AN ABSTRACT OF THE THESIS OF

Diana Lynn Cook for the degree of Master of Science in Chemistry presented on.

Title: Synthesis of Polybenzimidazoles Containing Arylene Sulfone and Ether Linkages

Redacted for Privacy

Abstract approved: ____

R.W. Thies

Polybenzimidazoles were synthesized from 3,3'-diaminobenzidine (DAB) and dicarboxylic acids. The polymerizations using the dicarboxylic acid monomers were carried out in polyphosphoric acid (PPA) and phosphorus pentoxide/methansulfonic acid (PPMA) which acted as the solvent and condensing agent. The resulting polybenzimidazoles had inherent viscosities in the range of 0.12 to 0.84 dL/g. The products were generally of low molecular weight as indicated by low inherent viscosities. The products of the dicarboxylic acid monomers and DAB having the highest inherent viscosities and forming strong, flexible films were formed in the polymerizations using the purest monomers. The dicarboxylic acid monomers were synthesized to contain internal sulfonate and ether linkages which were intended to increase the flexibility and processibility of the resulting polymers. These monomers can be used in the preparation of several other types of polymers such as polybenzoxazoles and polybenzothiazoles.

Synthesis of Polybenzimidazoles Containing Arylene Sulfone and Ether Linkages

by

Diana Lynn Cook

A THESIS

submitted to

Oregon State University

in partial fulfillment of

the requirements for the

degree of Master of Science

Completed February 16, 1993

Commencement June 1993

APPROVED:

Redacted for Privacy

Professor of Chemistry in charge of major

Redacted for Privacy

Chairman of the Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented: February 16, 1993

Typed by author: Diana Lynn Cook

Thanks to,

Dr. Richard Thies

Dr. Peter Freeman

Dr. Gerald Gleicher

for their guidance

Roger Kohnert

Lilo Barofsky

Brian Arbogast

for their assistance in obtaining spectroscopic data

Dow Chemical

Oregon State University

for financial assistance

My fellow graduate students and friends

especially Dora Azmus, Alan Johnson and Susan Hatliveg

Jenny, Jesse and Cory

for their love, acceptance, patience,and encouraging support.

I would like to dedicate this effort to my father who encouraged me to always keep learning and taught me so many of the important things in life.

Table of Contents

List of Figures

List of Figures

List of Tables

List of Schemes

List of Schemes

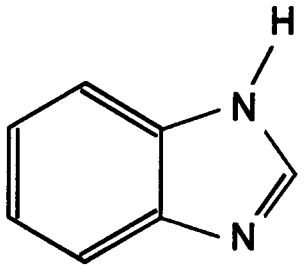
SYNTHESIS OF POLYBENZIMIDAZOLES CONTAINING ARYLENE SULFONE AND ETHER LINKAGES

INTRODUCTION

Properties of polybenzimidazoles

The polybenzimidazoles (PBIs) are a class of polymers that have incorporated in their structure the benzimidazole ring (shown in Figure 1).

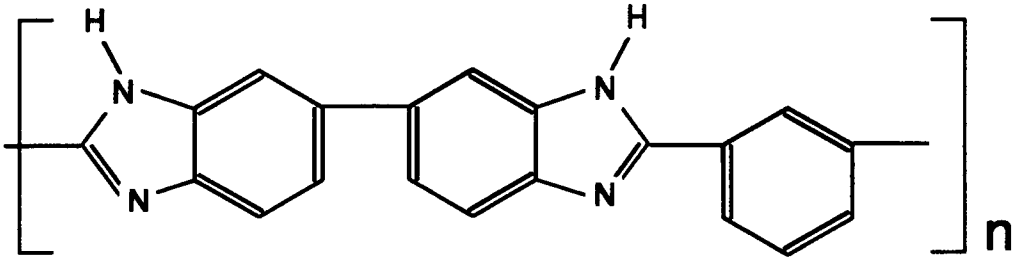
Figure 1. Benzimidazole Ring.



These polymers show good thermal stability and retain their mechanical properties at high temperatures. The polymers are generally yellow to brown solids, infusible up to 300-400°C, and with some degree of crystallinity detected in the more symmetrical types. Their heat resistance has made them good candidates for flame resistant fibers, and high temperature components.[1]

Presently the only readily available commercial polybenzimidazole is produced by the Celenese Corporation (shown in Figure 2).

Figure 2. Poly([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,3-phenylene).



This polymer is therefore the one chosen most frequently by researchers trying to find and perfect applications of PBIs. They have utilized PBI's to produce heat resistant resins and fibers, structural adhesives, battery separators (mainly aliphatic polymers), and foams (mainly aromatic polymers). PBIs show good adhesion as films cast from solution unto glass and this quality has lead to their use in glass composites and laminates. Woven cloth has been prepared using the Celanese PBI. The cloth is said to be comfortable (due to high moisture content) and have high flame resistance. Certain PBI fibers also show promise as reverse osmosis membranes. The use of PBIs as foams has been investigated and the 1,3-phenylene type provides a material having low-weight, high-strength, thermal stability and it is a machinable insulation that may find a use in the aerospace industry.[2]

Polybenzimidazoles are somewhat hygroscopic and can retain moisture even at temperatures exceeding 100°C, yet they are resistant to hydrolytic attack in acidic and basic media. They are generally of high molecular weight with a variation in molecular weight observed when different methods of polymerization are used.

The solubility of polybenzimidazoles is affected by several factors including solvent, molecular weight, moisture content and temperature. In general they are soluble in formic acid, sulfuric acid, and aprotic polar solvents such as DMF (dimethyl formamide), DMSO (dimethyl sulfoxide), NMP (1-methyl-2-pyrrolidinone) and DMAc (N,N-dimethylacetamide). Improved solubilities have been observed in solutions of 1-5% lithium chloride in the polar aprotic solvents. It has been demonstrated that the intrinsic viscosity of a PBI in N,N-dimethylacetamide decreases as the lithium chloride concentration in the solvent increases.[3] Although the solubilities are enhanced in these solvent systems, as the molecular weight of the polymer increases the possibility of solubility problems also increases. The presence of oxygen, sulfur, or sulfone bridges between the aromatic units improves solubility as well as enhancing the chain flexibility.[4,5] The presence of carbon-carbon or carbon-oxygen single bonds also enhance chain flexibility and solubility. The method used to prepare PBIs influences the solubility, and it has been shown that polymers prepared using low temperature methods often have greater solubilities than those prepared using high temperature methods.[6]

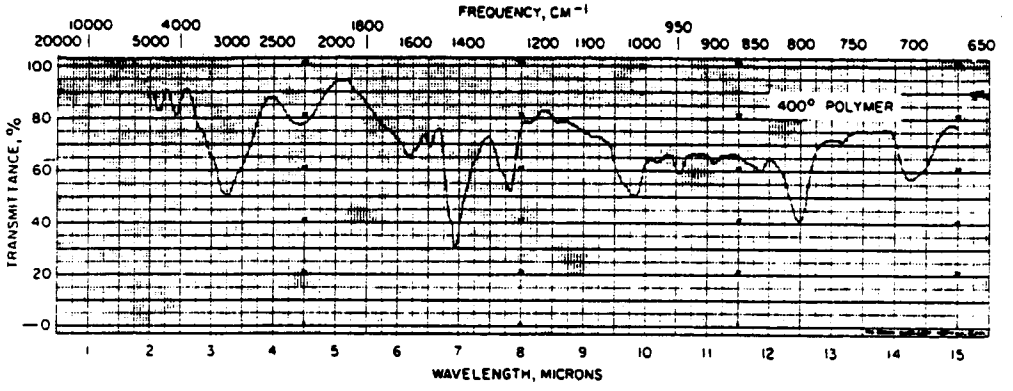
Viscosity measurements can vary depending on the solvent, moisture content of the polymer, temperature and lithium chloride concentration of the solvent.[3] For example, formic acid has been reported to give appreciably higher inherent viscosity values than dimethyl sulfoxide or sulfuric acid. The varying viscosity measurements of PBIs in dimethyl sulfoxide may be due to its hygroscopic nature. Experimental data indicates that increased water content of the solvent results in higher viscosity measurements.[3]

The viscosity of a polymer is directly related to temperature with an increase in viscosity observed at lower temperatures.

The aromatic PBIs have an intense absorption in the 330-350 nm range of the ultraviolet spectrum and this characteristic can be used to demonstrate the closure of the benzimidazole ring. The intermediate aromatic bis(Schiff base) formed as an intermediate in the dialdehyde method of preparing PBIs gives a characteristic band at 400-450 nm.[1,7]

The spectroscopic data utilized most frequently for the characterization of PBIs is infrared (IR) spectroscopy. Most polybenzimidazoles show absorptions near 800-820 cm^{-1} (CH out-of-plane bending), 1300 cm^{-1} (C-N stretching), 1450-1500 cm^{-1} (in-plane vibration), 1600-1640 cm^{-1} (combined C=C, C=N ring vibration), and 3350-3450 cm^{-1} (N-H stretching).[1,6,7] A typical IR of a polybenzimidazole is shown in Figure 3.

Figure 3. IR Spectrum of Poly([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,3-phenylene).



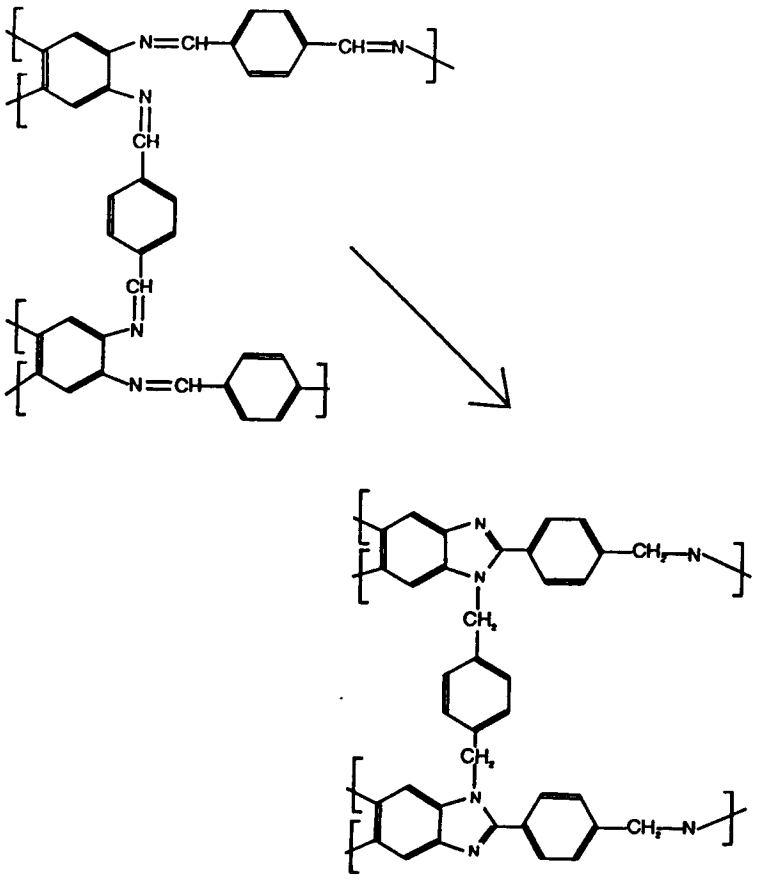
The stability of different types of PBIs can vary greatly but certain generalities can be made based on agreement between various groups that have done stability studies. Oxidative stability appears to be enhanced by 1,4-phenylene moiety over 1,3-phenylene groups. It has also been shown that thermal stability is slightly decreased by ether linkages.[1,4]

Commercial Aspects

Polymers are usually assessed according to their chemical structure, molecular shape, molecular weight and physical structure. The applications to which a polymer can be employed are directly related to these properties.

To illustrate, the molecular shape of a polymer can influence its ability to be processed. Molecular shape is classified as either linear, branched or crosslinked. Linear polymers are able to pack together into a crystal lattice better than branched polymers. Crosslinking can effect the properties of a polymer as well as its processibility. A low degree of crosslinking can impart elastic properties to the polymer while a high degree of crosslinking can make the polymer totally rigid and difficult to process.[8] Crosslinking has been observed in polybenzimidazole formation when unprotected dialdehydes were condensed with tetraamines in polar aprotic solvents.[9] The researchers Higgins and Marvel proposed that the crosslinking was due to the formation of aldehydine intermediates as diagramed in Figure 4.

Figure 4. Aldehydine Intermediate Forming Crosslinked PBI.



During the equilibrium between a ring open and ring closed polybenzimidazole the potential for crosslinking exists. The free amino groups can react with carbon atoms on other molecules and crosslinking may result. It is desired that reaction conditions be adjusted to favor the reaction of two adjacent amino groups of the amino monomers with the same carbonyl carbon.

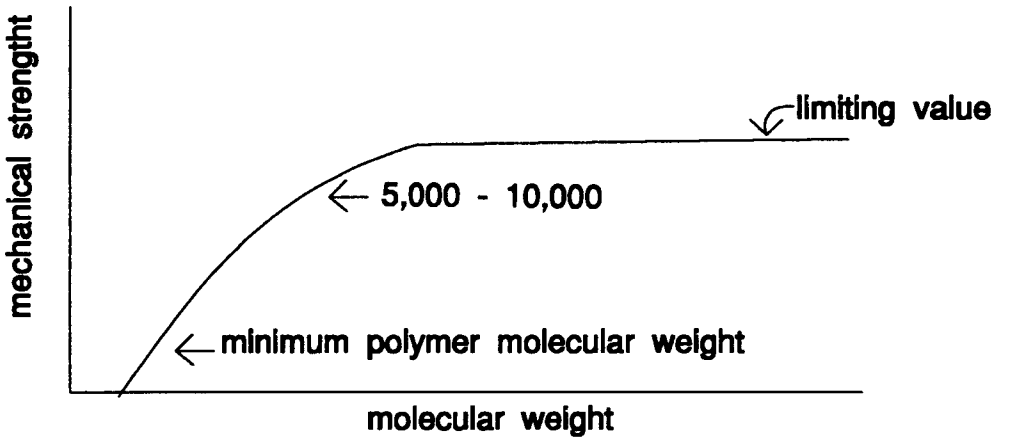
Several methods have been employed to increase the rate at which cyclization can occur and to limit the possiblity of crosslinking. One approach has been to limit the availablity of aldehyde monomer by slow

addition to the reaction mixture. In this way the aldehyde concentration is maintained at a minimum and the ring can close before another carbonyl group is encountered by the free amino group. Another approach involves decreasing the temperature of the reaction so the kinetics of the system are decreased and the polymer's movement is restricted and reaction with another aldehyde group is less likely.[1]

Changing the steric environment near the site of ring closure is another method that has been tried to help control the amount of crosslinking. The use of N-substituted amines has been attempted as a means to block one side of the intermediate so reaction with the nearest amino group would be favored. The N-substitution might also restrict chain movement therefore increasing the opportunity for the free amino group to cyclize with the same carbon. This method has the limitations of increased expense due to the difficulty of synthesizing the substituted di- or tetra-amines as well as slowing the rate of cyclization between the desired groups.[8]

The quality of a polymer is also affected by the polymers molecular weight. Most mechanical properties of polymers depend on and vary considerably with molecular weight. In order for the polymer to show any degree of mechanical stability a molecular weight of a thousand or so is required. The relationship between molecular weight and mechanical strength is diagramed in Figure 5.

Figure 5. The Relationship Between Molecular Weight and Mechanical Strength.



There are a variety of methods that can be used to measure the average molecular weight of a polymer. These include methods based on colligative properties, light scattering, viscosity, ultracentrifugation, and sedimentation. This research endeavor has utilized the viscosity of the polybenzimidazoles formed as an indicator of the molecular weight of the polymers. Most PBI researchers express viscosity as inherent viscosity (η_{inh}) measured at concentrations of 0.5 g/dL at 25-30°C. The inherent viscosity is measured at constant temperature by timing the movement of a polymer solution in a constant temperature bath through a viscosimeter and comparing this to the time required for the solvent to travel the same distance. The inherent viscosity is then calculated using the equation in Figure 6.

Figure 6. Inherent Viscosity Calculations.

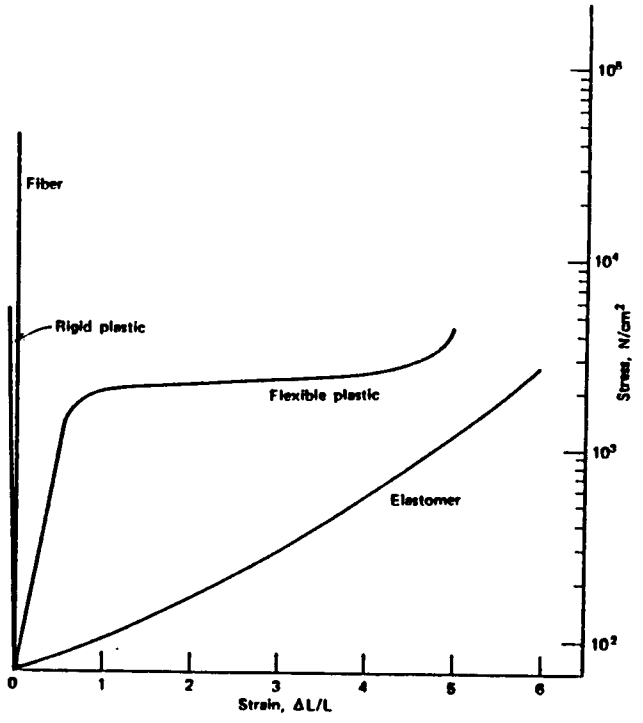
$t_{sample} / t_{solvent} = \eta_{rel}$ t = time through viscosimeter in sec.

