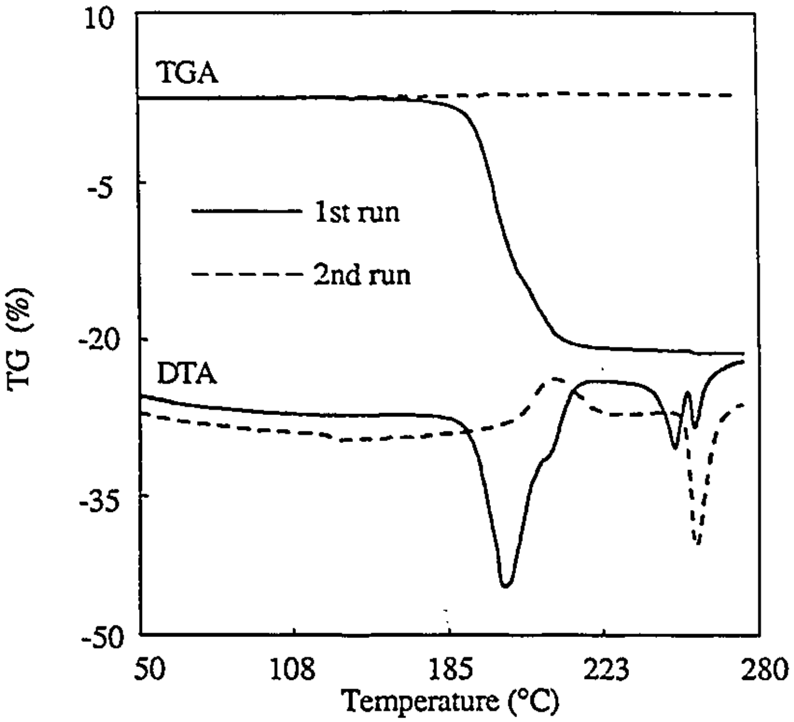


Figure 7.8 TG/DTA Analysis of bisethylacetals **7.18** ($R=CH_3$) under an atmosphere of nitrogen at heating rate 10 °C/min.

7.8 EXPERIMENTAL

General methods

Diphenylmethane, chlorobenzene, 4-chlorobenzyl chloride, 4,4'-diaminodiphenylmethane, benzene, aluminum chloride, ethylbenzene, benzylphenylether, deoxybenzoin, cyclohexene, 3,3-dihydro-2H-pyran, allybenzene, butyronitrile, Cu(I)Cl, KOH, $K_3Fe(CN)_6$ and oxygen were commercially available and were used without further purification. ^1H NMR spectra were taken in $CDCl_3$ solution on a Varian XL-200 instrument, and chemical shifts are given in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were recorded on a ZAB 2F HS spectrometer, ion source 240 °C and 70 eV electron impact, direct inlet: *m/z* (assignment). Melting points were determined on a Fischer-Johns melting point apparatus. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Ontario, Canada. HPLC analysis was performed on a Milton Roy CM 4000 instrument.

2,2',3'3',5,5'-Hexaphenylbiphenyl-4,4'-dioxyl (7.4)

A suspension of 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol **2.17a** (0.75 g, 1.2 mmol) and Ag_2O (1.12g , 0.048 mol) in chlorobenzene (50 mL) was placed in a 100 mL screw cap flask protected from light and the mixture was shaken in a Vibrax apparatus for 20 h. The resulting purple suspension was suction-filtered through a thin layer of Celite. The chlorobenzene was evaporated and the residue was then collected and dried under reduced pressure to give **7.4**; mp 212-214 °C.

^1H NMR (200 MHz , $CDCl_3$) δ 6.90-7.37 (m, 32 H, PhH);

UV-Vis (C_6H_5Cl) λ max 294, 508 nm (ε 13600, 49300).

MS (EI) *m/z* 640 (M^+).

Elemental analysis (%): Calculated for $C_{48}H_{32}O_2$: C, 90.28; H, 5.02 Found : C, 89.80, H 5.10.

The purple solid could not be recrystallized since it is extremely soluble in most organic solvents to give intensely purple-colored solutions. This is in strong contrast to 3,3',5,5'-tetraphenyldiphenoquinone obtained from 2,6-diphenylphenol which is extremely insoluble in all solvents.

Thermolysis of 2,2',3'3',5,5'-hexaphenyl-[1,1'-biphenyl]-4,4'-diyloxy

A chlorobenzene solution of 2,2',3'3',5,5'-hexaphenylbiphenyl]-4,4'-dioxyl (2 g, 3.12 mmol) was slowly heated to reflux under nitrogen at 130 °C and kept for 12 h. The solution changed from a deep violet to a light yellow color. The solution was concentrated by evaporation under reduced pressure. The resulting products were separated by flash chromatography (20 cm column) with 5% ethylacetate-hexane to afford three products. The first fraction contained **7.7** (0.55 g, 27.6%) which was recovered by evaporation of the eluent, and recrystallized from methanol and chloroform, mp 280-282 and 301-302 °C; ^{1}H nmr (200 MHz, $CDCl_3$) δ 6.92-7.76 (m, 30 H, ArH); MS *m/z* 638 (M^+). The second fraction was obtained as yellow crystals of **7.8** (0.45 g, 22.6%). This product was treated with a few drops of hydrazine in hot chloroform to give **7.8** which was recrystallized from ethyl acetate and hexane. mp 245-248 and 265-266 °C; ^{1}H nmr (200 MHz, $CDCl_3$) δ 5.14 (s, 1 H, OH), 6.82-7.78 (m, 31 H, ArH); MS *m/z* 640 (M^+). The third fraction was hexaphenylbiphenol **7.9** (0.8 g, 40%), which was recrystallized from chloroform-methanol and identified by comparison with an authentic sample **2.17a** (HPLC, ^{1}H nmr, mp, MS). mp 248-250, 258-260 °C; ^{1}H nmr (200 MHz, $CDCl_3$) δ 5.16 (s, 2 H, OH), 6.97-7.32 (m, 32 H, ArH); MS *m/z* 642 (M^+).

4,4'-Dichlorodiphenylmethane

The literature procedure was modified as follows [22]. In a 100 mL three-necked round bottomed flask equipped with a mechanical stirrer, dropping funnel and nitrogen gas inlet topped by a calcium chloride drying tube were placed a mixture of aluminum chloride (0.31

g. 2.3 mmol) and chlorobenzene (55 g). The flask was cooled to -2 to -5 °C in ice water/acetone under nitrogen atmosphere. A solution of 4-chlorobenzyl chloride (20 g, 0.12 mol) in chlorobenzene (40 g) was added dropwise over 30 min to the cooled slurry. After an additional 30 min, the mixture was washed with water, dried over $MgSO_4$, filtered, and the solvent was evaporated. Distillation of the crude product was carried out under reduced pressure using a Kugelrohr apparatus. The ratio of 4,4'-dichlorodiphenylmethane to 2,4'-dichlorodiphenylmethane was 87% : 13% as determined by HPLC.

4-Chlorodiphenylmethane

This reaction followed the procedure used for dichlorodiphenylmethane. Benzene (35 g) and aluminum chloride (0.31g, 2.3 mmol) were placed in a 100 mL flask and a 4-chlorobenzyl chloride (20 g, 0.12 mol) solution in benzene (15 g) was slowly added. The product was characterized by ^1H NMR. ^1H nmr (200 MHz, $CDCl_3$) δ 3.87 (s, 2 H, CH_2), 6.81-7.23 (m, 5 H, ArH)

4,4'-Dimethoxydiphenylmethane

4,4'-Dihydroxydiphenylmethane (10g, 50 mmol), dimethylsulfate (7g, 55 mmol) and NaOH (5g, 125 mmol) were added to ethanol (60 mL). The reaction was refluxed for 12 h. The mixture was washed with a solution of chloroform and H_2O. The chloroform layer was isolated and the chloroform removed by evaporation. The crude product was purified by using a Kugelrohr apparatus. The product was a liquid and the structure confirmed by ^1H NMR. ^1H nmr (200 MHz, $CDCl_3$) δ 3.78 (s, 6 H, CH_2), 6.84-6.95 (d, 2 H, ArH), 7.07-7.13 (d, 2 H, ArH)

4,4'-Bis(phthalimido)-diphenylmethane

4,4'-Diaminodiphenylmethane (5 g, 25 mmol), phthalic anhydride (7.4g, 50 mmol) and triethylamine (0.65 mL, 5 mmol) were dissolved in toluene (70 mL). The reaction was heated to reflux for 3 h. The yellow solid precipitated out of solution. The solid was triturated 3 times with water (100 mL) and conc. hydrochloric acid (1 mL) and filtered. The product recrystallized from chloroform. mp >300 °C. The product was characterized by ^{1}H NMR. ^{1}H nmr (200 MHz, $CDCl_3$) δ 3.98 (s, 2 H, OH), 6.97-7.93 (m, 16 H, ArH)

General oxidation procedure (diphenylmethane)

To a stirred solution of butyronitrile (15 mL) was added 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol (0.71 g, 1.1 mmol), and CuCl (0.2 g, 2 mmol). The mixture was heated to 95 °C with oxygen bubbling into the solution. The reaction was maintained for 3 h to afford hexaphenylbiphenoxy radical **7.4** at which point diphenylmethane (2 g, 11.89 mmol) was added. The reaction was stirred for 12 h and benzophenone formation was monitored by HPLC. The mixture was concentrated by evaporation and the residue was purified by a short-path distillation using a Kugelrohr apparatus under reduced pressure. The product was identical to an authentic sample. mp 47-48 °C (lit. 48-49.5 °C).