η_{rel} = relative viscosity

$\eta_{inh} = \ln(\eta_{rel}) / c$ c = concentration in g/dL

The mechanical properties of a polymer are important when it comes to determining the general utility of a polymer. The mechanical properties of a polymer can be characterized by its stress-strain properties which are assessed in terms of its modulus, ultimate strength, ultimate elongation, and elastic elongation. The mechanical properties of a polymer can vary widely depending on the degree of crystallinity, the degree of crosslinking and the values of T_g (glass transition temperature) and T_m (crystalline melting temperature). Depending on these mechanical properties a polymer will be used as a fiber, flexible plastic, rigid plastic, or elastomer.[8] The relationship between stress-strain properties and polymer use is illustrated in Figure 7.

Figure 7. Stress-Strain Plot for a Typical Elastomer, Flexible Plastic, Rigid Plastic and Fiber.



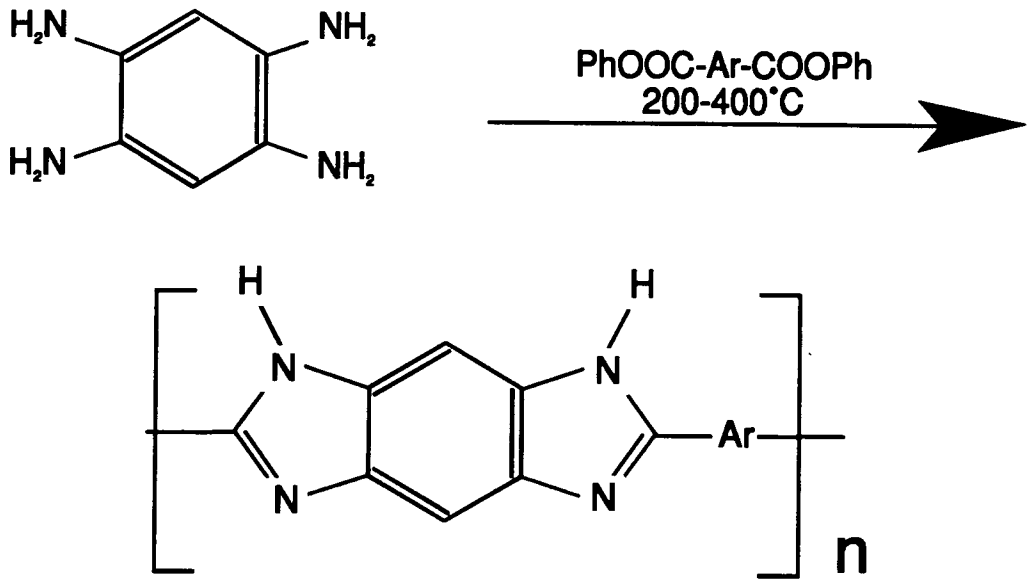
The mechanical properties of a polymer can be altered by physical and chemical means to allow polymers to serve a variety of functions.

The mechanical properties of a polymer are usually assessed by the researcher by preparing a film and performing tests on this film to determine its stress-strain characteristics. In this research a very rough indication of these properties is determined by evaluating the prepared films in terms of bendability versus brittleness, elasticity, and the relative strength of the film.

History of Polybenzimidazoles

The first polybenzimidazoles described in a patent in 1959, were synthesized by the condensation of aromatic bis-o-diamines with aliphatic dicarboxylic acids. The first all-aromatic polybenzimidazoles were reported in 1961 by Carl S. Marvel.[1] Marvel's approach involved melt poly-condensation of 3,3'-diaminobenzidine or 1,2,4,5,-tetra amino benzidine with the diphenyl ester of a large number of aromatic dicarboxylic acids (shown in scheme 1).

Scheme 1. Marvel's Polycondensation Approach.



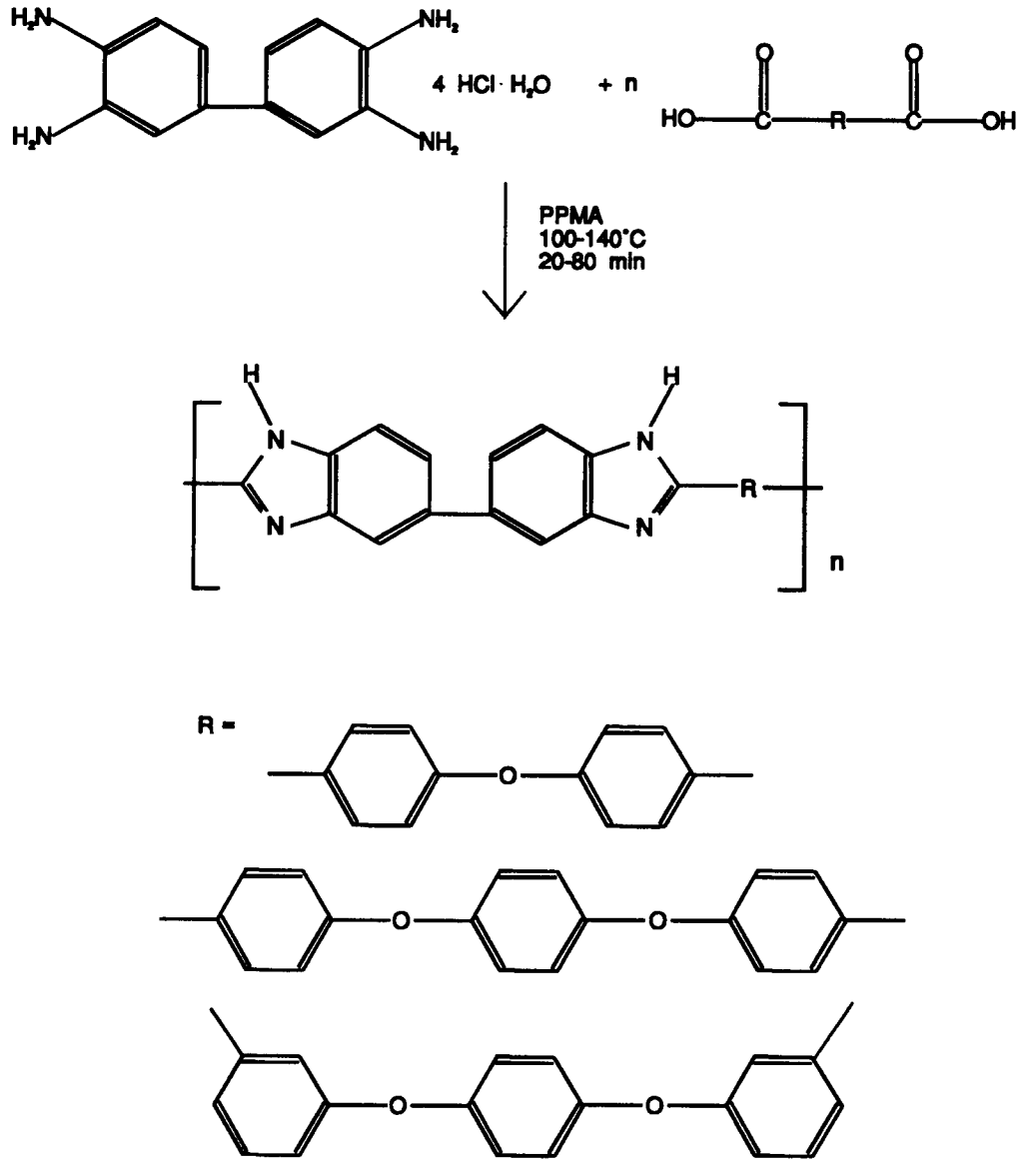
The reaction was carried out by heating equimoler amounts of tetraamine and diphenyl ester under nitrogen at temperatures that gradually increased from 200 to 300°C. Around 200°C the evolution of phenol occurred and the viscosity increased steadily until the reaction

mixture solidified. After reaction under reduced pressure for a short period of time, to drive the reaction by the removal of phenol, the polymeric solid was pulverized and heated for several hours at temperatures of 350-400°C under vacuum. This resulted in a fully aromatic polybenzimidazole of high molecular weight. The high molecular weight was not achieved unless this solid-state reaction step was included. This polymerization method was harsh and therefore not readily applicable to many monomers.[1,6] Since this work, several polybenzimidazoles have been synthesized using a variety of methods in an effort to synthesize PBIs that have the desired thermal stability, oxidative resistance and increased processibility. By 1969 over 15 tetraamines and about 60 dicarboxylic acid derivatives had been condensed to PBIs.[10]

Other methods were then pursued that might overcome some of the disadvantages of melt polymerization. High and low temperature solution condensations were explored by several research groups. These polymerization reactions were carried out in solvents having high boiling points or in acidic media such as polyphosphoric acid (PPA) and phorphorus pentoxide/methane sulfonic acid (PPMA).[11,12,13]

In the early sixties a method was introduced by Iwakura that utilized poly(phosphoric acid) as the solvent for high temperature solution polymerization of polybenzimidazoles.[13] This method was successful using other acidic media such as phosphorus pentoxide/methane sulfonic acid (PPMA). Some of the polymers prepared by Ueda utilizing PPMA are illustrated in Figure 8.[14]

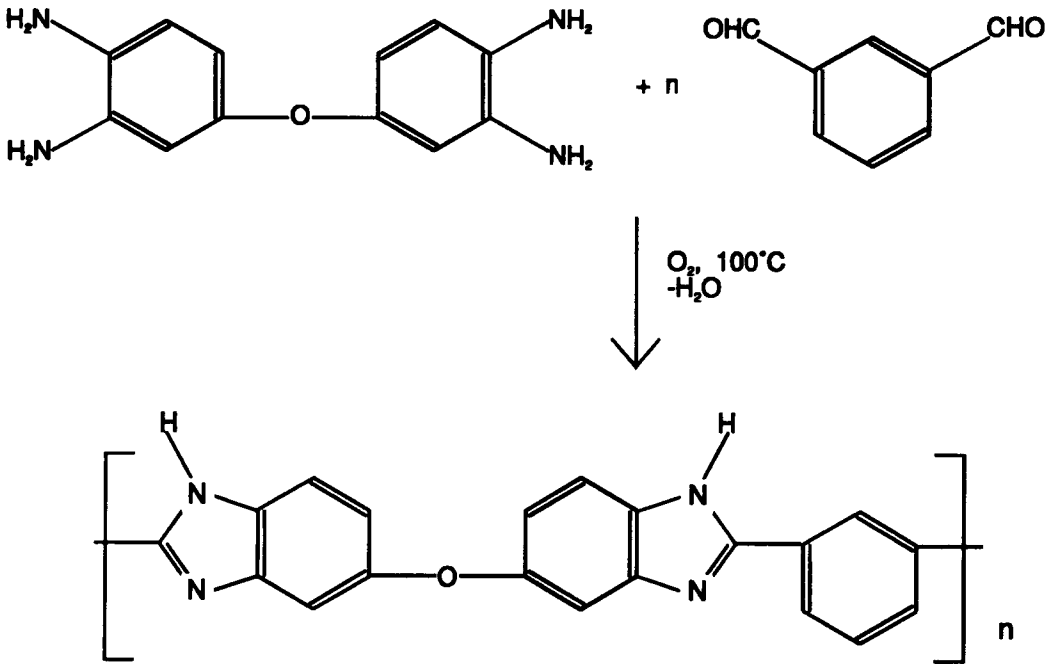
Figure 8. Solution Polymerizations Using PPMA.



The polymerization methods using acidic media eliminate the ability to isolate a prepolymer intermediate, and therefore their use is limited to applications were the products are used directly such as spinning and film casting. One must also consider the stability of the proposed monomers in a hot acidic media.

In 1963 a patent filed by D'Alelio[15] presented a low temperature polymerization method for the synthesis of PBI from aromatic bis(o-amines)s and free dialdehydes in dimethylacetamide and similar solvents. This polymerization scheme is shown in Scheme 2.

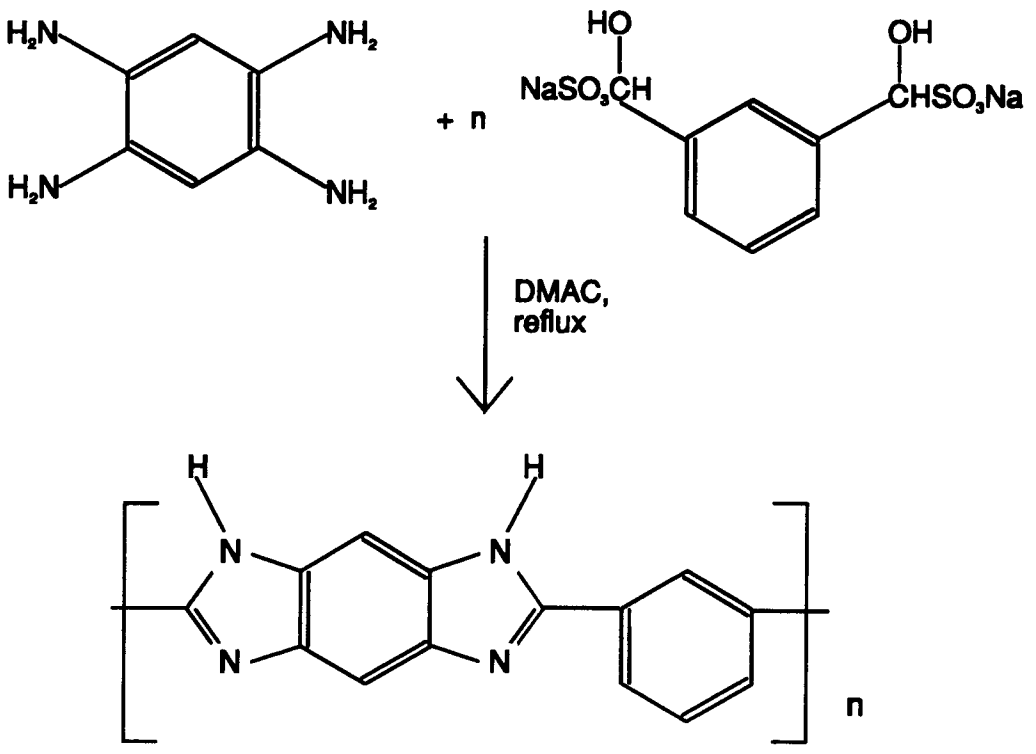
Scheme 2. Low Temperature Polymerization of Bis(o-amines)s and Dialdehydes.



This method permits the formation of PBIs from monomers too unstable thermally or chemically for the use of melt or acidic media polymerization methods.

Work done by Higgins and Marvel involving the condensation of tetraamines with bis(bisulfite) adducts of isophthalaldehyde has been successful under mild conditions and short reaction times producing products with moderate inherent viscosities (see Scheme 3).[9]

Scheme 3. Polybenzimidazole Synthesis from Tetraaminobenzene and Bisulfite Adduct of Isophthalaldehyde.



Dudgeon *et al.* prepared polybenzimidazoles from bisothoesters and DAB in DMSO with pyridine as a stablizer at temperatures as low as 100°C. These polymers showed properties similar to those of PBIs prepared using solid state melt polymerization.[5]

Solution polymerization of dialdehydes and tetraamines in phenol, veratrol, N, N-dimethylaniline, N,N-dimethylacetamide and other amide solvents have shown limited success. These polymerizations are usually carried out in a two step process that involves formation of a prepolymer

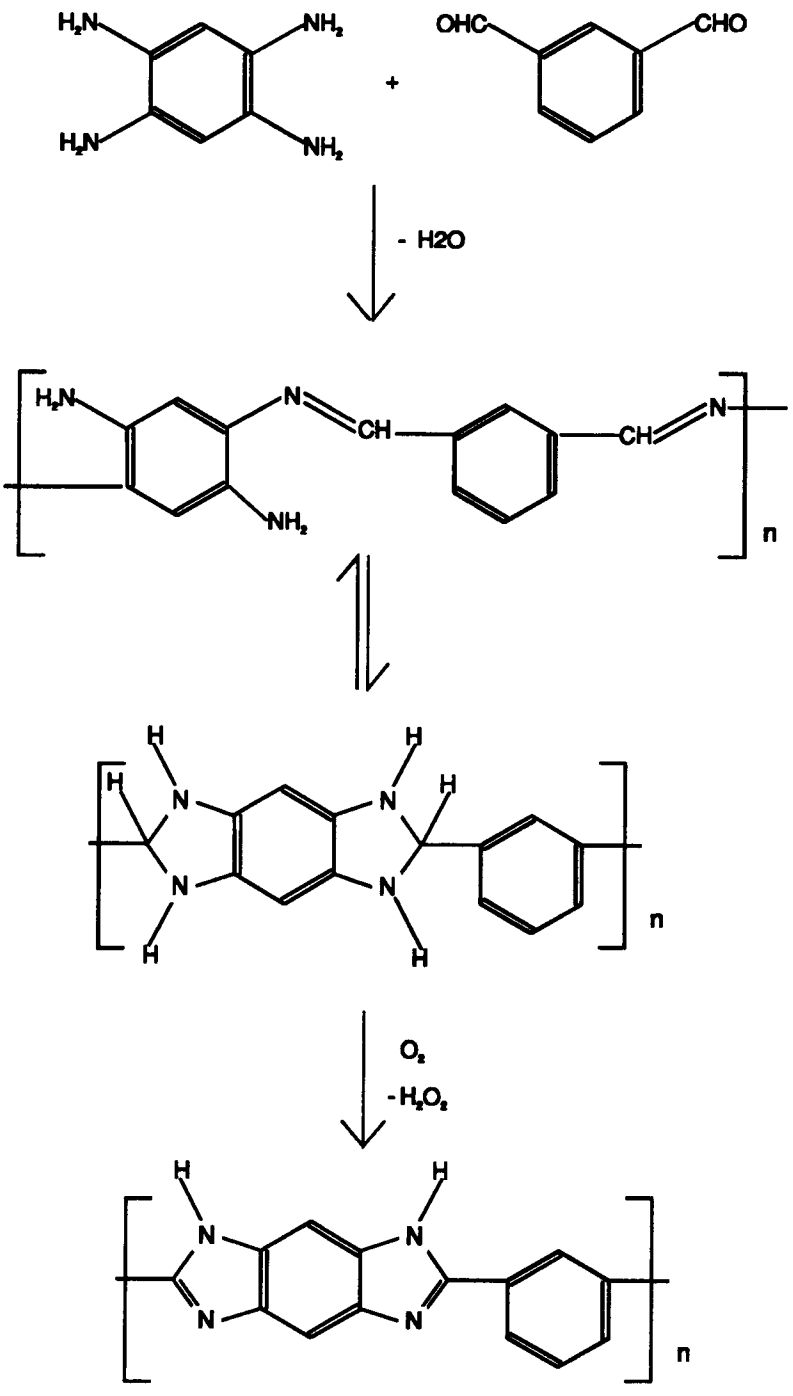
in the solvent under an inert atmosphere followed by heating of the isolated prepolymer with oxygen present.[16,17]

Successful application of this two step process was demonstrated by Neuse using a method for the preparation of PBIs that involved the initial formation of a tractable prepolymer at low temperature that was later converted to PBI. The advantages of this two stage synthesis are the formation of a tractable and processible prepolymer and the ability to use monomers that are sensitive to high temperatures. The two stage synthesis is outlined in Scheme 4.[1]

Recently, polybenzimidazoles have been synthesized using a non-aqueous suspension method. A patent application made by G. N. Milford[18] describes a process in which 3,4-diaminobenzoic acid was suspended in an inert organic continuous phase and polyphosphoric acid was then added forming a suspension. The dispersed phase consists of the monomer and sodium dodecylbenzene sulphonate which was thought to act as a surface active suspension stabilizer. The authors reported that upon heating the reaction mixture to 200°C for several hours polybenzimidazole particulates in high yields and various particles sizes were obtained.

Further progress in preparing spherical polybenzimidazoles using a non-aqueous suspension method have been achieved by Brock and Sherrington.[19] Their work involved the study of several compounds as potential stabilizers to provide some degree of steric stabilization to enhance the dispersion system. They prepared polymers using low molecular weight surfactants such as sorbitan monooleate (Span 80) and obtained relatively low molecular weight polymers.

Scheme 4. Two Stage Polybenzimidazole Synthesis from DAB and Dialdehyde.



The polymerizations using polymeric surfactants provided polybenzimidazoles in higher yields and higher molecular weights. Best results were obtained when carboxy-terminated polyisobutylene was used as a stabilizer. In this case the macromolecular product consisted of almost 100% spherical beads with a narrow particle size distribution. Although their work shows much promise some problems still remain. They point out that drops in viscosity during the heating cycle create changes in the flow pattern which result in inconsistent particles. They also point out that the solvent PPA is used as a commercial plasticizer for polybenzimidazoles and the polymer particles were soft when initially collected and hardened after the removal of acid. This means that the particles are softer and susceptible to deformation or agglomeration during the work-up steps.

Most current research is focused on finding ways to improve flexibility, molecular weight and solubility. The synthetic work initiated to accomplish these goals has taken a variety of approaches. For example, ether, sulfone and carbonyl links were introduced between the rings in the diaminobenzidine[20]; groups were attached to the amino nitrogen[21]; and aromatic and aliphatic silanes or siloxanes were placed in the backbone. [2]

Formation of Polymers

Most polymers are formed by step or chain polymerization. Chain polymerization usually involves addition reactions with the repeating unit and the monomer having the same composition. The monomers are usually alkenes, aldehydes or ketones in which the pi bonds in the

monomer can be replaced with a sigma bond in the polymer. It is characterized by a gradual change in monomer concentration and the formation of high molecular weigh polymer early in the reaction. It occurs via free radical, cationic or anionic reaction mechanisms and the reaction mixture contains monomer, polymer and the reactive species. These reactions are exothermic and sometimes need to be controlled by the addition of inhibitors and or retarders.

In step polymerization the monomers disappear quickly, but long reaction times are required for the formation of high molecular weight polymers. Step polymerizations usually involve condensation reactions in which atoms in the monomers are not present in the polymers, and a small molecule such as water, hydrochloric acid, or a salt are given off as biproducts. The monomers used in step polymerization reactions are bifunctional, containing two functional groups per monomer. For example, the formation of polyamides occurs by the condensation of a diamine with a diacid. The pattern of step polymerization is outlined in Figure 9.

Figure 9. Step Polymerization.

monomer + monomer -> dimer

dimer + monomer -> trimer

dimer + dimer -> tetramer

dimer + tetramer -> hexamer

etc. -> polymer

Figure 9 explains the observation that the monomers disappear rapidly, but formation of the high molecular weight polymer is slow. The polymerization involves several equilibrium reactions and high molecular weight polymer will not form unless the equilibrium is driven by the removal of the biproducts, or addition of a catalyst. Other conditions that enhance step polymerization are the purity of the monomers, temperature of the reaction, and concentration of the monomers.[22] The polymerization reactions studied in this research endeavor fall into the step polymerization category.

MECHANISMS OF POLYBENZIMIDAZOLE FORMATION

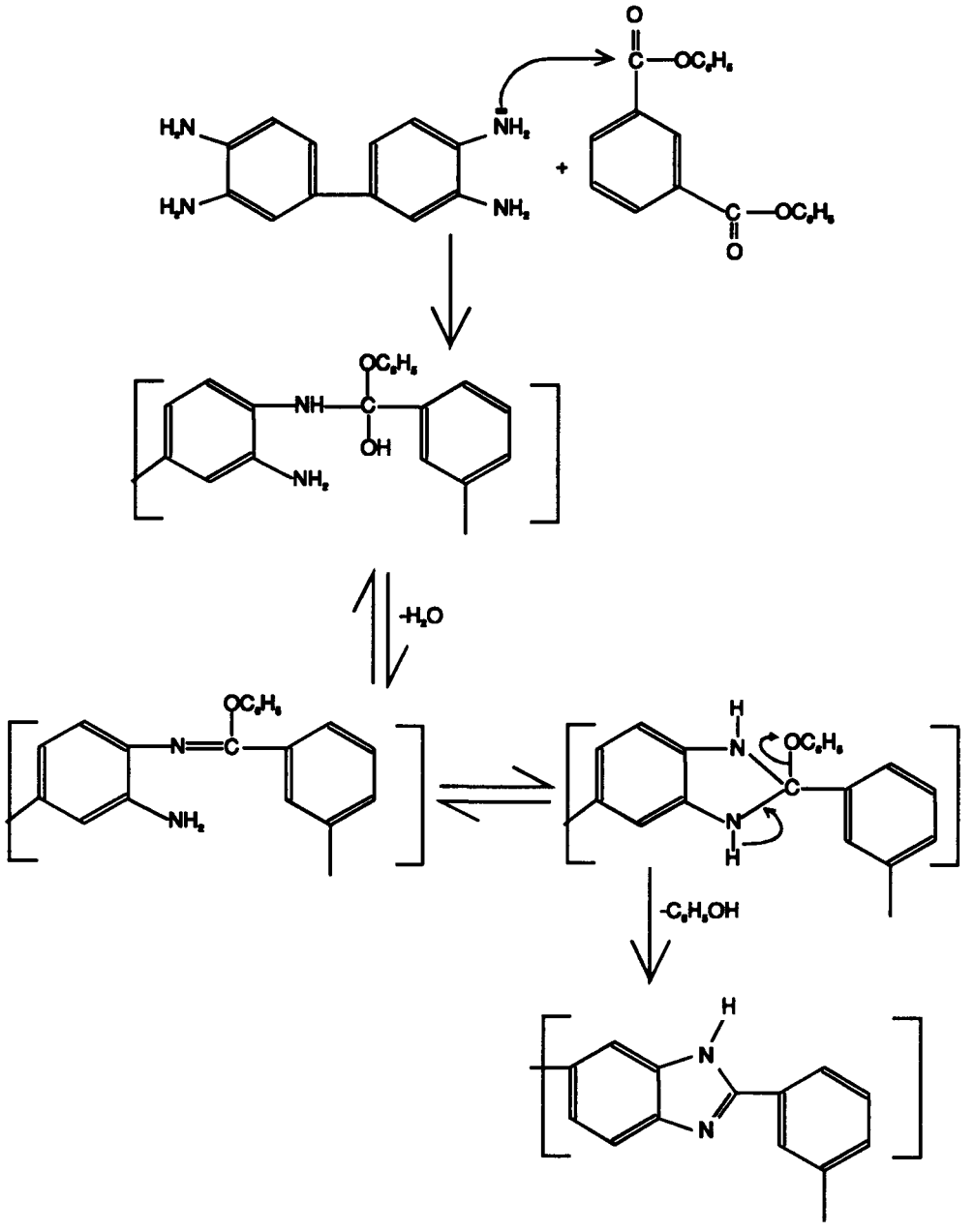
Diacid Derivatives plus Tetraamines: Melt Polymerization

Considering all the research work on PBI synthesis very little effort has been dedicated to elucidating the mechanism of the reaction. It was originally believed that the first step in polybenzimidazole formation was amidolysis of the phenyl ester to an aminoamide which then closed the ring by means of dehydration.

When attempts to synthesize the ester terminated polymer resulted in volatiles in excess of theory, it was proposed that the polyaminoamide intermediate was condensing with the unreacted phenyl ester to form polymer containing polyamide linkages instead of cyclizing to form polybenzimidazole. This assumption was believed based on the rate of amidolysis being more rapid than the rate of dehydration. So the intermediate polyamide would condense with the unreacted phenyl ester to evolve more phenol instead of cyclizing with liberation of water.

Currently there are two proposed mechanisms each based on differing studies and reaction conditions. The first of these is based on kinetic data and ultraviolet spectra and was proposed in 1964 by Levine and Wrasidlo.[23] This mechanism is presented in Scheme 5. The data on which this reaction mechanism is based were collected on samples that were polymerized in sealed capillary tubes. The tetraamine and phenol could be detected in the ultraviolet at 310 and 269 nm and a kinetic study was undertaken at 200°C and 260°C. The sealed tubes were immersed in a constant temperature hot water bath and removed at certain intervals

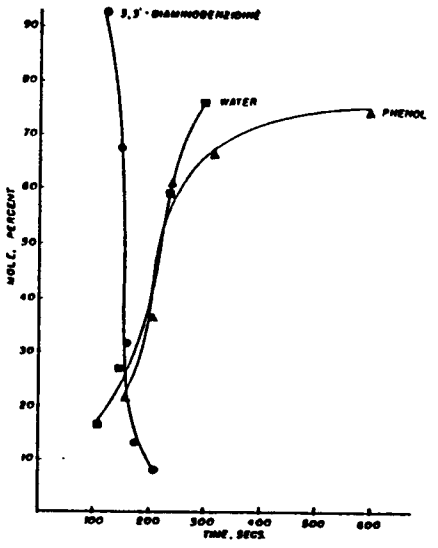
Scheme 5. Proposed Mechanism of Polybenzimidazole Formation.



and chilled rapidly, then broken under distilled water and brought to volume for ultraviolet spectroscopy. The ultraviolet spectra were recorded for phenol formation as a function of tetraamine consumption. The water formation was determined using vapor phase chromatograpy in which the

tubes were broken under methanol instead of water. This data is shown in Figure 10 for 200°C and 260°C.

Figure 10. Condensation of 3,3'-Diaminobenzidine and Diphenyl Isophthalate at 200°C.



The authors argued that a polyamide could not be an intermediate since the consumption of tetraamine did not occur simultaneously with phenol evolution. The curves also indicated that water evolution preceeds phenol evolution. This data may be questionable since it depends on the ability to dry the methanol used in the chromotography samples.

In summary, the authors indicated that the evolution of water occurred first resulting in the formation of a Schiff base intermediate and followed by the evolution of phenol and the formation of the polybenzimidazole ring.

The other mechanism was proposed in 1967 by Gray after his group investigated the prepolymeric species isolated at various stages of

polybenzimidazole formation from the reaction of amine and phenyl ester.[24] They also determined the rates of formation of volatile polymerization products at various stages of the reaction. To accomplish this investigation they utilized a variety of techniques including mass spectrometric thermal analysis, infrared and ultraviolet spectral analysis, elemental analysis, and thermogravimetric and differential thermal analysis of polymers and model compounds.

The chemistry of model systems suggests that the formation of polybenzimidazoles from amines and phenyl ester would be similar to ester saponification and basic hydrolysis of amides. These reactions are accelerated by electron-attracting groups and involve acyl-oxygen cleavage. The kinetics suggest a bimolecular rate determining step. Gray proposed a mechanism consistent with existing literature and the above considerations. Grey's proposed mechanism is outlined in Scheme 6. Gray's research provided some definitive evidence for his proposed mechanism. The mass spectrometic thermal analysis indicated that both water and phenol were evolved during the initial stages of the reaction, but the phenol was evolved in greater quantity. During the later stages of the polymerization reaction water was evolved in greater quantity and evolution of phenol ceased. The results of Gray's mass spectrometic thermal analysis (MTA) are presented in Figure 11. Along with data acquired by analysis of isolated intermediates the partially hydrated intermediate structures (**A** or **B**) proposed in this mechanism were substantiated.

Scheme 6. Gray's Mechanism of PBI Formation.