General procedure for the carbon-oxygen coupling reaction

In benzene (20 mL) was dissolved 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol (0.5 g, 0.78 mmol) at room temperature. A solution of $K_3Fe(CN)_6$ (2.4 g, 6.1 mmol) and KOH (0.34 g, 6.06 mmol) in distilled water (15 mL) was added and the two phases were stirred for 2 h. The color of the organic phase changed to dark-violet. To this mixture was added diphenylmethane (0.5 g, 3 mmol). The mixture was kept for 12 h at reflux temperature. Then it was cooled and washed with water (3x50 mL). The organic layer was separated and evaporated. The residue was recrystallized from ethyl acetate-hexane to give the carbon-oxygen coupled compound. mp 243-245 °C; ^{1}H nmr (200 MHz, CDCL$_3$) δ 5.10 (s, 2 H, -CH), 6.27-7.11 (m, 27 H, ArH); MS *m/z* 974 (M$^+$)

Polymerization of 2,2',3,3',5,5'-hexaphenylbiphenyl]-4,4-diol and 2,2-bis(4-benzyloxyphenyl)-propane

In benzene (20 mL) was dissolved 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol (1.0 g, 15.6 mmol) at room temperature. A solution of $K_3Fe(CN)_6$ (3.0 g, 7.6 mmol) and KOH (0.43 g, 7.6 mmol) in distilled water (15 mL) was added. The mixture was stirred for 2 h and then 2,2-bis(4-benzyloxyphenyl)-propane (1.27g, 3.12 mmol) added. The reaction was kept for 12 h at reflux temperature. The organic layer was collected and washed with water (3x50 mL). The organic layer was concentrated and precipitated in methanol. The resulting product was filtered and dried. The dried polymer was dissolved in chloroform and reprecipitated in methanol. The resulting polymer was dried under vacuum.

General procedure for the t-butylation of primary alcohols (Preparation of t-butoxymethylbenzene)

The literature procedure was modified [39]. To a solution of benzylalcohol (92.47 mmol, 10 g) in benzene(100 mL) Amberlyst H-15 was added and isobutylene bubbled into the reaction mixture at room temperature. The progress of the reaction was monitored by HPLC and thin layer chromatography. When no more alcohol was present the Amberlyst was filtered off and potassium carbonate was mixed into the filtrate which was mixed. The inorganics were filtered and the filtrate was evaporated under reduced vacuum. The resulting product yields ranged from 90-100 % and their structures were confirmed by ^{1}H NMR.

Carbon-Oxygen coupling reaction

The 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4-diol (0.5 g, 0.78 mmol) dissolved in benzene (20 mL) at room temperature. A solution of $K_3Fe(CN)_6$ (2.4 g, 6.1 mmol) and KOH (0.34 g, 6.06 mmol) in distilled water (15 mL) added. The mixture was stirred for 2 h and t-butylethylether (0.49 g, 3 mmol) added. The reaction was kept for 20 h at reflux temperature. An additional $K_3Fe(CN)_6$ (1.2g, 3.05 mmol) and KOH (0.17, 3.03 mmol) were added and maintained 20 h. The mixture was washed with water (3x50 mL). The organic layer was separated and evaporated, and the residue was recrystallized from chloroform-methanol.

Detection of aldehydes

Into the nmr tube were added the above difunctional acetal (10 mg) and a catalytic amount of aqueous HCl in $CDCl_3$ with TMS. The quartet peaks (CH_3-C$\underline{H}$O) appeared at 9.75-9.80 ppm and the methylene (CH_3-C$\underline{H}$-O-t-Butyl) disappeared at 4.29-4.41 ppm.

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CHAPTER 8

REDOX POLYMERS

8.1 INTRODUCTION

All living organisms, animal and plant, function by virtue of polymeric redox systems. Among these systems are the host of oxidases, reductases, and the other enzymes that carry out reactions in which electrons are removed from or introduced into reagent and product molecules [1,2]. In addition, there are a number of modified natural products and artificial systems that fall into this class which are of industrial interest. For example, there are many dyes which, fixed on fibers, comprise polymeric redox systems. Potential uses of redox polymers as antioxidants, nondiffusing stabilizers, free radical scavengers, oxygen in boiler feed water, ion exchangers and catalysts for reactions have been suggested [3,4,5].

Polymer reagents offer the advantages of easy mechanical separation of regenerable reagents from products by filtration or flow in column techniques and the possibility of using excess reagent to shift the equilibrium toward the product [6]. The redox systems must be chemically stable, reversible, and redox capacity must be sufficiently high. They should be easily regenerable using inexpensive reagents without side reactions. Oxidation-reduction polymers, or redox polymers, are high molecular weight substances that can transfer or exchange electrons when in contact with reactive ions or molecules. Inherently, redox polymers are potential ion exchangers. For each electron that is transferred, a net

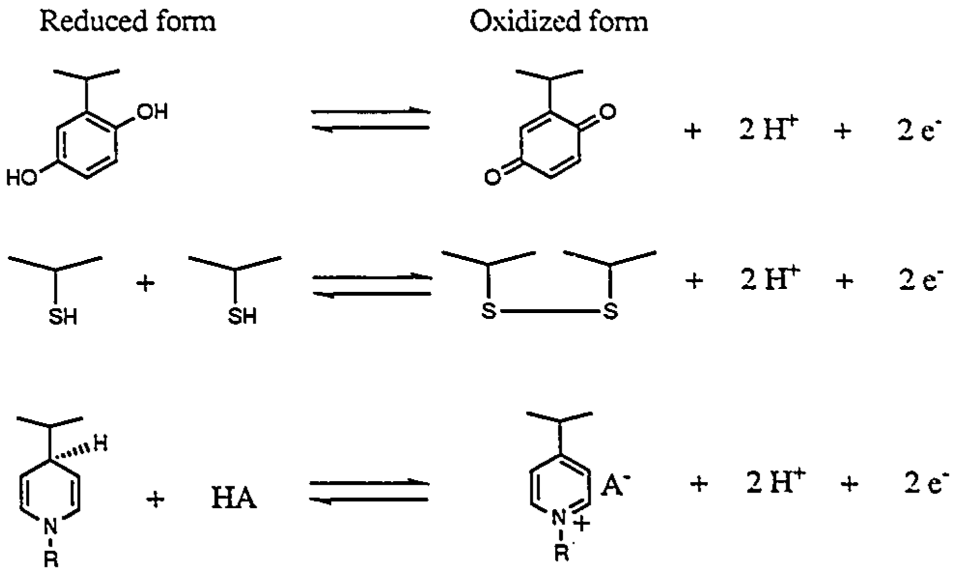


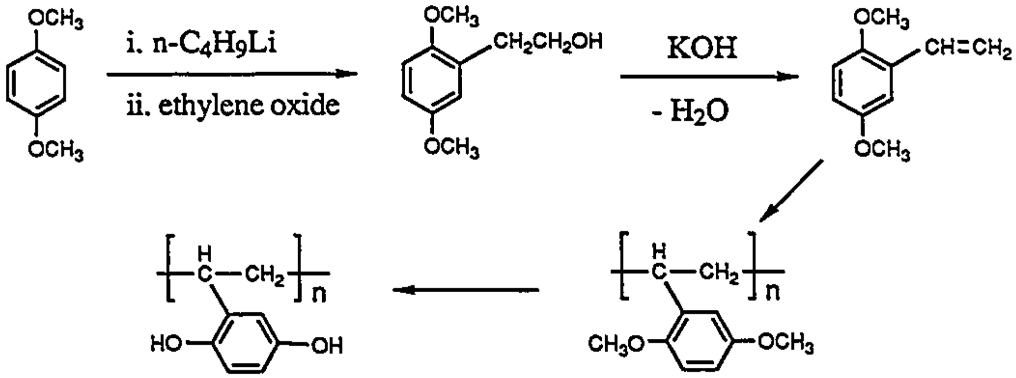
Figure 8.1 Representive oxidation-reduction reactions.

positive charge is developed (or lost) or a positively charged ion is lost (or gained), as shown by the representative type reactions in Figure 8.1. The first organic functional redox systems were the hydroquinone-quinone, thiol-disulfide, and hydropyridine-pyridinium groups as shown in Figure 8.1. The thiol-disulfide type [7] was initially ruled out because the oxidation would introduce crosslinking or other constraints which would add complications to the interpretation of results. The pyridinium redox [8] systems, though interesting from a natural products point of view, also were ruled out of the initial work. This system would cause experimental difficulties because of its extreme sensitivity to environmental conditions. The hydroquinone-quinone system [9,10] appeared most suitable for in this area since it is known to be rapidly reversible, and since a great deal of fundamental work had been done with hydroquinone and its derivatives.