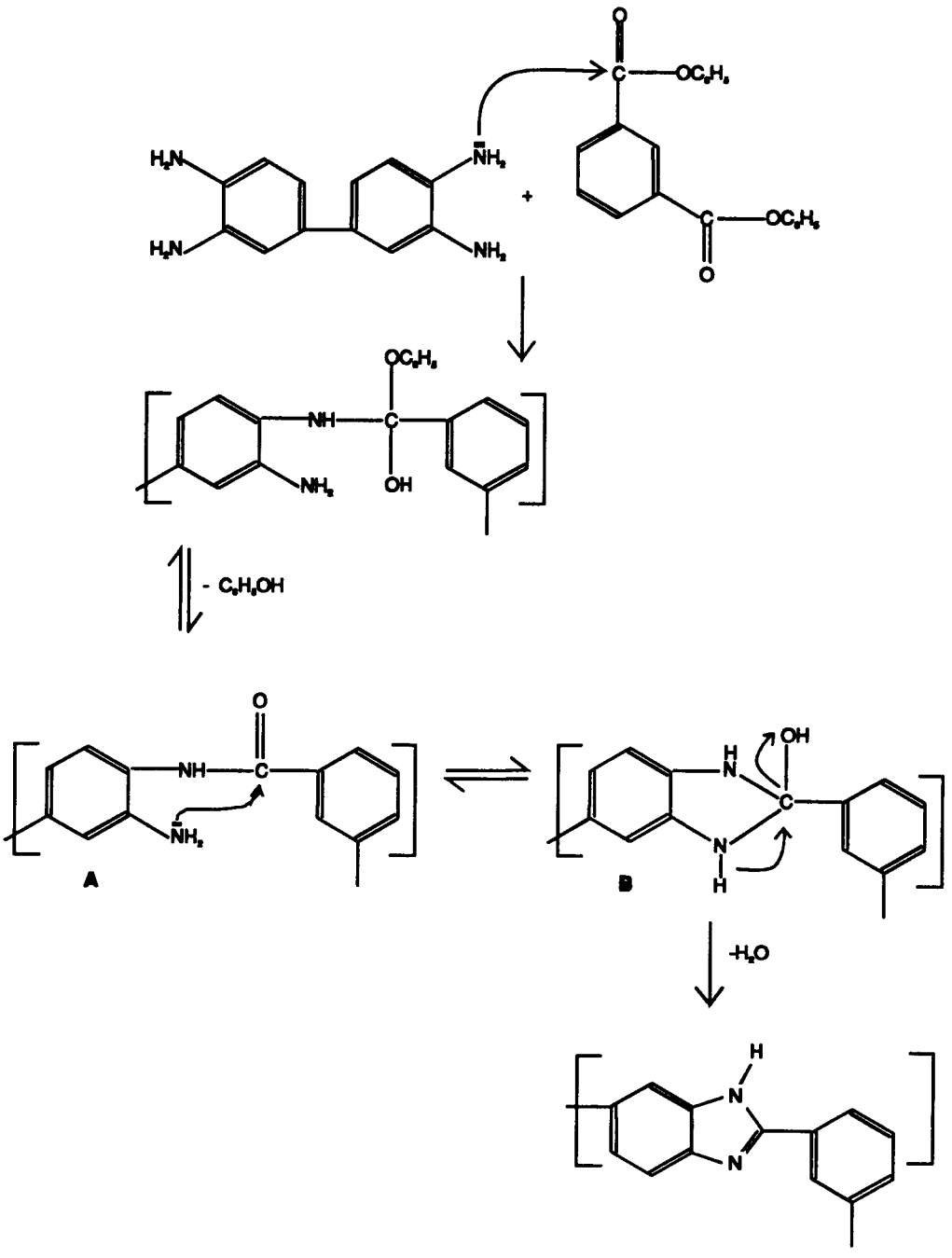
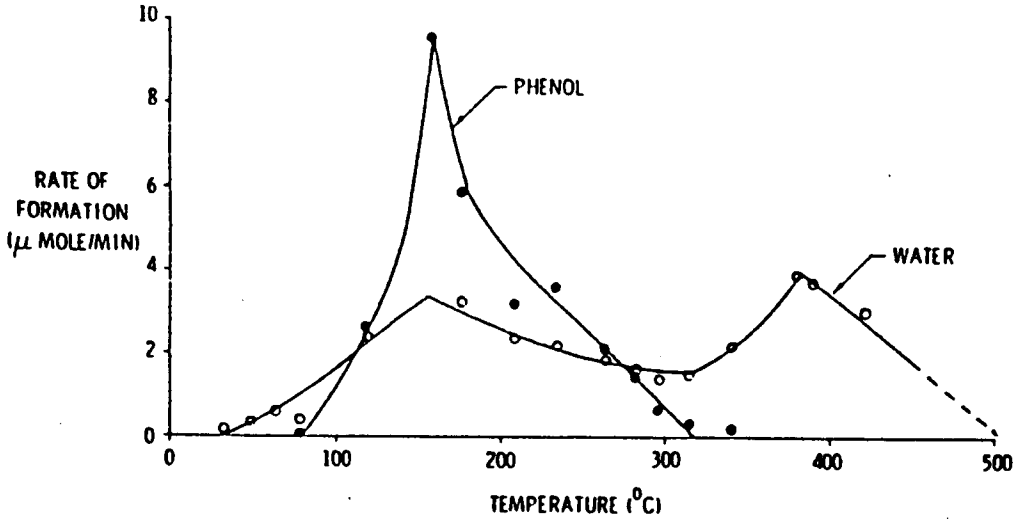


Figure 11. MTA of Diphenyl Isophthalate-Tetraaminobiphenyl Mixture.



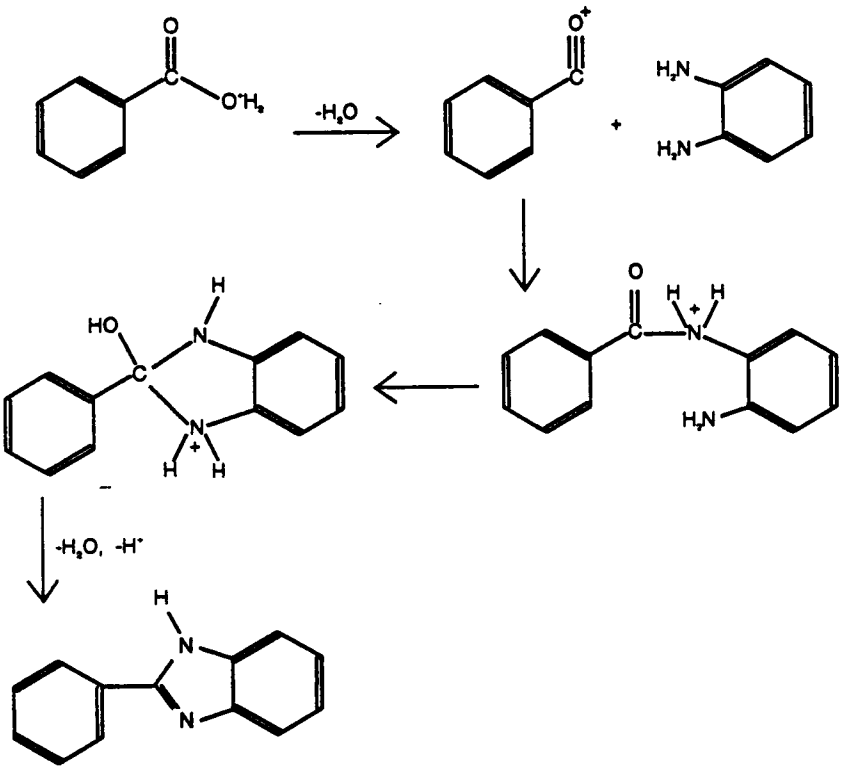
Although the two mechanisms suggested for melt polymerization differ one must consider that each investigation was carried out under differing reaction conditions and different methods were employed to make the measurements. The methods employed by Wrasidlo and Levine measure the evolution of water by collection under methanol which is extemely difficult to dry completely. They also ran their reactions at relatively low temperatures and it has been demonstrated that cyclization is often incomplete at temperatures as high as 260-300°C.[1]

The mechanism may also vary depending on the monomers and the conditions of the reaction. Currently, the literature shows interpretation of results based on both proposed mechanisms.

Diacids plus Tetraamines: Acidic Solvent Polymerization

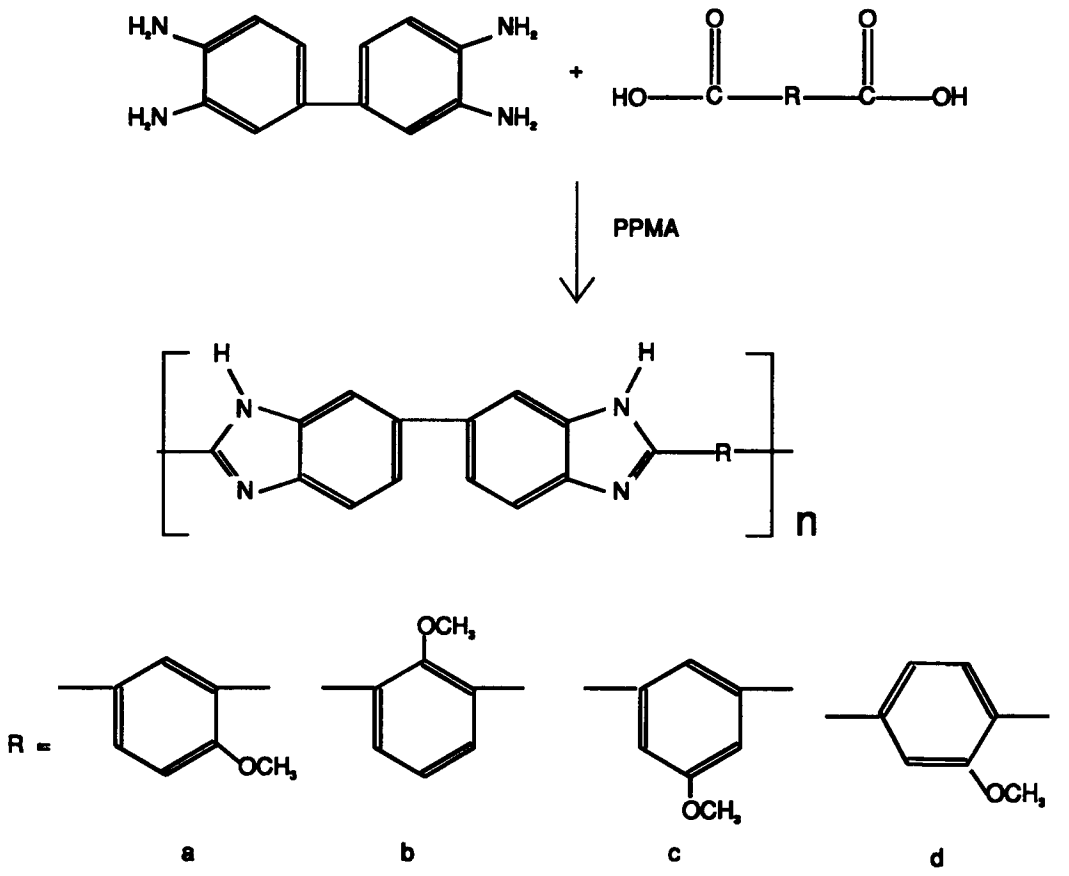
The literature includes very few studies directed at determining the mechanism of polybenzimidazole formation under conditions other than melt polymerization. Mechanisms for the formation of PBIs in acidic solutions have been proposed but not investigated thoroughly. For example, the synthetic pathway to aromatic PBIs in PPMA was proposed to procede through an acylium ion as the rate-determining step. This intermediate could withstand the strongly acidic medium unlike the intermediates in the mechanisms for melt polymerization. The proposed mechanism of PBIs formation in PPMA is outlined in Scheme 7.[16]

Scheme 7. Synthetic Pathway to PBI's in PPMA.



Some evidence for this mechanism is found in the work of Ueda *et al.* which demonstrated that electron-withdrawing groups on the aromatic diacid results in poor polymerization. This is due to the destabilization of the acylium ion intermediate by the electron-withdrawing groups. In order to further test this hypothesis, Ueda synthesized PBIs from methoxyphthalic acids which were expected to give more stable acylium ions due to the electron-donating methoxy group.[25] This experiment is summarized in Scheme 8.

Scheme 8. Polymerization of 3,3'-Diaminobenzidine and Methoxyphthalic acids.

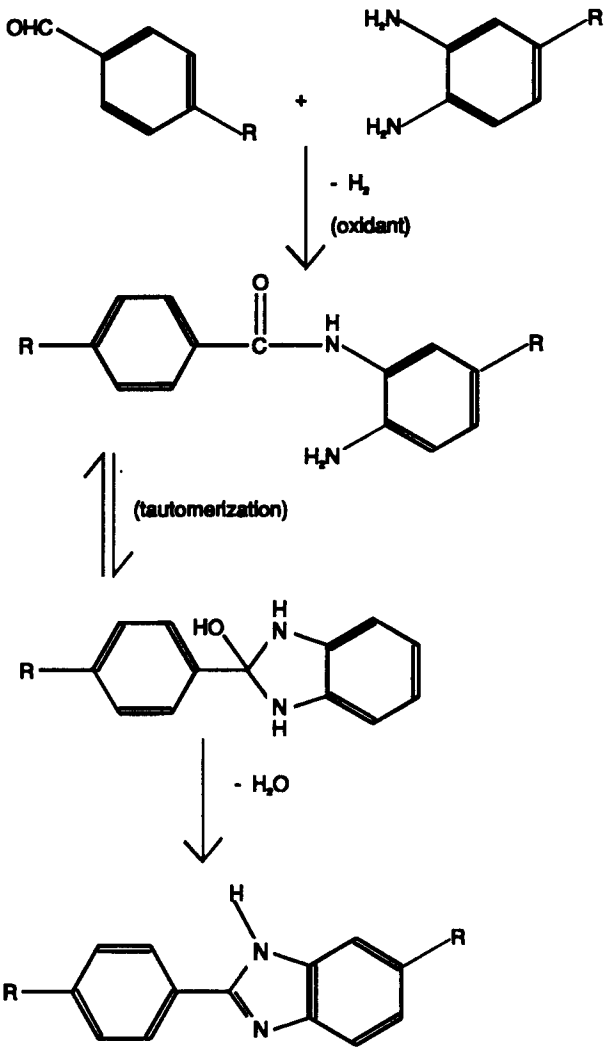


The results of this experiment demonstrated that the isomers in which the methoxy substituent was meta to one or both of the carboxylic acid groups gave significantly lower yields than the systems in which the methoxy group was ortho or para to both the acid groups. These results help substantiate the hypothesis of an acylium ion intermediate in acidic solution polymerization of polybenzimidazoles.

Dialdehydes plus Tetraamines: Polar, Aprotic Solvent Polymerization

Two mechanisms have been proposed for the reaction of dialdehydes and tetraamines in polar, aprotic solvents. To date the necessary kinetic research that is needed to substantiate either of these mechanisms has not been done. The first of these proposed mechanisms is presented in Scheme 9. The amide intermediate seems unusual since one would not normally predict aldehyde and amine to react to form an amide. The explanation for this amide intermediate may be the presence of an oxidant in the reaction system. It has been demonstrated that amides are formed by the reaction of aldehydes and amines in the presence of oxidants, such as nickel. Dialdehyde and tetraamine polymerizations are often conducted in the presence of oxidants like iron trichloride with oxygen gas or air. The dehydration of the amide intermediate would then result in PBI formation.

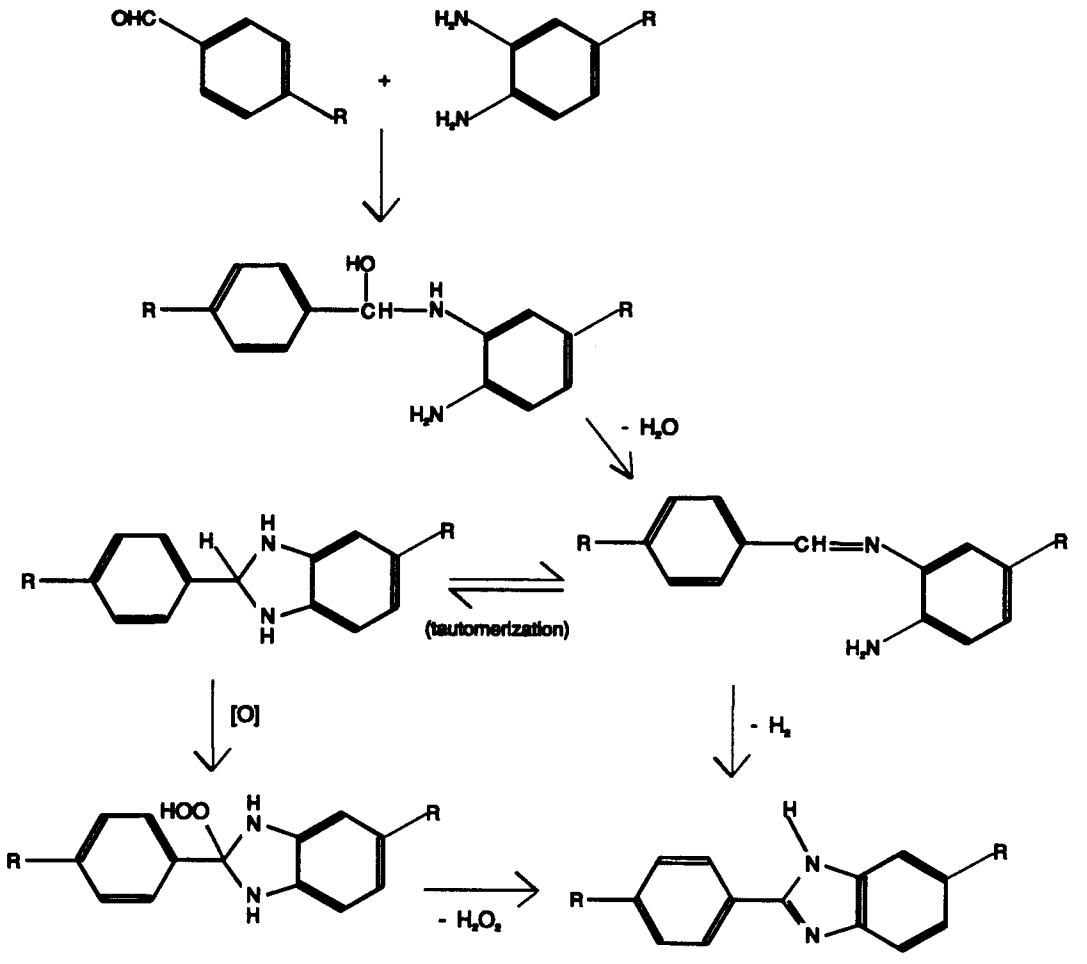
Scheme 9. Mechanism 1 of Dialdehyde plus Tetraamine Polymerization.



The second mechanism for PBI formation via aldehydes and tetraamines is shown in Scheme 10. This mechanism includes an azomethine intermediate. The presence of such an intermediate has been substantiated by the isolation of polyazomethine intermediates by several research groups using solution polymerization systems.[26, 27] Research conducted by Coville and Neuse on the oxidative cyclodehydrogenation of aromatic bis(o-aminoanils) adds credence to the above mechanism which

proposes an azomethine intermediate that then cyclizes to a benzimidazole.[27]

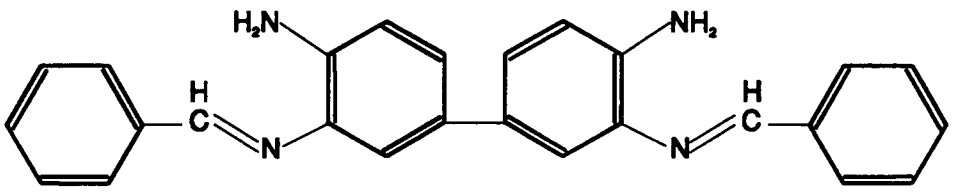
Scheme 10. Mechanism 2 of Dialdehyde plus Tetraamine Polymerization.