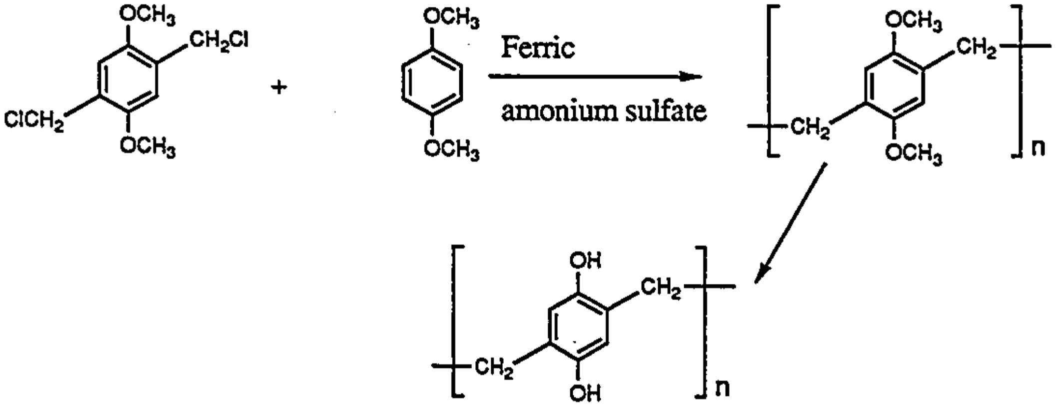
8.1.1 SYNTHESIS OF REDOX POLYMERS

A variety of synthetic methods exist for the preparation of redox polymers [9,11]. These may be divided into two classes: methods for preparing the desired polymers by polymerization of the appropriate monomers, and methods whereby preformed polymers are chemically modified [12]. Both methods permit the synthesis of polymeric structures with many sites capable of accepting or donating electrons. The oxidation-reduction groups may form part of the polymer backbone [9,13], or may be attached as substituents

Scheme 8.1



The oxidation-reduction groups attached as substituents on the polymer backbone

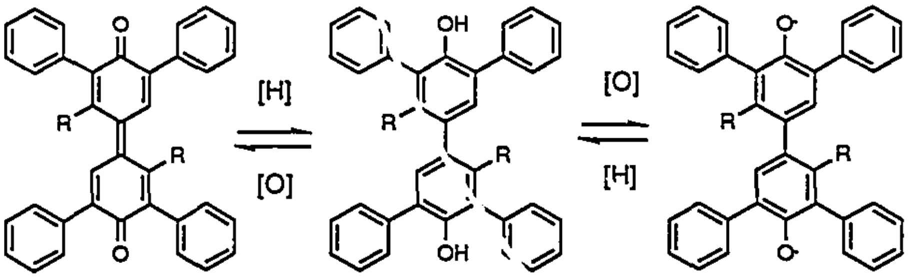


The oxidation-reduction groups form part of the polymer backbone on the backbone of polymer [8]. Redox polymers of the first type exhibit effects due to the constraints of being part of the backbone as compared to the latter type where the redox group is a substituent on the backbone (Scheme 8.1). In addition, differences in chemical and physical properties may be expected between linear polymers, which may be put into solution, and are accessible to reaction and crosslinked polymers. Also, classical condensation reactions permit more variations in syntheses. Treatment of bishydroxyalkylquinones with biscarboxylic acid chlorides in tetrahydrofuran-pyridine gave polyester quinones. With phosgene, polycarbonate quinones were prepared. These polymers dissolve in organic solvents and can be reversibly oxidized and reduced. We picked the route in which the oxidation-reduction groups formed part of the polymer backbone. Monomer synthesis, followed by condensation polymerization, has the advantage that the composition of the product is known with increased certainty, and the product is readily characterized.

8.1.2 STRATEGY AND GOAL

Highly hindered biphenols such as **8.1a** and their oxidized forms constitute powerful oxidation-reduction systems (Scheme 8.2). In the oxidized form these compounds exist as intensely colored diphenoquinones **8.2a** [14] or biphenoxy radicals **8.3b** [15,16] and are effective oxidizing agents, for example, in the oxidative coupling of 2,6-disubstituted phenols to yield biphenols of type **8.1a** and in the conversion of diphenylmethane into 1,1,2,2-tetraphenylethane [17]. Diphenoquinones such as **8.2a** (R = H) are formed as the C-C coupled by-product in the oxidative polymerization of 2, 6-diarylphenols [18] but they can be prepared as the principal products if the oxidation reaction, which requires molecular oxygen and a copper catalyst, is performed at 100 °C using butyronitrile or benzonitrile as the ligand and solvent [19]. The diphenoquinone **8.2a** is insoluble in the nitrile solvent mixture and precipitates out of the solution as a dark green solid which in solution is orange

Scheme 8.2



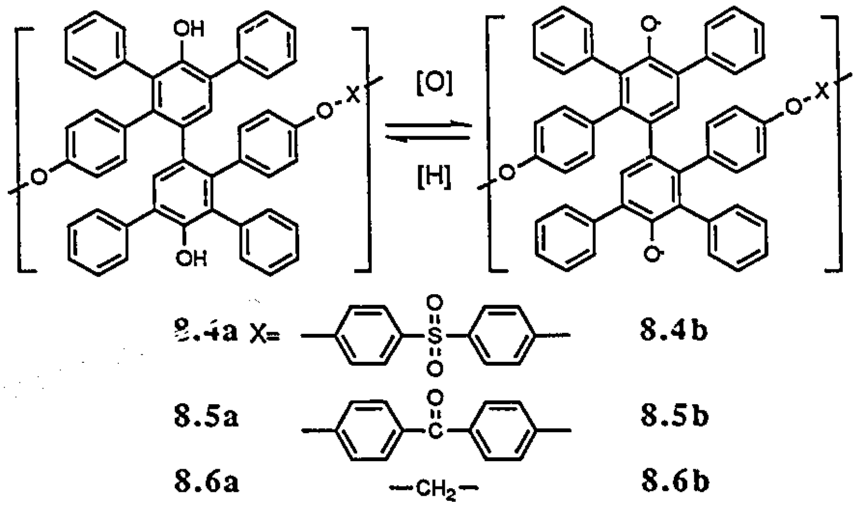
8.2a R=H
8.2b R=Ph

8.1a R=H
8.1b R=Ph

8.3a R=H
8.3b R=Ph

colored. The same oxidative coupling reaction conditions can be successfully applied for the conversion of 2,3,6-triphenylphenol into 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol **8.1b** [20]. The introduction of the phenyl rings on the 2 and 2' positions places a geometrical constraint on the molecule which results in non-coplanarity of the biphenyl moiety which reduces its crystallinity and increases the solubility of **8.1b** relative to **8.1a**. In contrast to the diphenoquinones the oxidized form of **8.1b** is very soluble and probably exists as the biphenoxy radical **8.3b** rather than the diphenoquinone **8.2b** because of the lack of coplanarity. Biphenoxy radicals of this type are more powerful oxidizing agents than the diphenoquinones and they are presently under active investigation in our laboratory. In addition to good solubility **8.1b** would be expected to show high thermal and oxidative stability since it is completely aromatic. With these properties highly sterically hindered biphenols such as **8.1b** should be interesting redox monomer units for the preparation of oxidation-reduction polymers. Redox resins containing hydroquinone or other redox systems have been prepared [21] but despite patents describing their applications these polymers have seen little commercial utility probably because the materials that have been synthesized are not very thermally stable and have relatively low redox potentials [22]. A polymer containing these highly hindered aromatic biphenols as

Scheme 8.3



repeating units linked by diphenylsulfone or benzophenone moieties or a methylene bridge (Scheme 8.3) should have high stability and should be usable at elevated temperatures and be chemically stable. The preparation of a redox polymer of this type is the object of the investigations which we report in this section. The synthesis of functionalized 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol and its polymerization to polymers **8.4a**, **8.5a**, and **8.6a** is described. Preliminary studies in this area were carried out in this laboratory by Dr. Hellena Nardin Carvalho.