Their work involved the solution condensation of 3,3'-diaminobenzidine with benzaldehyde in the absence of moisture and air using either DMAc, DMSO, ethanol or N-methylpyrrolidone as the solvent. They were able to

verify the formation of the structure in Figure 12 in the dissolved state using spectroscopic data.

Figure 12. Azomethine Intermediate.



In the NMR spectrum, the 2-proton peak of the azomethine links are found near 8.6 ppm, the 4-proton resonance of the amino groups appears at 5.2 ppm and the ortho protons of the terminal end give a 4-proton signal at 7.9 ppm. In contrast, the phenyl group in the 2 position of the imidazole ring would give a 4-proton signal near 7-7.5 ppm. This structure was also confirmed by IR and UV data.

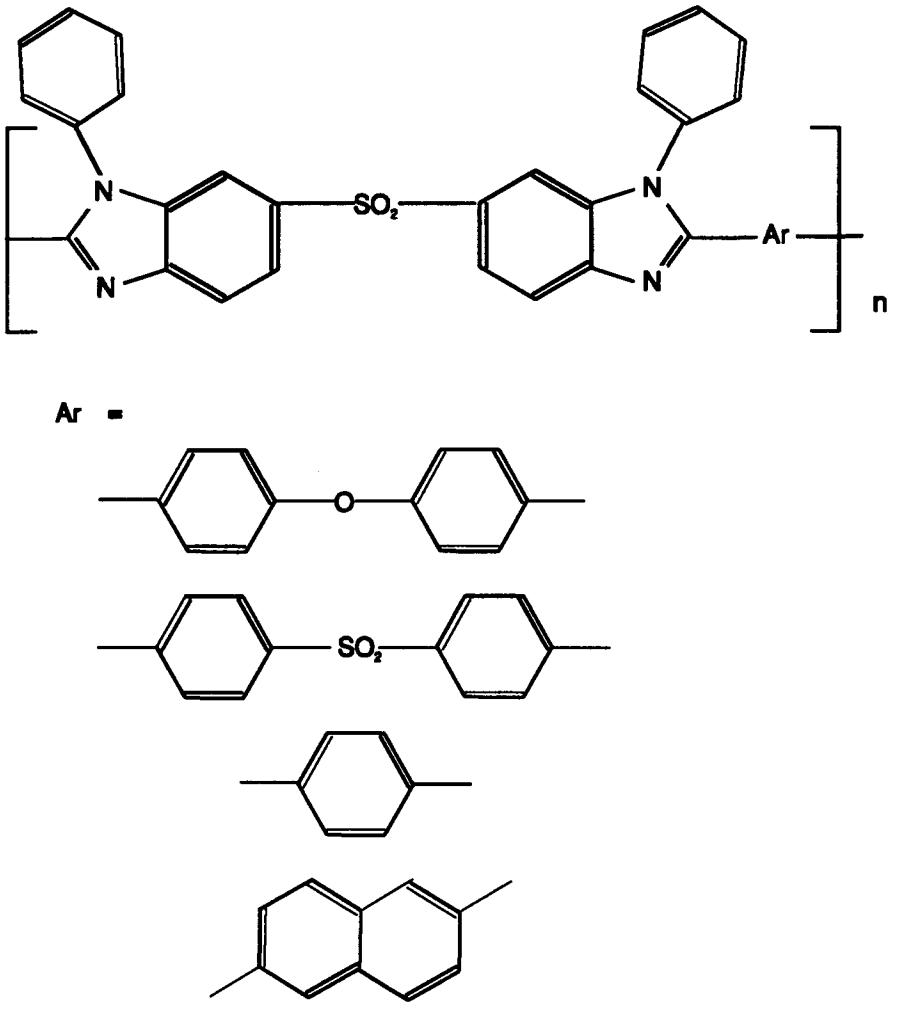
The oxidative cyclodehydrogenation of the azomethine intermediate structure was then brought about by agitation in air at 60°C for 3 hours. The resulting benzimidazole was also confirmed by spectrometric analysis. This work also indicated suitable conditions for low temperature solution polymerization of aldehydes and tetraamines to form polybenzimidazoles.

RECENT DEVELOPMENTS IN PBI SYNTHESIS

Recent work in PBI synthesis has taken a variety of approaches. For example, Smith and coworkers have had success in preparing PBI's that were soluble in DMAc and provided films with excellent room temperature properties using nucleophilic displacement reactions.[28] Their approach involved the synthesis of monomers containing the benzimidazole ring and terminating in hydroxyl groups. The bis[2-(4-hydroxyphenyl) benzimidazole]s were prepared from aromatic bis(o-diamine)s and phenyl 4-hydroxybenzoate. These monomers in the form of the alkali metal bisphenates were condensed with activated difluorides to form polybenzimidazoles in yields greater than 90%. This synthetic approach avoids the possibility of crosslinking that can occur during the benzimidazole ring formation.

As previously mentioned many research groups have focused on overcoming problems of chain stiffness and increasing polymer solubility. Korshak *et al.* have reported the synthesis of N-substituted polybenzimidazoles with increased solubilities due to the beneficial effect of the phenyl side-group substitution. Their results include several polymers with flexibilizing ether and sulfone groups in the polymer chain.[17] A sample of these polymers is illustrated in Figure 13. Until recently N-substituted PBIs were studied comparatively little due to problems encountered using classical synthetic methods. These problems were especially difficult to overcome when working with N,N'-disubstituted aromatic tetraamines. The efforts mentioned above showed some

Figure 13. N-Substituted Polybenzimidazoles

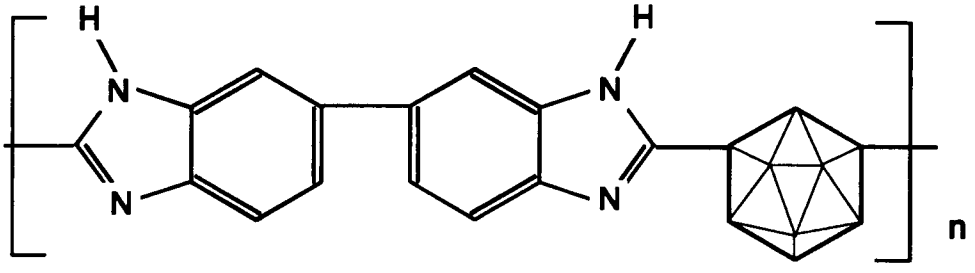


promise in improved polymer properties; therefore, Kane's group sought to prepare N-substituted PBIs using a different synthetic route.[21] They condensed a tetraamine bis-carbamate derivative and a dicarboxylic acid with the mild dehydrating agent polyphosphoric acid trimethylsilyl ester (PPSE). Their efforts resulted in PBIs with viscosities in the range of 0.23-0.46 dL/g that formed very brittle films. Next they condensed tetraamine with bis-acid chlorides in NMP to form poly(o-

anilinobenzanilides) which were cyclized to the desired PBIs in PPA. The polymers formed were the same as those formed in the previous section except the viscosities ranged from 0.73-1.17 dL/g and provided clear, self supporting films.

Some unique polybenzimidazoles have been synthesized by Neuse and coworkers. They reacted 3,3'-diaminobenzidine with a large carborane dialdehyde to produce a low molecular weight polymer that was stable up to temperatures of 500°C. The synthesis was difficult due to reaction condition restrictions resulting from the easy cleavage of the C-C bond between the benzimidazole ring and the carborane cage. This cleavage occurred when the temperature of the reaction was to high or the reaction time was too long. Neuse explained this bond cleavage in terms of the increased steric requirements and electron deficient nature of the carborane cage. The steric interaction destabilizes the bond and the carborane cluster withdraws electrons from the benzimidazole ring further increasing the instability of the C-C bond. The carborane containing polybenzimidazole is illustrated in Figure 14.[29]

Figure 14. PBI containing carborane cluster.



RESULTS AND DISCUSSION

This research project was directed at preparing a series of compounds containing various combinations of ether and sulfone linkages, in an effort to increase the solubility and processibility of the resulting polybenzimidazoles. These linkages were incorporated into the PBIs as a constituent of diacid monomers. The diacids were synthesized by a variety of methods mainly involving nucleophilic aromatic substitution reactions and electrophilic aromatic substitution to synthesize the precursers.

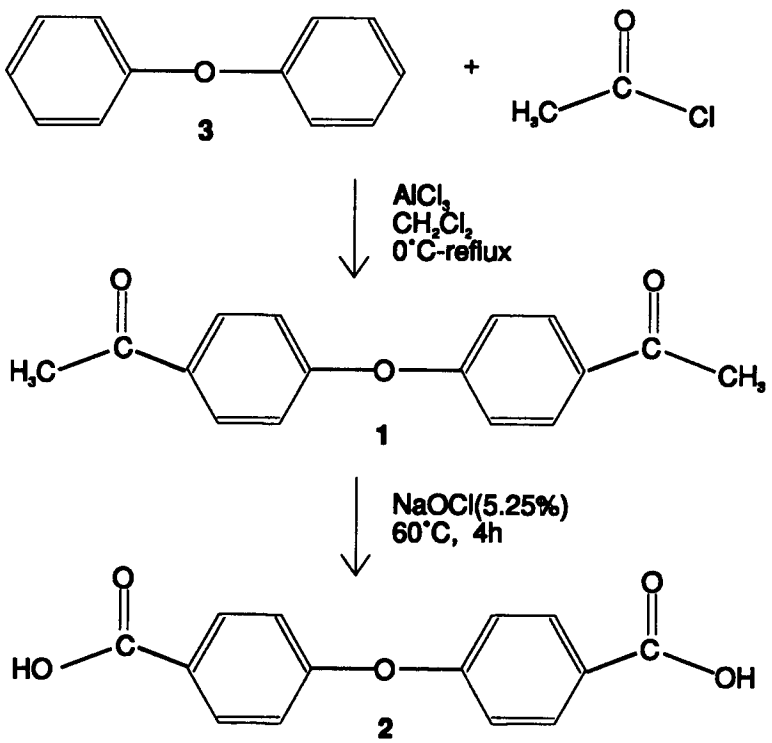
The secondary goal was the formation of polybenzimidazoles using a one step process that was less time consuming and/or more effective than melt or two step polymerization methods. Ueda has previously described one step polymerization methods using diacids and tetraamines in a condensing agent/solvent system of polyphosphoric acid (PPA) and an alternate method using phosphorous pentoxide/methane sulfonic acid (PPMA).[11, 13, 14] This method would allow for polymerization and oxidative ring formation concurrently in a single step. These polymerization methods were used to prepare the desired PBIs and comparisons of viscosities and film qualities were made.

Synthesis of Monomers

The incorporation of the ether and sulfone linkages into the polymers was accomplished by incorporating these functionalities into dicarbonyl monomers. The monomer 4,4'-oxybis[benzoic acid] (**2**) was prepared

using a synthesis described by Mulvaney *et al.* which involved the Friedel Crafts reaction of diphenyl ether with acetyl chloride in carbon disulfide catalyzed by aluminum chloride,[30] followed by oxidation of the bis (4,4'-acetyl)diphenyl ether (**1**) to the diacid via a haloform reaction (Scheme 11). Using carbon disulfide as the solvent for the Friedel Crafts reaction presented problems of rapid solvent evaporation and extremely low yields of the desired product. The reaction was subsequently repeated using dichloroethane as the solvent and a 70:30 mixture of product to starting material was obtained. The best results were obtained using dichloromethane as the solvent during acylation; the resulting 4,4'-oxybis[benzoic acid] (**2**) was recrystallized from ethanol as a pure light yellow crystalline solid.

Scheme 11. Synthesis of 4,4'-Oxybis[benzoic acid] (**2**).



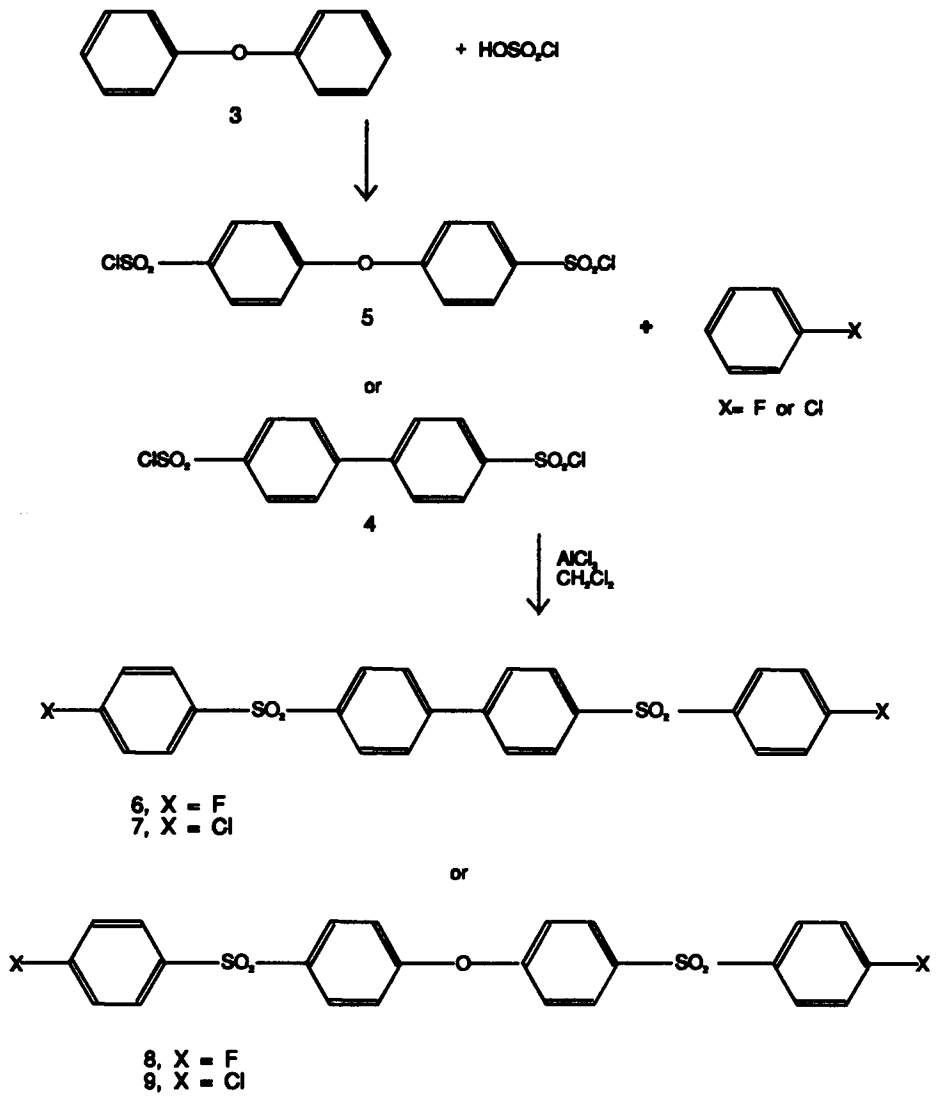
The remaining monomers were synthesized using a general approach involving the preparation of dihalides containing a series of sulfone linkages and then forming the ether linkages during the nucleophilic aromatic substitution reaction of these dihalides with the potassium salt of 4-hydroxy benzoic acid or the corresponding methyl ester.[31]

The initial dihalides were synthesized by way of Friedel Crafts reactions of either fluorobenzene or chlorobenzene with dihalide precursors as outlined in Scheme 12.

The aluminum chloride acts as a catalyst in the formation of the active electrophilic species $ArSO_2^+$. Previous research has demonstrated that aryl sulfonium ions ($ArSO_2^+$) are capable of substituting both activated and deactivated aromatic rings. The electrophilic species then attacks the halobenzenes favoring the position para to the halogen. Halogens are weak electron withdrawing groups which decrease the electron density of the aromatic ring and reduce the reactivity to electrophiles. Since fluorine is more electronegative than chlorine, the reaction with fluorobenzene would be expected to occur slowly as compared to the reaction with chlorobenzene. Although the halogen substituents can deactivate the ring to electrophilic substitution, they are still ortho and para directing due to their ability to resonance stabilize the intermediate sigma complex.

Both the dichlorides and difluorides were prepared so experiments to determine the halides effect on the formation of the diacids could be investigated. Generally, the difluorides were obtained as crystalline solids in higher yields than the dichlorides . The NMR, IR and mass spectrum conclusively showed that diadducts of the desired purity had formed.

Scheme 12. Preparation of Dihalides.



These dihalide precursers were than used in the synthesis of the diacid monomers.