8.2 PREPARATION OF MONOMER AND POLYMERS

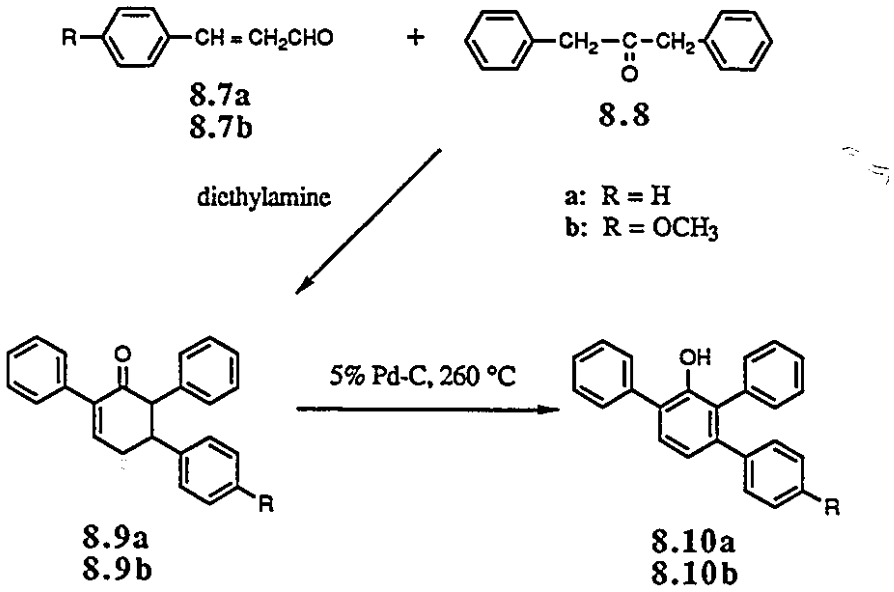
8.2.1 SYNTHESIS OF MONOMER

The preparation of 2,3,6-triphenylphenol **8.10a**, which is the starting material for **8.1b**, has been previously described [23,24]. It consists of the condensation of dibenzylketone

8.8 with cinnamaldehyde **8.7a** in the presence of diethylamine to give the intermediate cyclohexenone followed by a dehydrogenation reaction (Scheme 8.4). This same strategy would also be convenient for the preparation of a 3-(4-methoxyphenyl)-2,6-diphenylphenol **8.10b** which could then be dimerized by oxidative coupling to give the biphenol **8.11a.** A 4-methoxy substituent seemed an appropriate choice since the methoxy group would most likely be stable to the conditions of the subsequent C-C coupling reaction and could be easily removed before the polymerization reaction.

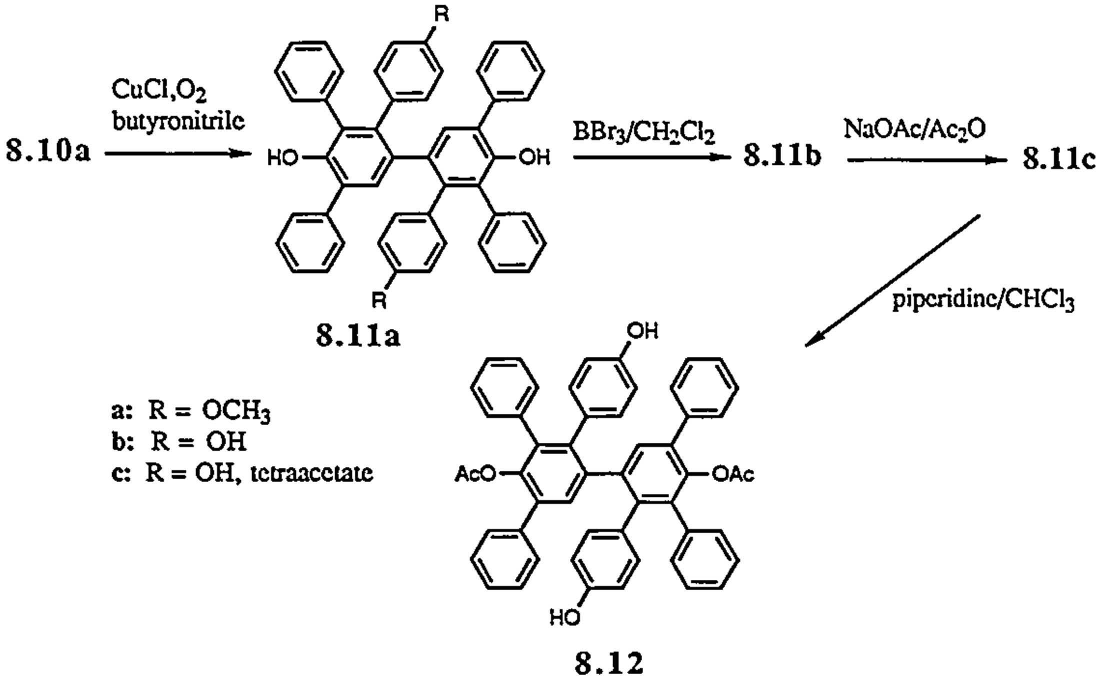
The condensation reaction of trans-4-methoxycinnamaldehyde **8.7b** with dibenzylketone 8.8 in the presence of diethylamine afforded a mixture of two compounds with very close retention times formed in approximately equal amounts (HPLC) in an overall yield of 96%. One isomer **8.9b** was obtained pure by fractional recrystallization (Scheme 8.4). The mixture of isomers **8.9b** was aromatized by heating at 250-260 °C with (5%) Pd on charcoal to give **8.10b** in approximately 82 % yield after recrystallization from ethyl acetate.

Scheme 8.4



The oxidative coupling of **8.10** gave **8.11a** in 73 % yield (Scheme 8.5). The reaction was catalyzed by CuCl (I) in butyronitrile heated at 95 °C, under vigorous stirring with O_2 bubbling through the reaction mixture. As the reaction proceeded the mixture became purple due to the formation of the biphenoxyradical which was formed along with **8.11a.** Addition of hydrazine at the end of the reaction converted the oxidized form into the biphenol **8.11a.** Cleavage of the methoxy group of **8.11** was performed with 5.7 moles of BBr_3 in CH_2Cl_2. The stirred mixture was kept at 0 °C for one hour and then for half

Scheme 8.5



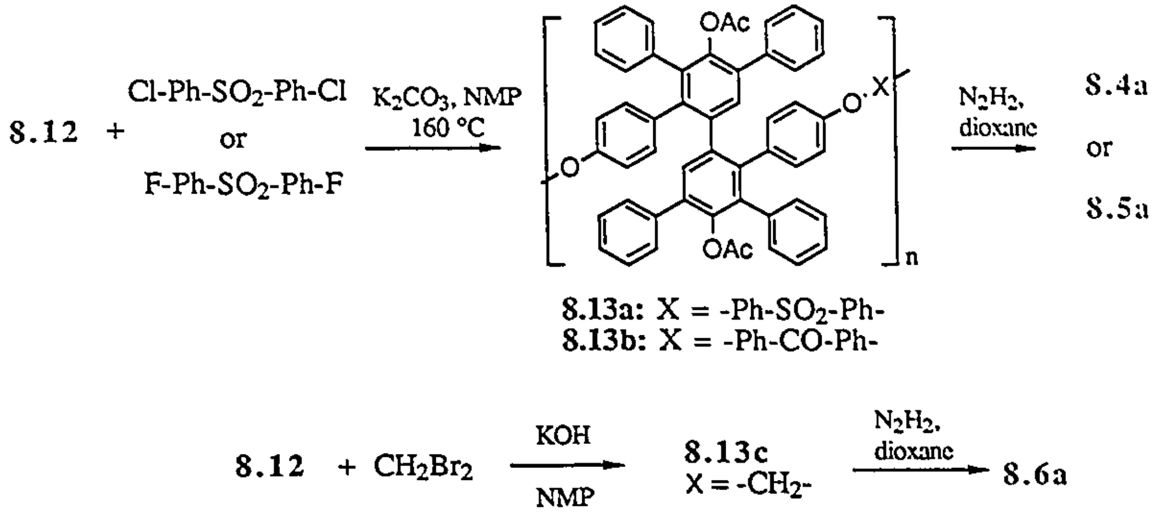
hour at room temperature to obtain **8.11b.** There was some difficulty in achieving a complete reaction even when up to 6.50 moles of BBr_3 were used. Similar difficulty has been found in removing this functionality from polymers in which it has been used to protect phenolic groups [25]. Protection of tetraphenol **8.11b** with acetic anhydride in the presence of potassium acetate afforded the tetraacetoxyhexaphenylbiphenol **8.11c** in

82 % yield after recrystallization from ethyl acetate. The less hindered acetate groups of the tetraacetate derivative **8.11c** could be selectively deprotected by using piperidine as a base. The resulting product **8.12** was obtained in 90% yield. ^{1}H and ^{13}C chemical shifts of the unhindered phenolic groups and the hindered acetate groups were clearly shown. The unhindered phenolic hydroxyl signals appeared at 5.12 ppm while the signals ($OCO\underline{C}H_3$), 2.20 ppm (^{1}H) and 21.11 ppm (^{13}C) of hindered acetate disappeared and the signals ($OCO\underline{C}H_3$) of hindered acetate remained at 1.50 ppm (^{1}H) and 20.21 ppm (^{13}C).

8.2.2 SYNTHESIS OF REDOX POLYMERS

We attempted to polymerize the tetraphenol **8.11b** directly by reaction with 4,4'-difluorophenylsulfone or 4,4'-difluorobenzophenone in NMP with potassium carbonate to give the poly(aryl ether) or by the reaction with methylene bromide to give the polyformal. Although the unhindered phenolic groups are considerably more reactive than the hindered phenolic groups there is still enough reactivity in the latter so that branching and eventually crosslinking occurs. Thus, we were not successful in making high molecular weight polymers. Wang recently demonstrated the synthesis of poly(aryl ether)s using masked biphenols in which the phenolic groups, protected as acetates or carbamates, were hydrolyzed during the reaction to generate the phenoxide ions in situ [26]. Direct polymerization of the tetraacetate **8.11c** under these conditions, on the expectation that the unhindered acetate groups would be selectively deprotected, was partially successful. However, high molecular weight polymers were not obtained. The polymerization of the selectively protected diacetate **8.12** with 4,4'-difluorophenylsulfone or 4,4'-difluorobenzophenone carried out in NMP with potassium carbonate at 165 °C for 30 hours (Scheme 8.6) was much more successful. During the reaction the acetate groups were partially deprotected. The resulting polymers **8.13a** and **8.13b** were completely deprotected with hydrazine to give polymers (85 % yield), **8.4a** and **8.5a**. The polyformal

Scheme 8.6



8.13c was prepared from **8.12** with excess of CH_2Br_2 and potassium hydroxide in NMP at 95 °C for 7 hour. In this case deprotection of the acetate groups did not occur during the polymerization reaction.

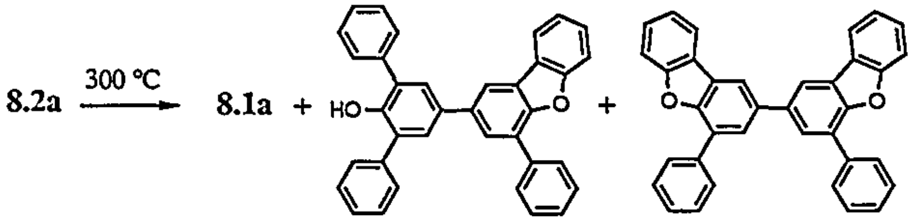
8.3 RESULTS AND DISCUSSION

8.3.1 PHYSICAL AND THERMAL PROPERTIES

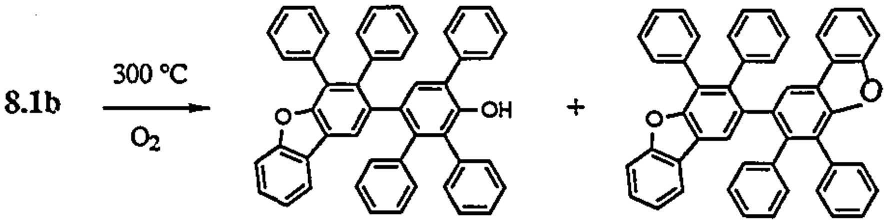
Properties of the polymers **8.4a, 8.5a, 8.6a** are listed in Table 8.1. These polymers have excellent solubility at room temperature in organic solvents such as methylene chloride, NMP and DMSO. The glass transition temperatures of polymers **8.4a, 8.5a, 8.6a** are in the range of 226-259 °C (Figure 8.2). Inherent viscosities and weight average molecular weights determined by GPC vs polystyrene standards are 0.11-0.23 g/dL and 10,000-56,800 respectively. The UV-Visible spectra of reduced (**8.3b, 8.6a**), and oxidized monomers (**8.3b, 8.11**) and the reduced (**8.4a, 8.5a**) and oxidized polymers (**8.4b,** 8.5b) are shown in Table 8.2. The reduced forms show one band at 290-300 nm, which is assigned to π-π* transition, while the oxidized forms show two bands at 290, 500-530 nm, which are π-π* and n-π* transitions. The n-π* transition of **8.4b, 8.5b** are shifted about 30 nm compared to the corresponding **8.3b**, due to the electronic effect of methoxy group.

8.3.2 THERMAL BEHAVIOR OF POLYMERS

The polymers have excellent thermoxidative stability in the range of 477-526 °C (5 % weight loss) in air and in nitrogen (Figure 8.3). Polymers **8.4a, 8.5a** show better thermal stability than **8.6a**. Phenols are generally not considered to be thermoxidatively stable materials therefore it is surprising that the stability of these materials as measured by TGA in air is comparable to the stability in nitrogen. It has been previously shown [27] that when **8.2a** is heated to 300 °C three products are formed (eq 8.1). The dibenzofuran containing molecules **8.14** and **8.15** must result from the attack of a phenoxy radical on the pendent phenyl groups. A similar reaction showed in chapter 7 when the biphenoxy



8.14 **8.15** (8.1)



8.16 **8.17** (8.2)

radical **8.3b** is heated and we have also determined that at 300 °C in the presence of air the biphenol **8.1b** is slowly oxidized to give the monodibenzofuran and bisdibenzofuran containing molecules as principal products (eq 8.2). The resulting polymers **8.4a** and **8.5a**, after treating 5 h under air atmosphere, are not soluble in $CHCl_3$, NMP and DMSO. However the polymers **8.4a** and **8.5a** treated under nitrogen are soluble in same solvents. Polymers **8.4a, 8.5a** and **8.6a** presumably resulted from the intramolecular ring closure reactions to give the stable dibenzofuran moieties in the polymer at the elevated temperatures.

8.4 CONCLUSIONS

The 2,2'-bis(4-methoxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol **8.11a**, was prepared by the oxidative coupling of 3-(4-methoxyphenyl)-2,6-diphenylphenol **8.10b**. The oxidative coupling reaction was carried out in the presence of molecular oxygen, copper (I) chloride catalyst and butyronitrile as ligand and solvent. Its oxidized form **8.11** constitutes a powerful oxidation reduction system (see next chapter). The unhindered acetoxy groups of the tetracetoxybiphenol **8.11c** were selectively deprotected with piperidine in high yield. We could polymerize **8.12** with 4,4'-difluoro-diphenylsulfone and 4,4'-difluoro-benzophenone by using K_2CO_3 in NMP. Polyformal **8.6a** was synthesized by the reaction of **8.12** and methylene bromide with KOH as base. The polymers **8.4a, 8.5a** show thermal stability (5 wt % loss) above 500 °C under nitrogen and air. At 300 °C the polymers were cyclized by an intramolecular reaction under air atmosphere.

Table 8.1 Physical and Thermal Properties of Polymers

Polymer	ηinh[a]	$Mw^b x10^3$	Mw/Mn	Tg^c(°C)	TGA^d(°C) N_2/Air
8.4a	0.21	40.0	7.5	259	518/515
8.5a	0.23	56.8	6.3	251	526/525
8.6a	0.11	10.0	8.3	226	481/477

[a] Inherent viscosity was measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

[b] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

[c] Tg was determined by DSC at heating rate 20 °C/min under nitrogen (flow rate 50 mL/min).

[d] Temperature at which 5% weight loss was determined by TGA at heating rate 10 °C/min under air or nitrogen (flow rate 200 mL/min).