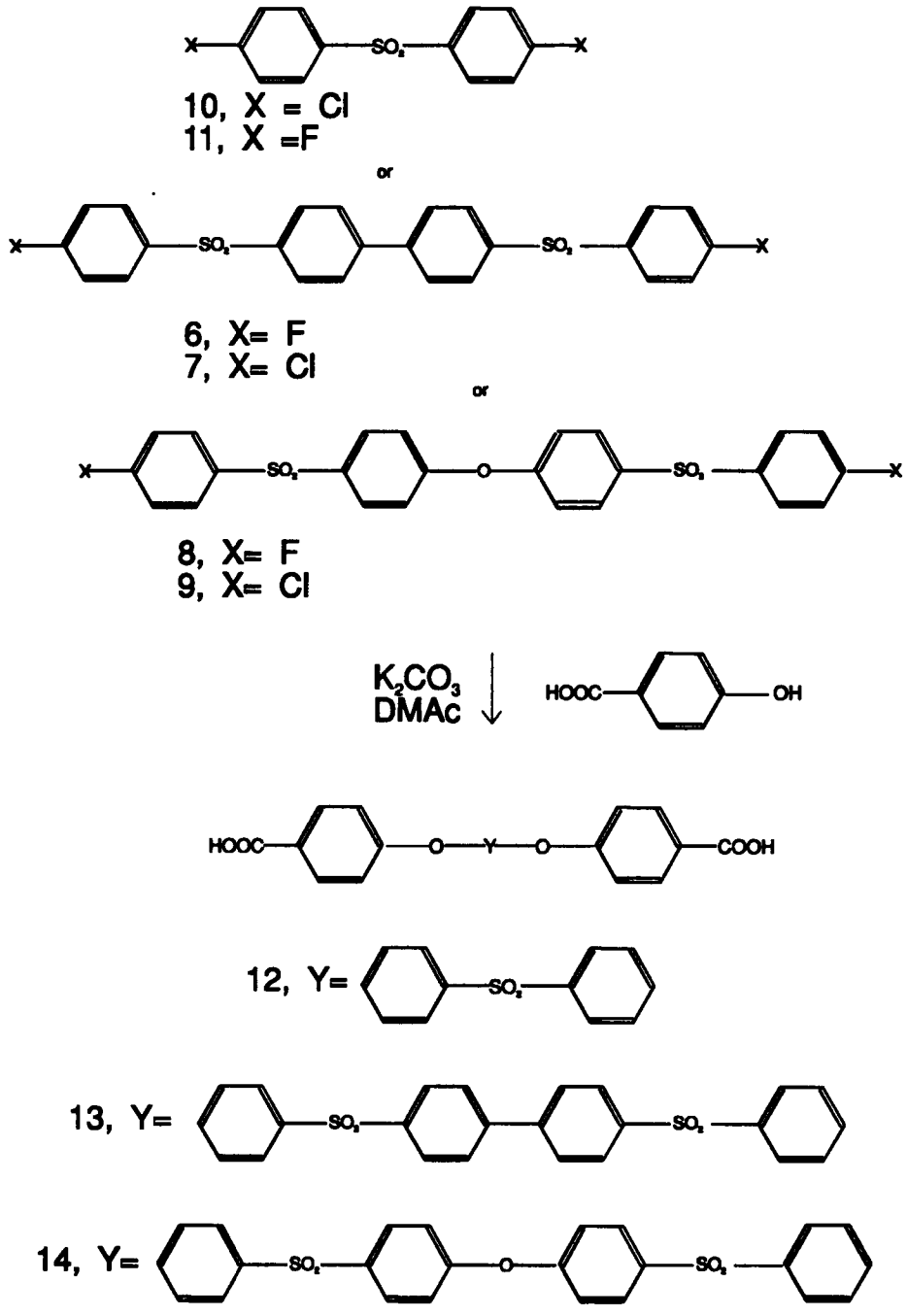
The diacid monomers were synthesized using a modification of Idage's method for the synthesis of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]bis [benzoic acid] (**12**) by the reaction of dichloride (**10**) with the dipotassium

salt of 4-hydroxybenzoic acid.[32] This method required reaction times of up to 80 hours and only worked efficiently with the lower molecular weight dichlorides. In an effort to decrease the required reaction time, the difluoride (**11**) was used in place of the dichloride (**10**). It has been demonstrated that fluorine is a better leaving group than chlorine in nucleophilic aromatic substitution reactions. This alteration in the synthesis did not improve the method to any appreciable extent. The general synthetic scheme is shown in Scheme 13.

To determine the most effective solvent the reaction was attempted in DMSO, DMF, and DMAc. The highest yields were obtained using DMAc. The reaction was sensitive to water content and toluene/DMAc azeotrope was utilized to remove the water liberated in the formation of the dipotassium salt. When applying this synthetic route with high molecular weight dihalide precursers difficulties arose. The reaction gave the diadduct as the major product with the low molecular weight dihalides and the monoadduct with the higher molecular weight dihalides. This is accounted for by the intermediate formation of a monoadduct salt that was difficult to keep in solution as its molecular weight increased. The reaction was only successful with vigorous mechanical stirring over long reaction periods at temperatures of 140-160°C. A mixture of the mono and diadduct products was still obtained that proved difficult to purify.

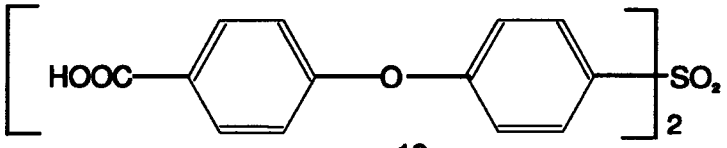
In an effort to avoid the formation of the salt intermediate, to keep the reactants in solution, and to form products that were more easily separated from impurities the potassium salt of 4-hydroxy methyl benzoate was employed as the nucleophilic species. This resulted in the formation of the desired diesters in higher yields with only a minor impurity

Scheme 13. Synthesis of Diacids.

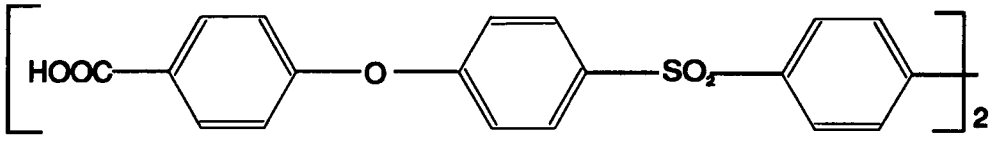


of the monoesters. The diesters could then be converted to the diacids during the work up by heating the products in acidic solution for thirty minutes. The diacids prepared by this synthesis are listed in Figure 15.

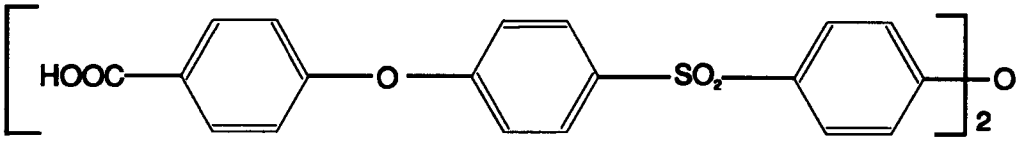
Figure 15. Diacid Monomers.



12



13



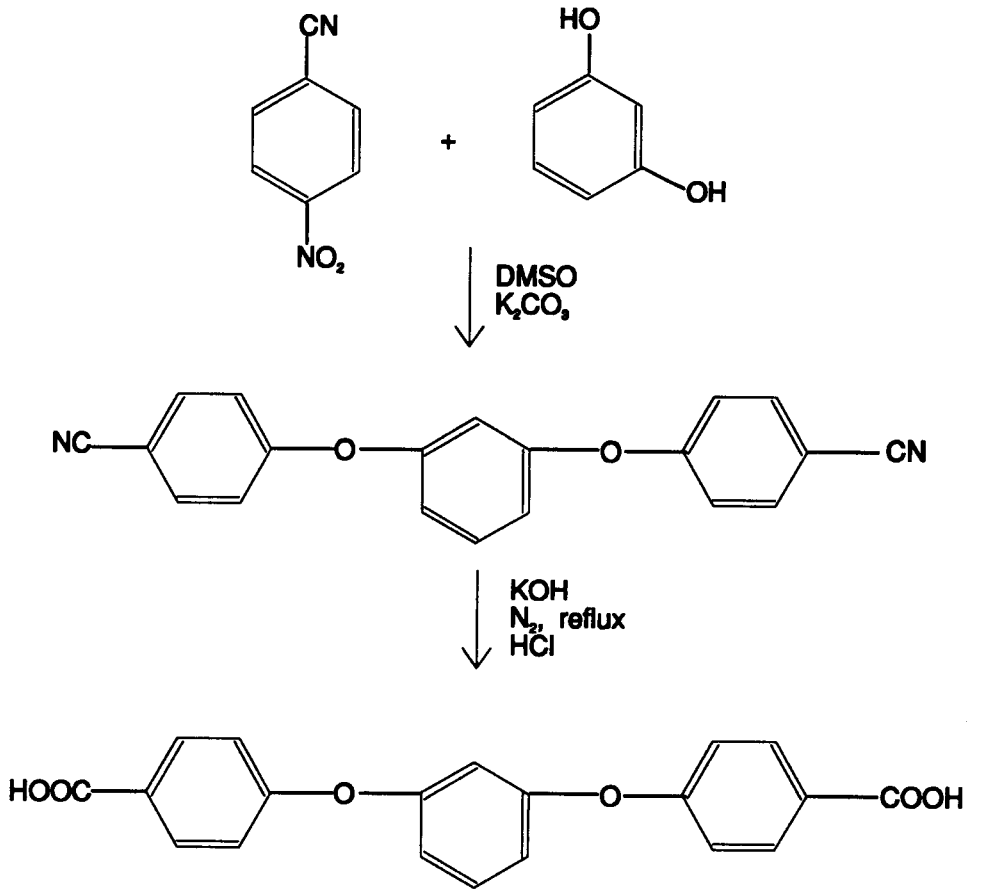
14

The synthesis resulted in a series of compounds with increasing amounts of ether and sulfone linkages. Compound **12** has been previously synthesized by Idage, while compounds **13** and **14** are unique to this research endeavor.

The initial success achieved in preparing 4,4'oxybis[benzoic acid] (**2**) lead to the pursuit of a diacid monomer containing two ether linkages as shown in Scheme 14. This compound had initially been prepared by Robert C. Evers *et al.* and used in the formation of polybenzoxazoles,

polybenzimidazoles and polybenthiazoles.[32] Evers' group prepared the *p-m-p* diphenoxybenzene structure by the base promoted reaction of 4-nitrobenzonitrile with resorcinol. The initially formed dinitrile resulting from this nitro-displacement reaction was converted to the corresponding diacid by reaction with base under refluxing conditions followed by acidification of the resulting dipotassium salt. The product was obtained as a white powdery solid which could not be purified further by recrystallization (Scheme 14).

Scheme 14. Evers' Synthesis of 4,4'-(1,3-Phenylenebisoxy) bis[benzoic Acid].



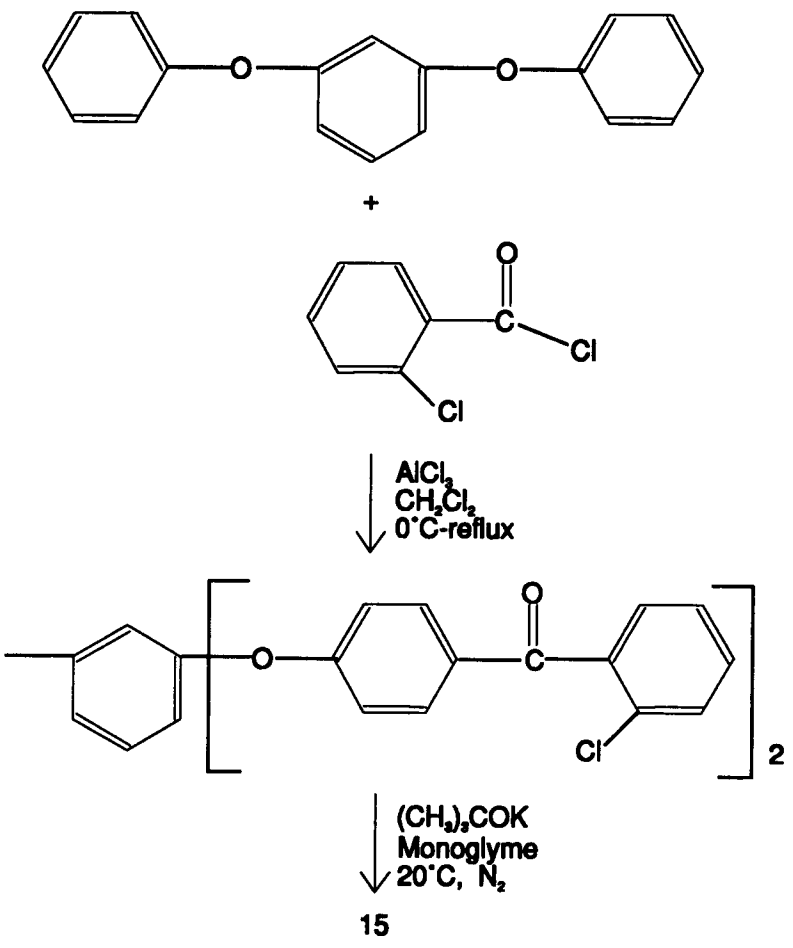
The yield obtained was modest (64%); therefore, a synthetic approach that could result in higher yields was pursued. Preliminary experiments involved the acylation of 1,3-diphenoxybenzene with acetyl chloride in dichloromethane in an effort to synthesize bis[4,4'-acetyl]-1,3-diphenoxybenzene. ^{1}H-NMR results indicated that acylation had occurred on all three of the aromatic rings. The product would have a third functional group in the monomeric unit and its use in polymerization reactions would result in crosslinking.

It was thought that the use of a more sterically hindered acylating reagent could restrict reaction on the central aromatic ring and provide the desired diacetylated product. 2-Chlorobenzoyl chloride was selected as the acylating agent for several reasons. It is more sterically hindered than acetyl chloride, it has been demonstrated that cleavage of benzophenones with chlorine atoms in the two position are readily cleaved, and this cleavage is accomplished with high yields of the corresponding acids.[33] The synthesis was proposed as presented in Scheme 15.

The work of Davies, Derenburg and Hodge suggests that in the 2-chloro benzophenone type structures there is a strong electron-withdrawing inductive effect and a steric effect that would favor cleavage of the bond to the ring bearing the chloro substituent. For example, their research yielded benzoic acid (99%) from cleavage of 2-chloro benzophenone.[33]

Efforts to synthesize 4,4'-(1,3-phenylenebisoxy)bis[benzoic acid] using this approach resulted in a mixture of isomers. The ^{1}H-NMR of the crude

Scheme 15. Proposed Synthesis of 4,4'-(1,3-Phenylenebisoxy) bis[benzoic acid].



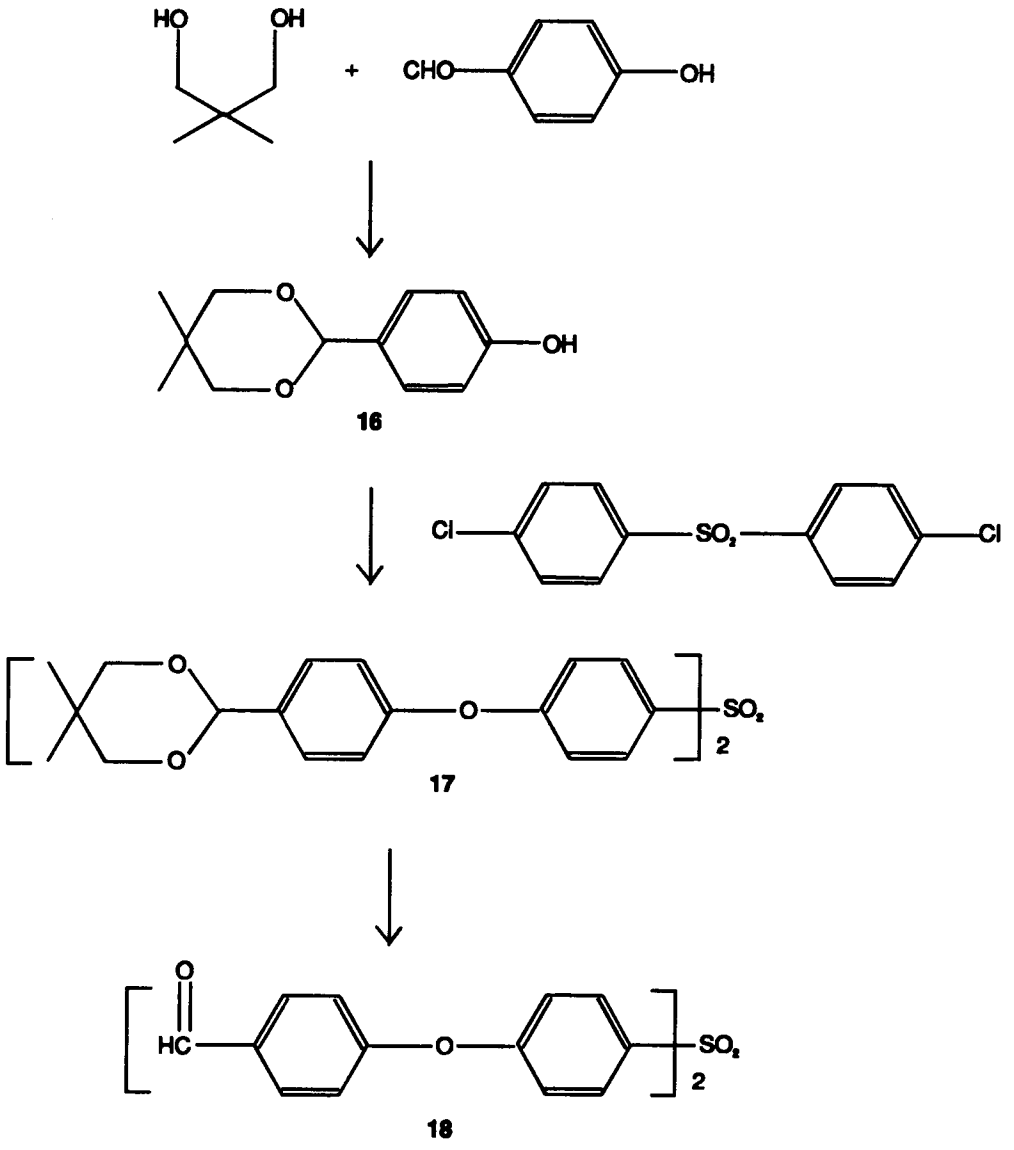
15

product indicated that tri-acylation had occurred. Separation of the isomers by flash chromatography proved ineffective.

Earlier work in these laboratories by Dora Azmus indicated that dialdehydes could be used to synthesize PBIs of good quality using a two step solution polymerization method, so efforts were made to prepare a dialdehyde containing ether and sulfone linkages.[16] Scheme 16 illustrates

the synthetic route used to synthesize 4,4'-[sulfonylbis(1,4-phenyleneoxy)] bis[benzaldehyde] (**18**).

Scheme 16. Synthetic Route to 4,4'-[Sulfonylbis(1,4-phenyleneoxy)] bis[benzaldehyde].



The protection of the aldehyde as the acetal initially proved difficult until the reaction conditions were adjusted to allow for removal of water from the reaction flask as the catalyst was slowly added. This eliminated the side reactions such as polymerization that occurred when the catalyst was added too rapidly and the reaction was driven to product by the removal of water. Meskens reports that electron-donating substituents in the para position hinder acetal formation.[34] The equilibrium constants for acetal formation decrease from p-bromobenzaldehyde to benzaldehyde to p-anisaldehyde. The isolated product mixture was further purified by flash chromatography to give acetal **16** as a crystalline solid. The nucleophilic aromatic substitution reaction of the acetal with the dichloride gave a mixture of mono and diadduct (**17**), the resulting product mixture was stirred with hydrochloric acid to deprotect the dialdehyde (**18**). A mixture of products was obtained which were separated by flash chromatography.

The tetraamine monomer used in this research was 3,3'-diaminobenzidine which is readily available commercially and was purchased from Aldrich. This tetraamine is toxic and carcinogenic so it must be handled with care. It is susceptible to oxidation and usually requires recrystallization, but once purified and dried, it can be stored for long periods under nitrogen.

Synthesis of Polymers

The basic approach used to synthesize polybenzimidazoles in this research used the solution polymerization of tetraamines and dicarboxylic

acids in a one step process that results in concurrent condensation and ring formation.

Several researchers have routinely synthesized polybenzimidazoles in polyphosphoric acid and methane sulfonic/polyphosphoric acid in order to avoid the high temperatures required for melt polymerization that can result in decarboxylation of monomers with free carboxylic acid groups.[1] The potent dehydration properties of polyphosphoric acid allow reaction to proceed at much lower temperatures. The success of PPA as a condensing agent for making PBIs has been demonstrated in synthetic organic chemistry several times. For example, polyphosphoric acid has been used to prepare 2-substituted benzimidazoles from o-phenylenediamine and carboxylic acids.[12] Since the mid sixties it has been utilized by Ueda and others for solution polymerization in macromolecular systems.

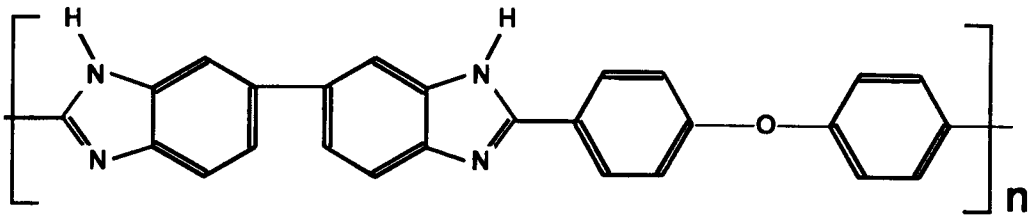
Polyphosphoric acid can be prepared by heating phosphoric acid and phosphorus pentoxide on a steam bath for 2-4 hours to their equilibration point. The PPA can age upon storage and become less effective as a condensing agent.

Methane sulfonic acid/phosphorus pentoxide can be prepared by the heating of methane sulfonic acid and phosphorous pentoxide at 60°C until all the phosphorous pentoxide has dissolved. This reagent is light sensitive but has been shown to remain effective after storage or discoloration.

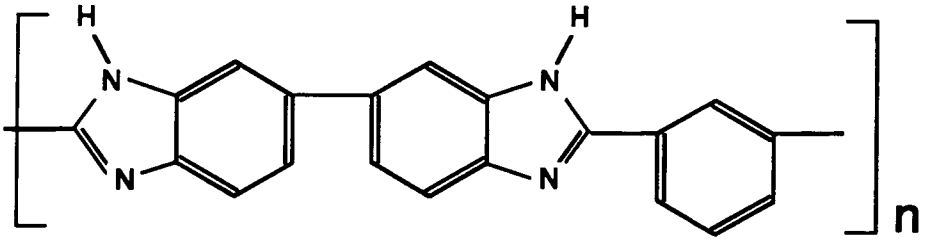
Model Compound Investigations

In an effort to refine the techniques and methods used to prepare polybenzimidazoles using PPA and PPMA, the polymers (**19** and **20**) shown in Figure 16 were synthesized as reported by Ueda.[25]

Figure 16. Poly([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,4-phenyleneoxy-1,4-phenylene) (**19**).



Poly([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,3-phenylene) (**20**).



Polymer **19** was prepared by the condensation of 4,4'-oxybis[benzoic acid] (**2**) with 3,3'-diaminobenzidine in PPA and PPMA. Condensation of this monomer with 3,3'-diaminobenzidine (DAB) in PPA gave a polymer with an inherent viscosity of 0.25 dL/g (25°C, DMAc) and poor film quality. This polymerization was then attempted in PPMA and a polymer with an inherent viscosity of 0.23 dL/g (25°C, formic acid) and poor film quality

was obtained. These results were poor compared to Ueda's measured inherent viscosity of 3.63 dL/g (30°C, methane sulfonic acid) for polymer **19** prepared under similar reaction conditions. The values are not directly comparable due to the different temperatures at which the viscosities were measured as well as the difference in viscosity solvent used, but a rough comparison was made in order to assess the efficiency of the reaction conditions.

Polymer **20** was then investigated as a more economical and time efficient way to evaluate the reaction conditions and refine the polymerization method. Commercially available (Lancaster Synthesis Inc.) isophthalic acid was condensed with DAB and or DAB-HCl in PPA and PPMA and polybenzimidazoles having viscosities indicative of a high molecular weight were obtained using both solvents. The results of these experiments are presented in Table 1.

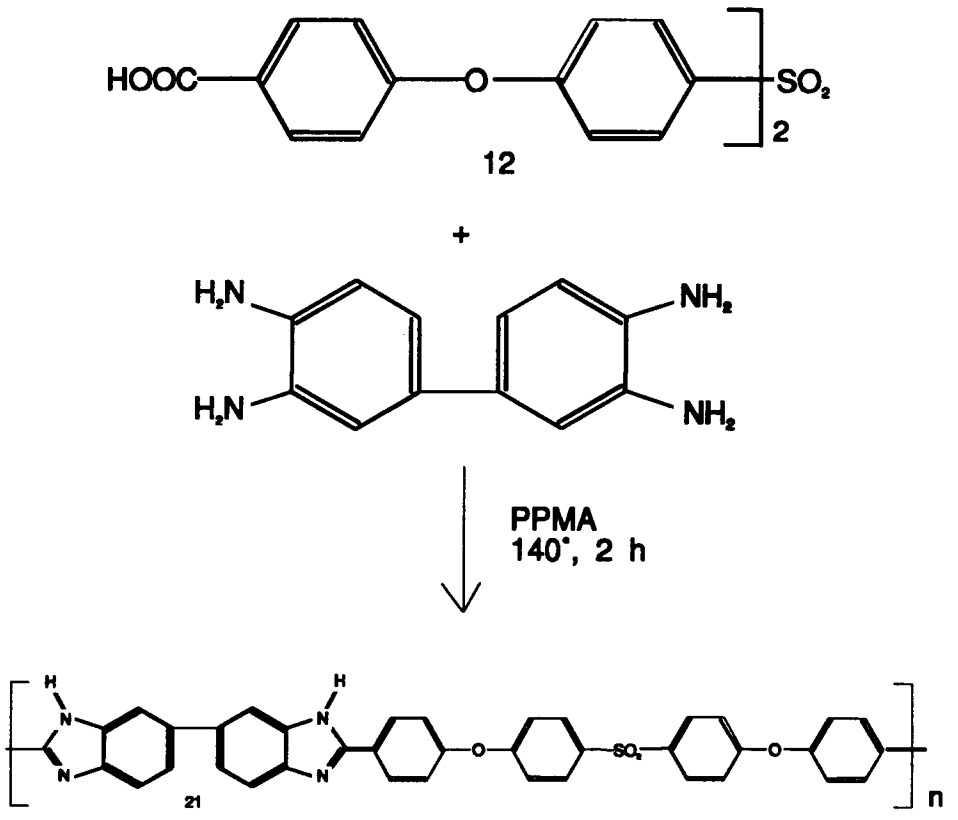
Table 1. Polymerization Reactions of Isophthalic Acid and 3,3'-Diaminobenzidine

reaction time	temperature	solvent	η_{inh}	viscosity conditions
16 h	160°C	PPA	1.16dL/g	DMAc/4%LiCl,25°C
12 h	140°C	PPMA	1.33dL/g	DMAc/4%LiCl,25°C

The polymerization in PPMA resulted in a polymer that could be formed into a bendable film. The results of these polymerization reactions were encouraging and work was begun to synthesize polybenzimidizoles using the other diacid monomers containing ether and sulfone linkages.

The initial polymerizations were conducted at a temperature of 140°C for two hours using equimoler amounts of 3,3'-diaminobenzidine and **12** as outlined in Scheme 17.

Scheme 17. Polycondensation in PPMA.



The resulting polymer had an inherent viscosity of 0.13 dL/g (formic acid, 25°C) indicating the formation of a low molecular weight polymer that provided a brittle film. The conditions were not very stringent in precluding of oxygen and water. Many polymerization reactions are extremely sensitive to water content and the tetraamine employed in these reactions is susceptible to oxidation in the presence of air.

The reaction was repeated using precautions that exclude air and moisture from the reaction vessel and reagents. This resulted in the formation of a polymer with an inherent viscosity of 1.62 dL/g (formic acid, 25°C) indicating a moderately high molecular weight that could be formed into a bendable film. The UV results indicated that the benzimidazole ring had formed and IR compared favorable to previously synthesized PBI's. Results of the elemental analysis indicated that the polymer formed contained inpurities. This has been a major problem in solution polymerizations using PPA and/or PPMA as the solvent. The removal of all the phosphorus from the polymer is extremely difficult to accomplish and has been known to effect the elemental analysis as well as oxidative stability tests.[6] The acids can also attack the glass and introduce silica into the polymer which can also contribute to a poor analysis.

The polymerization was attempted using 3,3'-diaminobenzidine tetrahydrochloride in order to exclude the oxidation of the amine as a factor contributing to the low viscosity of the polymers formed. The procedure was varied in the following manner. 3,3'-Diaminobenzidine tetrahydrochloride was dissolved in polyphosphoric acid at 120°C in a flask equipped with a stirrer under a stream of nitrogen, and bubbles of hydrogen chloride gas were eliminated gradually. The aromatic carboxylic acid component was added to this solution and the temperature was increased to 140°C. The reaction mixture developed a blue or violet fluorescence and gradually became viscous. After several hours the polymer was isolated by pouring the solution into water, washing with alkaline solution, rinsing with water and drying.

The resulting polymer was fibrous and black and was insoluble in DMSO, DMAc, sulfuric acid and formic acid. A viscosity was therefore not determined and crosslinking of the polymer was indicated. These poor results are probably due to the extensively long reaction time and the impurities in the diacid monomer.

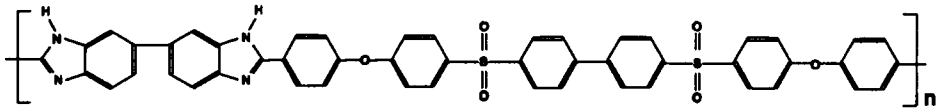
The results obtained thus far indicated that the optimum reaction conditions had not been attained and so a series of experiments were conducted using monomer (**13**) at differing time intervals and temperatures. The polymerizations were carried out using 3,3'-diaminobenzidine and **13** under the conditions indicated in Table 2.

Table 2. Polymerization of 3,3'-Diaminobenzidine and **13**

exp.	reaction time	temperature	solvent	η_{inh}	conditions
a	2.0 h 0.5 h	70°C 100°C	PPMA	0.84dL/g	DMAc, 25°C
b	1.0 h 0.5 h	100°C 140°C	PPMA	0.12dL/g	DMAc, 25°C
c	1.0 h 5.0 h	100°C 140°C	PPMA	0.25dL/g	DMAc, 25°C

The results of the above experiments suggest that polymerization proceeds to a higher degree when the reaction is conducted at a lower temperature and over a shorter reaction time. The polymer resulting from experiment **a** (Figure 17) was soluble in DMF, DMAc, sulfuric acid and formic acid.

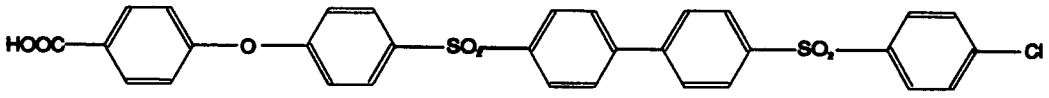
Figure 17. PBI **22.**



A film was prepared in DMF using a concentration of 33 mg/mL. This film was bendable, not brittle and could be folded without breaking until creased. The film was slightly elastic when pulled from each side. A film of this polymer was also prepared in DMAc at a concentration of 2 mg/mL using the solution from the viscosimeter and this film was also bendable and flexible. The film at lower concentration was not as strong and was easily broken.

It should also be noted that the diacid monomer used in experiment **a** was of high purity and crystalline structure. The diacid monomer used in experiments **b** and **c** was from a batch that showed a less than 1% impurity of the monoadduct by NMR analysis. This may also be a factor in the attainment of a higher degree of polymerization in experiment **a** than in **b** or **c**. The presence of impurities in the monomers can effect the polymerization in several ways. First, if the monoadduct pictured in Figure 18 were present, it would provide only one reactive functional group and the reaction of this end group with the tetraamine would result in a low molecular weight polymer because one endgroup would no longer be reactive.

Figure 18. Monoadduct of Diacid Monomer **13**.

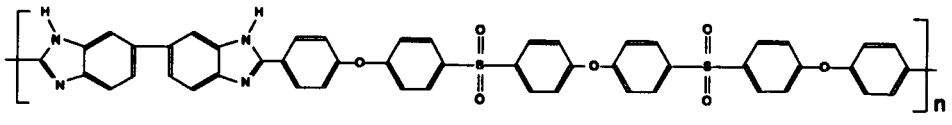


13

The polymerization would then be limited to polymer growth on only one end of the growing polymer chain. Therefore, the presence of only a minor impurity can greatly decrease the molecular weight of the resulting polymers formed during the reaction. The elemental analysis of the polymer prepared in experiment **a** gave poor results.

The polymerization method used in experiment **a** was then utilized to prepare PBI from 3,3'-diaminobenzidine and diacid monomer (**14**). The resulting polymer **23** (Figure 19) has an inherent viscosity of 0.20 dL/g (25°C, DMAc) and as expected provided a brittle film at a concentration of 100 mg/mL. The polymerization was then repeated using a reaction time of 5 hours and this also resulted in a polymer of low molecular weight as indicated by the low inherent viscosity and poor film quality.

Figure 19. PBI **23.**



The low degree of polymerization achieved with diacid monomer (**14**) and DAB can be attributed to impurities present in the diacid monomer. The 1H-NMR of this monomer indicates a purity of 93 percent. The degree of

polymerization is greatly affected by minor impurities. Further purification of this monomer may be accomplished by flask chromatography using an organic solvent system that is gradually acidified as elution fractions are collected.