Table 8.2 UV-Visible Absorptions and Absorption coefficients*

Polymers	λmax (nm)	ε mol x 10^{-4}($M^{-1}Cm^{-1}$)
8.1b	302	1.44
8.3b	294, 508	1.36, 4.93
8.4a	290	3.23
8.4b	290, 530	3.06, 0.64
8.5a	290	3.81
8.5b	292, 530	4.02, 0.63
8.11a	290	2.61
8.11	292, 528	3.15, 2.78

* Measured in chlorobenzene at room temperature.

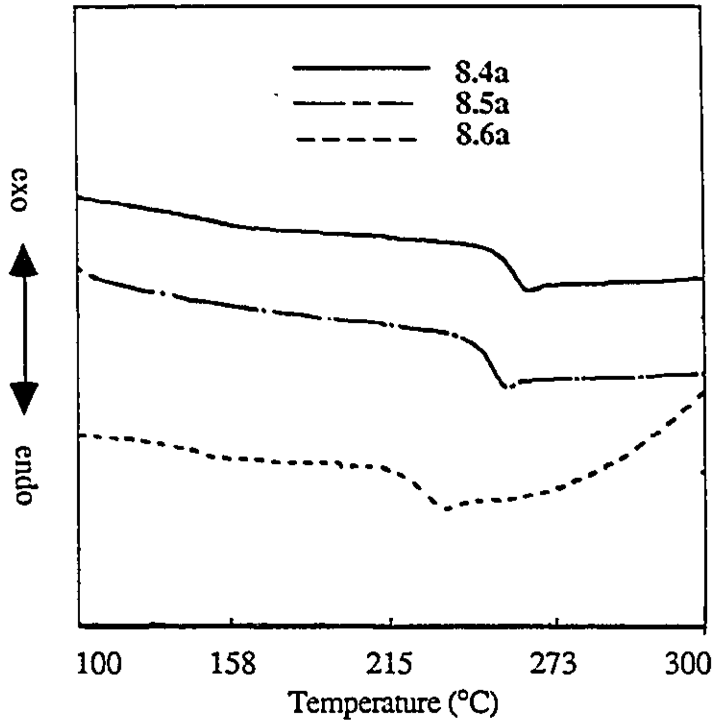


Figure 8.2 DSC Analysis of polymers **8.4a**, **8.5a** and **8.6a** under an atmosphere of nitrogen.

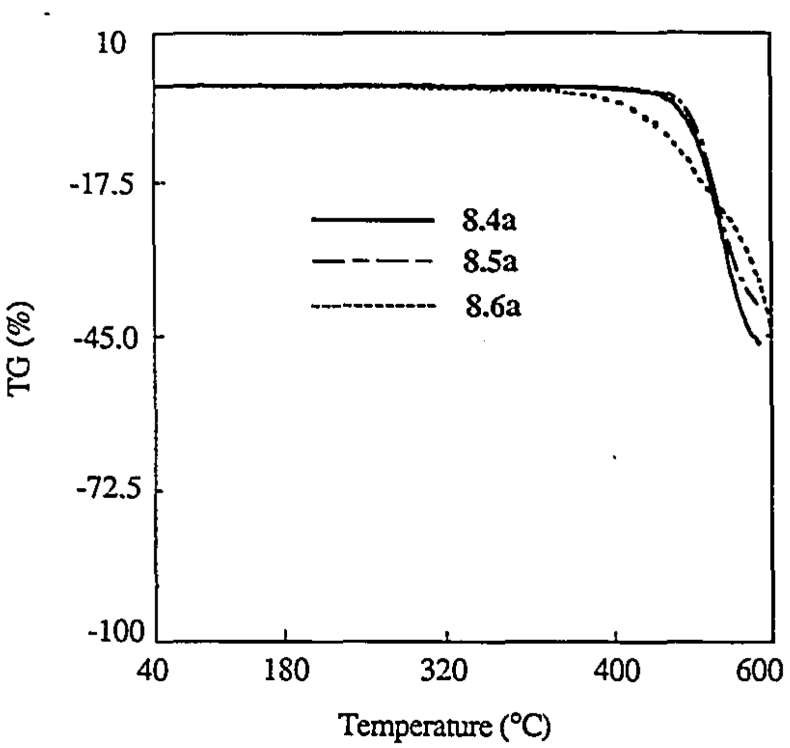


Figure 8.3 TGA thermograms of polymers **8.4a**, **8.5a** and **8.6a** under an atmosphere of nitrogen.

8.5 EXPERIMENTAL

General Procedures

Toluene and NMP were distilled before use from calcium hydride. K_2CO_3 was dried in an oven at 130 °C. 4,4'-Dichlorodiphenylsulfone and 4-methoxycinnamaldehyde were obtained from commercial suppliers. Melting points were determined in a Fisher John's melting point apparatus. Infrared spectra were recorded using Analet AQS-60 FTIR spectrometer in $CDCl_3$. UV spectra were obtained on an Unicam-SP-800 instrument. ^1H and ^{13}C NMR spectra were determined on either a 200 MHz or a 300 MHz XL Varian NMR spectrometer using $CDCl_3$ containing tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane on the δ scale. Microanalyses were done by Guelph Chemical Laboratories Ltd., Ontario, Canada. Mass spectra were recorded on a Du Pont 21-492 B mass spectrometer. HPLC analysis was performed on a Milton Roy CM 4000 instrument. Molecular weights were determined by gel permeation chromatography using polystyrene as a standard with chloroform as solvent on a Waters 510 GPC with a UV detector and with four µ-Styragel columns (500, 10^4, 10^5, and 100 Å) in series. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Seiko SSC5200 thermal analysis system (TG/DTA 220 and DSC 220) with a heating rate of 10 or 20 °C per minute in air and nitrogen atmospheres.

Monomer synthesis

2,2',3,3',5,5'-Hexaphenylbiphenyl-4,4'-dioxyl (8.3b)

The preparation was described in Chater 7.

3-(4-Methoxyphenyl)-2, 6-diphenylcyclo-2-hexenone (8.9b)

Trans-4-methoxycinnamaldehyde **8.7b** (25 g, 0.142 mol) 1,3-diphenylacetone **8.8** (29.9 g, 0.142 mol) and diethylamine (20 mL) were magnetically stirred in a 250 mL flask at room temperature under a nitrogen atmosphere. The reaction proceeded exothermically to form a thick melt which then solidified to form a yellow solid. The solid was triturated with ethanol and then filtered. The resulting solid was magnetically stirred in hot ethanol for 3 h. After cooling, the solid was filtered and dried in a vacuum oven to yield an approximately equimolar mixture of two isomeric compounds (48.1g, 0.136 mol, 96 % yield). The mixture is used without separation of the isomers for the next step. Recrystallization from ethyl acetate-petroleum ether yielded a single isomer **8.9b**: mp 168-170 °C.

^{1}H NMR (200 MHz , CDCl$_3$) δ 2.87-2.97 (m, 2 H), 3.60-3.80 (m, 2 H), 3.74 (s, 3 H), 4.05 (dd, *J* =1.5, 12 Hz, 1 H), 6.70-6.75 (d, 2 H), 7.00- 7.55 (m, 12 H).

IR (CDCl$_3$) 1674 (C=O), 1611 (conjugated C=C), 1250 cm-1 (CH$_3$O);

MS (EI) *m/z* 354 (M$^+$);

Elemental analysis (%): Calculated for $C_{25}H_{22}O_2$: C, 85.29; H, 5.68; Found: C, 84.98; H, 6.02.

3-(4-Methoxyphenyl)-2,6-diphenylphenol (8.10b)

In a three neck round bottom flask equipped with a condenser, a thermometer, and a nitrogen inlet were placed **8.9b** (20 g, 56 mmol) and 5% Pd on charcoal (1.3 g). This mixture was melted and heated up to 250-260 °C for 40 min. While stirring magnetically temperature was brought down to room temperature and approximately 300 mL of hot ethyl acetate was added. This mixture was stirred magnetically to ensure that all the product was dissolved and filtered while hot. The catalyst collected on the filter was washed several times with small portions of hot ethyl acetate. The solutions were combined and evaporated and the residual solid was recrystallized to form a light pink solid. Drying in the vacuum oven for several hours yielded **8.10b** 16.3 g (46 mmol, 82% yield): mp 173-175 °C.

^{1}H NMR (200 MHz , CDCl$_3$) δ 3.78 (s, 3 H, CH$_3$O), 5.32 (s, 1H, OH), 6.70 (d, *J* =8.8 Hz, 2 H), 7.02 (d, *J* =8.8 Hz, 2 H), 7.05-7.60 (m, 12 H, ArH);

IR (CDCl$_3$) 3536 cm^{-1} (OH, free) 1247 cm^{-1}.

MS (EI) *m/z* Calculated: 352.1463, Found: 352.1479.

Elemental analysis (%): Calculated for $C_{25}H_{20}O_2$: C, 85.29; H, 5.68; Found: C, 84.94; H, 6.02.

2,2'-Bis(4-methoxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol (8.11a)

The phenol **8.10b** (16 g, 46 mmol), butyronitrile (200 mL) and CuCl (1.6 g, 14 mmol) were placed in a 500 mL three-necked flask equipped with condenser and mechanical stirrer. This mixture was heated up to 100 °C and stirred vigorously while molecular O_2 was bubbled into the flask. The solution gradually changed to a deep violet color. After 5 h, the mixture was allowed to cool down to room temperature giving a precipitate which was filtered. The solid was dissolved in hot chloroform and filtered while hot. The catalyst collected was washed with hot chloroform several times. The filtrate was evaporated and the residue was recrystallized from a mixture of methanol and chloroform. The violet product is a mixture of biphenoxy radical **8.3b** and biphenol **8.1b**. The resulting product was reduced with a small amount of hydrazine in chloroform at reflux for 6 h. The solvent was evaporated and the solid was recrystallized from CHCl$_3$-MeOH to give **8.11a** (73% yield); mp 305-307 °C.

^{1}H NMR (200 MHz , CDCl$_3$) δ 3.78 (s, 6 H, CH$_3$O), 5.05 (s, 2 H, OH), 6.50-7.50 (m, 30 H, ArH);

^{13}C (300 MHz, CDCl$_3$) δ 58.34, 115.54, 128.91, 130.13, 130.38, 131.31, 131.41, 131.75, 132.50, 134.24, 135.03, 135.57, 136.11, 136.77, 138.84, 140.88, 143.14, 151.10, 160.34;

IR (CDCl$_3$) 3534 cm^{-1} (free OH), 1245 cm^{-1} (CH$_3$O).

MS (EI) *m/z* 702 (M^+).

Elemental analysis (%): Calculated for $C_{50}H_{38}O_4$: C, 85.47; H, 5.47; Found : C, 84.90; H, 5.49;

2,2'-Bis(4-methoxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-dioxyl (8.11)

A suspension of biphenol **8.11a** (0.50 g, 0.71 mmol) and Ag_2O (0.65 g, 2.94 mmol) in chlorobenzene (50 mL) was shaken in a screw cap 100 mL flask protected from light in a Vibrex apparatus for 24 h. The resulting purple suspension was filtered through a thin layer of Celite and the solvent evaporated under reduced pressure. The solid recovered was dried under reduced pressure to give oxidized form **8.11** as a dark purple crystalline powder; mp 200-202 °C.

^1H NMR (200 MHz , $CDCl_3$) δ 3.84 (s , 6 H, CH_3O), 6.90-7.28 (m, 30 H, ArH);

^{13}C (300 MHz, $CDCl_3$) δ 55.35, 114. 09, 131.81, 134.16, 135.46, 135.38, 136.30, 141.28, 144.11. 147.44, 127.02, 127.40, 127.73, 128.44,129.45, 130.60, 132.3, 159.35, 184.02;

UV-Visible (C_6H_5Cl) λ max 292, 528 nm (ε 31500, 27800);

IR ($CDCl_3$) 1250 cm^{-1} (OCH_3).

Elemental analysis (%): Calculated for $C_{50}H_{36}O_4$: C, 85.71; H, 5.14; Found : C 85.78 ; H, 5.49 ;

MS (EI) *m/z* 700 (M^+).

2,2'-Bis(4-hydroxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol (8.11b)

In a flask equipped with a drying tube was placed the biphenol **8.11a** (11.65 g, 17 mmol) and methylene chloride (20 mL). The suspension formed was stirred at 0 °C under a nitrogen atmosphere while a 1M solution of BBr_3 (85 mL, 85 mmol, 5.7 eq) was injected through a septum. The mixture was stirred for 1h at 0 °C, and allowed to warm up to room temperature and stirred for an additional 30 min. The mixture which turned into a thick gel was poured into ice and stirred magnetically. An additional amount of methylene chloride was added to facilitate the phase separation. The partially emulsified organic phase was filtered and the solid recovered washed on the filter with methylene chloride. The product recovered (10.20 g, 15 mmol, 88% yield) was 95% pure (HPLC). Recrystallization from ethyl acetate -hexane and extensive drying yielded **8.11b** (82 %), mp 309-311 °C.

^{1}H NMR (200 MHz , CDCl$_3$) δ 4.82 (s, 2 H, OH, unhindered), 5.12 (s, 2 H, OH, hindered), 6.43 (d, 8 H), 7.05-7.56 (m, 22 H, ArH);

IR (CDCl$_3$), 3533-3593, 3600, 3628 cm^{-1}, intermolecularly bonded OH (unhindered), free OH (hindered).

MS (EI) *m/z* Calculated for $C_{48}H_{34}O_4$: 674.2457, Found 674.2460.

2,2'-Bis(4-acetoxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol-diacetate (8.11c)

The tetraphenol **8.11b** (2.69 g, 4 mmol) and potassium acetate (1.70 g, 18 mmol) were refluxed in acetic anhydride (30 mL) for approximately 4 hours. The mixture was first cooled under the tap and further cooled by the addition of some ice, and was then poured into a beaker with water (450 mL) and stirred for approximately 30 min. The precipitate formed was recovered and was washed several times with water and dried for several hours to give the tetraacetate **8.11c** (2.80 g, 3.32 mol, 83%), which could be recrystallized from toluene-hexane; mp 310-313 °C (which deteminded by DTA).

^{1}H NMR (200 MHz , CDCl$_3$) δ 1.61 (s, 3 H, OCOCH$_3$ hindered), 2.20 (s, 3 H, OCOCH$_3$, unhindered), 6.50-6.85 (m, 8 H), 6.90-7.70 (m, 22 H, ArH);

^{13}C (300 MHz, $CDCl_3$) δ 20.21 ($OCOCH_3$, unhindered), 21.11($OCOCH_3$, hindered), 119.18, 126.51, 127.08, 127.53, 128.29, 128.92, 130.50, 132.50, 133.68, 133.95, 135.34, 135.58, 136.27, 137.31, 138.56, 139.75, 145.0, 148.77, 168.91;

IR ($CDCl_3$) 1758 cm^{-1} (C=O, four acetates overlapped).

MS (EI) *m/z* Calculated for $C_{56}H_{42}O_8$, 842.2879, Found 842.2878.

2,2'-Bis(4-hydroxyphenyl)-3,3',5,5'-tetraphenylbiphenyl-4,4'-diol-diacetate (8.12)

In a 250 mL round bottom flask containing a magnetic stirring bar were added tetraacetate **8.11c** (15 g, 17.8 mmol), chloroform (150 mL), methanol (50 mL) and piperidine (15 mL) to allow selective deprotection of the less hindered acetate groups. The mixture was stirred for 4 h at reflux. After cooling additional chloroform (100 mL) was added and the mixture was extracted with water (100 mL) containing a small portion of hydrochloric acid, washed with water (2 x 100 mL) and dried over magnesium sulfate. The solvent was evaporated and the solid recrystallized from chloroform-hexane (90% yield): mp 295-297 °C.

^1H NMR (200 MHz , $CDCl_3$) δ 1.50 (s, 6 H, $OCOCH_3$, hindered), 5.12 (s, 2 H, biphenol), 6.09-7.42 (m, 30 H, ArH);

^{13}C (300 MHz, $CDCl_3$) δ 20.09 (-$OCOCH_3$), 144.48 (C-$OCOCH_3$), 156.39 (C-OH), 171.08 (-$OCOCH_3$);

IR ($CDCl_3$) 1756 cm^{-1} (C=O, acetates), 3532cm^{-1} (OH, biphenol);

MS (EI) *m/z* 758 (M^+);

Elemental analysis (%): Calculated for $C_{52}H_{38}O_2$: C, 82.30; H, 5.28; Found: C, 82.04; H, 5.28.

Polymer Preparation

Poly(ether sulfone) (8.4a)

The diacetoxybiphenol **8.12** (3 g, 3.95 mmol), 4,4'-difluorodiphenylsulfone (1.005 g, 3.95 mmol), NMP (16 mL) and toluene (10 mL) were placed in 50 mL three-necked flask, fitted with a Dean-Stark trap. While the reaction mixture was kept under nitrogen atmosphere at elevated temperature, potassium carbonate (0.71 g, 5.14 mmol) was added and the reaction was allowed to reflux. The water was removed at the azeotrope temperature and the reaction was continued for 30 h. After cooling chlorobenzene (10 mL) was added and the solution was filtered through a thin layer of Celite. The filtrate was precipitated in methanol (300 mL) and water (50 mL) containing a small portion of hydrochloric acid and the solid precipitate was collected by filtration. This material was dissolved in chloroform (20 mL) and added dropwise in methanol (300 mL). The polymer was separated and dried in a vacuum oven at 120 °C for 12 h (85% yield). The polymer contains both the protected acetates and the deprotected acetates which were characterized by NMR:

^{1}H NMR (200 MHz , $CDCl_3$) δ 1.64 (s, 6 H, $-OCOCH_3$), 5.14 (s, 2 H, -OH), 6.45-7.79 (m, 38 H, PhH).

In a 50 mL round bottom flask the resulting polymer (1.5 g) was dissolved in dioxane (25 mL) and treated with an excess of hydrazine under nitrogen. The mixture was stirred at room temperature for 24 h. The solution was extracted with chloroform and washed with water (3 x 100 mL) containing hydrochloric acid to give **8.4a**. The chloroform layer added dropwise was precipitated in methanol (200 mL), filtered and dried at 120 °C for 20 h under vacuum.

^{1}H NMR (200 MHz , $CDCl_3$) δ 5.16 (s, 2 H, -OH), 6.41-7.80 (m, 38 H, PhH).

8.5a was prepared in an identical fashion except that 4,4'difluorobenzophenone was used in lieu of 4,4'-difluorophenylsulfone.

Polyformal (8.6a)

Into a 100 mL round bottom flask equipped with a magnetic stirrer and condenser were charged diacetatebiphenol **8.12** (2g, 2.64 mmol), dibromomethane (1.1 g, 6.33 mmol) and NMP (6 mL). The reaction was carried out under nitrogen atmosphere. After a homogeneous solution was obtained, potassium hydroxide (0.324 g, 5.77 mmol) was added and the reaction was gradually heated up to 95 °C and kept there for 7 h. The mixture was allowed to cool to room temperature and filtered through Celite. The filtrate was added dropwise into methanol (200 mL) and water (50 mL) containing hydrochloric acid. The polymer was dissolved in chloroform and reprecipitated in methanol. This material was filtered and dried at 120 °C in a vacuum oven.

^{1}H NMR (200 MHz , CDCl$_3$) δ 1.63 (s, 12 H, overlapped -OCOCH$_3$ and C(CH$_3$)$_2$), 5.31(s, 2 H, CH$_2$), 6.45-7.81 (m, 34 H, PhH).

The deprotection was carried out with the resulting polymer (1g), excess of hydrazine and dioxane (15 mL) at room temperature for 24 h under nitrogen atmosphere. The mixture was extracted with chloroform and washed with water (3 x 100 mL) containing a small portion of HCl. The polymer **8.6a** was extracted and precipitated in methanol and dried at 120 °C for 24 h in a vacuum oven (89% yield).

^{1}H NMR (200 MHz , CDCl$_3$) δ 1.63 (s, 6 H, C(CH$_3$)$_2$), 5.12 (s, 2 H, -OH), 5.35 (s, 2 H, CH$_2$), 6.42-7.79 (m, 34 H, PhH).

Oxidation of Polymers

The polymer **8.4a**, Ag$_2$O (8 mmol per g of polymeric material) and chlorobenzene in a sealed bottle were shaken in a Vibrex apparatus for 24 h. The purple suspension was filtered through Celite and concentrated before precipitating into MeOH. The precipitate was left to coagulate for a few hours and then collected. The oxidized polymer **8.4b** was recovered in quantitative yield.

UV-Visible (C$_6$H$_5$Cl) λ max 290, 530 nm (ε 30600, 6360).

^{1}H NMR (200 MHz , CDCl$_3$) δ 6.50-7.80 (ArH).

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CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

This objectives of this research project were to study polymers containing hindered pendent groups on their rigid backbones. The contributions to knowledge derived from this research, which have been discussed in detail in the chapters (2-8), are briefly summarized in this section.

The first part of the research involved the synthesis of hindered biphenols which contain substituents in the 2,2' positions of the biphenyl group and of hindered hydroquinones which contain additional substituents. The biphenols were prepared from hindered phenols by oxidative coupling using oxygen and Cu(I)Cl in butyronitrile. The dihedral angles in the biphenyl rings of 2,2'-disubstituted biphenols are almost 90 °. Thermal analysis of the biphenols revealed that these materials exhibit polymorphism and that crystals initially formed were transformed into the stable forms at elevated temperatures. The hindered phenols were also oxidized with oxygen in the presence of a catalytic amount of N,N'-bis(salicylidene)-1,2-ethylenediaminocobalt(II) (Salcomine) to give benzoquinones. Subsequent reduction with hydrazine led to hydroquinones.

The polymers (poly(ether sulfone)s and poly(ether ketone)s) were synthesized from the reaction of the prepared biphenols/and hydroquinones with 4,4'-difluorophenylsulfone and 4,4'-difluorobenzophenone by condensation polymerization. The prepared polymers show considerably enhanced glass transition temperatures over those of the unsubstituted analogs and are soluble in common organic solvents such as methylene chloride, chloroform and DMSO at room temperature. The incorporation of a noncoplanar biphenyl moiety increases the disorder along the polymer backbone thereby reducing interchain interactions and this is the key to enhanced solubility. The glass transition temperatures increase due to the

the key to enhanced solubility. The glass transition temperatures increase due to the hindrance of chain rotation resulting from the 2,2'-substitution. Polyesters were also prepared from the reaction of the biphenols and hydroquinones with isophthaloyl dichloride and terephthaloyl dichloride in the presence of a zinc catalyst at high temperature. These polymers showed poor solubility since they very rigid molecules because of steric interactions between the ortho pendent phenyl groups and the carbonyl moieties. Introduction of the substituents significantly increased the Tg and Tm of these polymers due to the chain stiffness.

The second part of this research involves the study of polyimides. A series of bisanhydrides were prepared via the nitro-displacement reaction of hindered biphenols and N-methyl-4-nitro-phthalimide, followed by a ring opening reaction with KOH and subsequent anhydride formation. The polyimides were prepared from the reaction of the prepared dianhydrides and *m*- and *p*-phenylenediamine by using a two-step condensation polymerization. The polymers exhibit good solubility in common organic solvents. The Tg's of the polymers increased considerably above those of the known unsubstituted polymers. The polyimides from *m*-phenylenediamine show better miscibility with polycarbonate compared to the polyimides from *p*-phenylenediamine.

In the third part of this research, the chemistry of 2,2',3,3',5,5'-hexaphenylbiphenyl-1,1'-dioxyl has been studied. The 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-dioxyl is stable in solid form and in solution, and has excellent solubility. These biphenoxy radicals cyclized by intramolecular ring forming reactions at approximately 150 °C. The oxidation potential of the biphenol was found to be about -300 mV. Diphenylmethanes were oxidized to benzophenones with oxygen in butyronitrile solvent in the presence of a Cu(I)Cl catalyst by using 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol as a co-catalyst. These reactions were carried out in neutral conditions. Under basic conditions in the presence of $K_3Fe(CN)_6$, and absence of oxygen, the reaction of diphenylmethanes and 2,2',3,3',5,5'-hexaphenylbiphenyl-4,4'-diol gave C-O coupled products. Primary alcohols which can be readily converted to their corresponding t-butylethers react with 2,2',3,3',5,5'-hexaphenylbiphenyl-1,1'-dioxyl under the above conditions to give acetals. The acetals can be readily converted to the corresponding aldehyde and the parent biphenol in the presence of acid. This therefore represent a new method for convertion of primary alcohol to aldehyde. Polymers which may be applicable as photoresists were obtained from monomers containing two methylene groups.

Modified biphenols were synthesized for application as REDOX polymers. 3-*p*-Methoxyphenyl-2,6-diphenylphenol was prepared using a similar synthetic route to the one previously used for 2,3,6-triphenylphenol and was then converted to the biphenol by oxidation coupling. After demethylation the tetraphenols were acetylated and the resulting tetraacetates were selectively deprotected to yield the less hindered acetates with piperidine . The diacetate biphenols were polymerized with methylene bromide, 4,4'-difluorophenylsulfone and 4,4'-difluorobenzophenone by condensation polymerizations. The biphenol moieties of the polymers were oxidized to the polymeric radicals which showed λmax (530 nm). The polymers undergo intramolecular cyclization in air at high temperature.