Polymerization reactions using the dialdehyde monomer synthesized via the diacetal were not pursued at this time due to time constraints and purification problems, but success using a solution method for the polymerization of dialdhydes and tetraamines has been reported in this lab by Azmus.[16]

CONCLUSIONS

This research effort has resulted in the formation of three previously unreported monomers which can be utilized in the formation of a wide variety of polymers. These monomers can incorporate ether and sulfone linkages into the polymer backbone thereby increasing the solubility of the resulting polymer and enhancing its processibility. Attempts to synthesize polymers from these monomers has provided a new polybenzimidazole (**22**) with acceptable manufacturing characteristics as indicated by viscosity and film quality.

EXPERIMENTAL SECTION

General Procedures

Spectral measurements utilized a Nicolet 510P (FT) infrared, Hewlett Packard 8452 U.V., Bruker 300 or 400 MHz NMR, Varian MAT 311 (EI), Finnigan mass spectrometer, and Kratos MS 50 FAB.

Polymer Film Preparation: The polymer sample was dissolved in solvent at a concentration range of 15 mg/mL to 33 mg/mL. The solutions were placed on a glass plate and heated to 60°C for 2 hours. The sample was then placed under vacumm and the temperature was increased to 120°C and drying was continued for 16 hours. The polymers of a viscosity over 0.5 dL/g easily peeled off the glass plate. Films from polymers with a lower viscosity were removed by placing the slide in water and/or scraping them off the plate with a razor blade. These films were them redried in vacuo at 100°C overnight.

Purification of Reagents

Dimethylsulfoxide (DMSO): Reagent grade DMSO was stirred over CaH_2 for one day and then fractionally distilled from fresh CaH_2. The middle fraction was collected and stored over freshly activated 3A molecular sieves; bp 184-189°C (lit.[35] bp 189°C).

Dimethylacetamide (DMAc): Reagent grade DMAc was stirred with BaO for several days, refluxed with BaO for 2 h, and distilled under reduced pressure. The middle fraction was collected and stored over

freshly activated 3A molecular sieves; bp 56-59°C/11mmHg. (lit.[35] bp 58.0- 58.5°C/11mmHg).

Polyphosphoric acid (PPA): This reagent was used as received from Kodak Laboratories.

Phosphorus pentoxide/methane sulfonic acid (PPMA)[36]: Was prepared by the following procedure. Methane sulfonic acid (Aldrich) 30 mL was placed in a clean dry flask under nitrogen and stirred with a magnetic stir bar. To this flask 4.4 g of phosphorus pentoxide (weighed out in a dry box) was added and the temperature was increased to 60°C. The phosphorus pentoxide gradually dissolved in 1 to 3 h. The reagent was stored in a stoppered flask under nitrogen. Slight yellowing occurred on long storage but did not appear to affect the efficacy of the reagent.

Dichloromethane: HPLC grade was stirred with $CaCl_2$ and then distilled from CaH_2 and the middle fraction was collected and stored over freshly activated 3A molecular sieves away from light; bp 38-44°C. (lit.[35] bp 40.0°C)

Chlorobenzene: Reagent grade chlorobenzene was supplied by J.T. Baker and was distilled from CaH_2; bp 130-132°C. (lit.[35] bp 131.7°C)

3,3'-Diaminobenzidine (DAB) was supplied by Aldrich and dried in a vacuum oven prior to use; mp 173-176°C. (lit.[35] mp 172-174°C)

3,3'-Diaminobenzidine tetrahydrochloride dihydrate (97%) was supplied by Aldrich and used as received.

Aluminum chloride, anhydrous was supplied by Mallinckrodt and used as received. The aluminum chloride was weighed under nitrogen to ensure dryness.

Phosphorus pentoxide: Reagent grade phosphorus pentoxide was supplied by J.T. Baker and used as received. All quantities used were weighed out under nitrogen.

Diphenyl Ether (3) was supplied by Matheson Co. and used after the purity was verified by proton NMR and melting point; mp 26-30°C (lit.[37] mp 24- 28°C)

Acetyl chloride (99%) was used as received from Aldrich (lit.[35] bp 52°C)

Potassium fluoride was supplied by Aldrich and dried at 100°C under vacuum for 4 h prior to use.

Potassium carbonate (99%) was supplied by E.M. Science and was dried under vacuum prior to use.

Isophthalic acid was supplied by Lancaster Synthesis Inc. and used as received; mp 342-346°C. (lit.[35] mp 345-348°C)

4,4'-Dichlorodiphenyl sulphone (10), (98%) supplied by Aldrich was used as received; mp 143-147°C. (lit.[37] mp 145-148°C)

4-Hydroxybenzoic acid (99%) supplied by Aldrich was checked for purity by proton NMR and melting point and used as received; mp 215-217°C. (lit.[37] mp 214-215°C)

1,1'-Biphenyl-4,4'-disulfonyldichloride (4), (97%) was supplied by Aldrich and used as received.

4,4'-Difluorodiphenyl sulphone (11) was supplied by Lancaster Synthesis Inc. and used as received.

1,4 Dioxane was supplied by Aldrich and stored over 3A molecular sieves for use in recrystallizations.

Acetic acid (100%) was supplied by Mallinckrodt and used as received for recrystallizations.

Chloroform HPLC grade was used as received from Mallinckrodt for recrystallizations.

Chlorosulfonic acid supplied by Aldrich was checked for purity by proton NMR and used as received.

2-Chlorobenzoyl Chloride supplied by Aldrich was checked for purity by proton NMR and found to contain traces of acid and was stirred with CaH_2 and distilled.

1,3-Diphenoxybenzene supplied by Aldrich was checked for purity by proton NMR and melting point and used as received.

2,2-Dimethyl-1,3-propanediol (99%) supplied by Aldrich was dried under vacumn overnight and stored under nitrogen.

Methyl 4-hydroxybenzoate (99%) supplied by Aldrich was checked for purity by proton NMR and melting point and used as received; mp 124-127°C. (lit.[37] mp 126-128°C)

4-Hydroxybenzaldehyde (96%) supplied by Aldrich was checked for purity by proton NMR and melting point and used as received; mp 114-118°C. (lit.[37] mp 117-119°C)

Synthesis of Monomers

Bis[4,4'-acetyl]diphenyl Ether (1)[38]. Diphenyl ether 1.0 g (5.87 mmol) was dissolved in 1.04 mL (14.5 mmol) of acetyl chloride, and 10 mL of dichloromethane under nitrogen. In another clean dry flask at 0°C (ice bath), 3.25 g (24.4 mmol) of aluminum chloride, was stirred in 10 mL

of dichloromethane. The diphenyl ether solution was added dropwise to the aluminum chloride suspension and an orange to yellow suspension resulted. The ice bath was replaced with a heating mantle, the reaction vessel was fitted with a reflux condenser and the solution was refluxed for 12 h. The resulting brown residue was allowed to cool and stirred with an excess of cold 10% hydrochloric acid. The suspension became light yellow. The mixture was extracted with chloroform and concentrated in vacuo. Thin-layer chromatography indicated the formation of more than one product and the mixture was separated using flash chromatography (30% EtOAc:70% Hexane). A white crystalline solid was obtained; mp 91-92°C (lit.[30] mp 99-100°C); yield = 64%. Rf=0.30 (30% EtOAc:70% Hexane). ^{1}H-NMR (DMSO-d_6) δ 8.02 (d, J=8.7 Hz, 4H), 7.18 (d, J=8.7 Hz, 4H), 2.36 (s, 6H); ^{13}C-NMR (DMSO-d_6) δ 196.6, 159.6, 132.8, 130.9 (quadruple intensity), 118.7 (quadruple intensity), 26.7 (double intensity); IR (KBr) 1678 (C=O), 1595, 1269 (Ar-O-Ar), 827 cm^{-1}; MS (relative intensity) m/e 254 (34), 239 (100).

4,4'- Oxybis[benzoic Acid] (2)[30,38]. A 1200 mL solution of 5.25% NaOCl (Clorox) was added to a clean dry flask fitted with a thermometer and a heating mantle. The solution was heated to 55°C and 3.0 g (11.8 mmol) of bis(4,4'-acetyl)diphenyl ether was added with stirring. The temperature was then increased to 60°C for 4 h. The reaction mixture cooled to room temperature and the excess hypochlorite was destroyed by adding 100 mL of a solution of 20.0 g sodium bisulfite in 100 mL of water. After cooling, the mixture was cautiously acidified by adding 8 mL of concentrated hydrochloric acid. The solution was filtered and the white solid obtained was washed with water until neutral. The solid was

recrystallized from acetic acid which gave 2.2 g; yield = 71%; mp 312-316°C; (lit.[30] mp 358-360°C; lit.[38] mp 364-365°C and mp 328-330°C); ^{1}H-NMR (DMSO-d_6) δ 12.89 (s, 2H), 7.98 (d, J=8.7 Hz, 4H), 7.14 (d, J=8.7 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 166.6, 159.5, 131.8 (quadruple intensity), 126.4, 118.7 (quadruple intensity); IR (KBr) 2999-2550 (carboxylic acid), 1684, 1597, 1425, 1315, 1292, 1254 (Ar-O-Ar), 937 cm^{-1}.

Alternative method for the preparation of 4,4'-Oxybis[benzoic Acid] (2)[39]. A clean dry flask was fitted with a thermometer and an ice bath and 11 g of sodium hydroxide in 25 mL water and 20 mL 1,4-dioxane was added. The solution was maintained at a temperature of 12°C or less while 3.4 mL of bromine was added dropwise over a period of ten minutes. In another clean dry flask 3 g (0.012mol) of bis(4,4'acetyl) diphenyl ether was dissolved in 20 mL of 1,4-dioxane and this solution was added dropwise to the NaOBr solution while the mixture was stirred vigorously by a mechanical stirrer. The temperature was then increased to 20-24°C and stirring continued for 1.5 h. The excess hypobromite was destroyed by adding 5 mL of a solution of 20.0 g sodium bisulfite in 100 mL of water. The reaction mixture was extracted three times with ethyl ether to remove the unreacted ketone (0.894 g of ketone was recovered). The aqueous phase was then acidified by adding 2 mL of concentrated hydrochloric acid. The solution was filtered and the white solid obtained was washed with water until neutral. The solid was recrystallized from acetic acid which gave 2.11 g; crude yield = 69%; mp 320-322°C; (lit.[30] mp 358-360°C; lit.[38] mp 364-365°C and mp 328-330°C); ^{1}H-NMR (DMSO-d_6) δ 12.95 (broad s, 2H), 7.99 (d, J=8.7Hz, 4H), 7.15 (d, J=8.7

Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 166.7, 159.5, 131.8 (quadruple intensity), 126.5, 118.7 (quadruple intensity); IR (KBr) 2999- 2550 (carboxylic acid), 1700, 1597, 1425, 1308, 1292, 1254 cm^{-1} (Ar-O-Ar).

Bis(4,4'-chlorosulfonyl)diphenyl Ether (5)[40]. To a clean dry 150 mL 3-neck flask equipped with a nitrogen inlet, gas outlet, thermometer and magnetic stirrer was added 24 ml of chlorosulfonic acid. The reaction vessel was cooled to 12°C using an ice and water bath and the temperature was maintained while 14 g (0.082 mol) of diphenyl ether was slowly added over a 30 min period. The reaction mixture was allowed to come to room temperature and stirring continued for 2 h. The solution was extracted with 100 mL of diethyl ether twice and the combined extracts were washed with water. The diethyl ether was removed by rotary evaporation and a white solid resulted that was dried in vacuo which gave 21.7 g; yield = 72.3%; mp. 114-116°C; ^{1}H-NMR (DMSO-d_6) δ 7.60 (d, J=8.4 Hz, 4H), 6.97 (d, J=8.2 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 157.0, 143.1, 127.8 (quadruple intensity), 118.6 (quadruple intensity); IR (KBr) 3103, 1573, 1486, 1374, 1244 (Ar-O-Ar), 1187, 1165 cm^{-1} (R-SO_2-R); MS (relative intensity) m/e 368 (28.6), 366 (39.1), 331 (100), 267 (22.0), 168 (73.9), 139 (35.5), 92 (18.7).

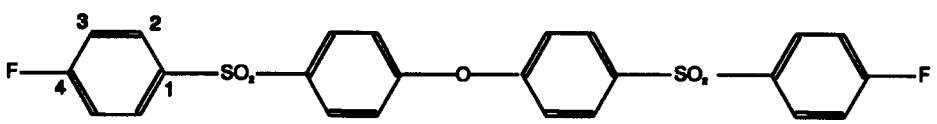
4,4'-Bis(4-fluorophenylsulfonyl)biphenyl (6). In an ice bath, under a nitrogen flow 10.0 g (0.028 mol) of 4,4'-biphenylsulfonyl chloride, 25 mL of fluorobenzene and 9.4 g (0.068 mol) of aluminum chloride were stirred for twenty minutes. The resulting suspension was bright yellow. The ice bath was replaced with a heating mantle and the reaction vessel was fitted with a reflux condenser and heated to 40°C. Hydrogen chloride gas was liberated upon heating. Within two hours the suspension was light yellow.

After two days the mixture was poured into an ice/concentrated hydrochloric acid mixture and stirred for fifteen minutes. The off-white paste was isolated in a Buchner funnel at reduced pressure. The paste was washed in water until neutral and recrystallized from chloroform. The resulting light yellow crystalline solid weighed 9.39 g; yield = 73.3%; mp 258-260°C; ^{1}H-NMR (DMSO-d_6) δ 8.07, (d, J=8.7 Hz, 8H), 7.94, (d, J=8.5 Hz, 4H), 7.47, (t, J=8.7 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 164.6 (d, J = 250 Hz), 143.26, 140.82, 137.24, 130.74 (d, J_{C2CF}= 9 Hz, double intensity), 128.68 (quadruple intensity), 128.06 (quadruple intensity), 117.08 (d, J_{C3CF} = 23 Hz, double intensity); IR(KBr) 3422, 3070, 1589, 1493, 1323, 1292 (R-SO_2-R), 1234 (C=C-F), 1154 (R-SO_2-R), 1107, 1072, 1003 cm^{-1}; high-resolution MS m/e 470.0457 (calcd for $C_{24}H_{16}F_2O_4S_2$, 470.0407).

4,4'-Bis(4-chlorophenylsulfonyl)biphenyl (7)[41]. In an ice bath, under a nitrogen flow 10.264 g (0.029 mol) of 4,4'-biphenylsulfonyl chloride, 60 mL of chlorobenzene and 9.31 g (0.070 mol) of aluminum chloride were stirred for twenty minutes. The resulting suspension was bright orange. The ice bath was replaced with a heating mantle and the reaction vessel was fitted with a reflux condenser. Hydrogen chloride gas was liberated upon heating. Within two hours the suspension was light orange to brown. After two days the mixture was poured into an ice/concentrated hydrochloric acid mixture and stirred for fifteen minutes. The off-white paste was isolated in a Buchner funnel at reduced pressure. The paste was washed in water until neutral and recrystallized from chloroform. The resulting white crystalline solid weighed 9.49 g; yield = 67%; mp 268-270°C (lit.[41] 274°C); ^{1}H-NMR (DMSO-d_6) δ 8.06 (d, J=8.4 Hz, 4H), 8.02 (d, J=8.5, 4H), 7.94 (d, J=8.5 Hz, 4H), 7.70 (d, J=8.5 Hz,

4H); ^{13}C-NMR (DMSO-d_6) δ 143.4, 140.5, 139.7, 139.0, 130.0 (triple intensity), 129.5 (triple intensity), 128.7 (triple intensity), 128.2 (triple intensity); IR(KBr) 3095-3068, 1592, 1475, 1396, 1327, 1322, 1314, 1280, 1148, 1104, 1093 cm^{-1}; MS (relative intensity) m/e 506 (19), 504 (36), 502 (74), 159 (95), 116 (100).

1,1'-Oxybis[4-[(4-fluorophenyl)sulfonyl]benzene] (8). In an ice bath, under a nitrogen flow 10.0 g (0.027 mol) 4,4'-bis(4-chlorosulfonyl) diphenyl ether (**5**), 20 mL of fluorobenzene and 9.0 g (0.068 mol) of aluminum chloride was stirred for 20 min. The resulting suspension was brown/gray. The ice bath was replaced with a heating mantle and the reaction vessel was fitted with a reflux condenser and heated to 40°C. Hydrogen chloride gas was liberated upon heating. After two days the mixture was poured into an ice/concentrated hydrochloric acid mixture and stirred for fifteen minutes. The resulting off-white paste was filtered off, washed with water until neutral, and dried in vacuo which gave 9.52 g; yield = 72.5%; mp 164-166°C; ^{1}H-NMR (DMSO-d_6) δ 8.03 (d, J=8.8Hz, 4H), 7.99 (d, J=8.8 Hz, 4H), 7.48 (t, J=8.7 Hz, 4H), 7.28 (d, J=8.7 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 164.6 (d, J_{CF}= 253 Hz), 159.3, 137.5, 136.3, 130.5 (d, J_{C2CF}= 9.8 Hz), 130.1 (quadruple intensity) , 119.8 (quadruple intensity), 116.9 (d, J_{C3CF}= 22.9 Hz); MS (relative intensity) m/e 486 (100), 375 (22.5), 327 (1.1), 143 (21.3), 127 (7.1), 95 (55.9); high-resolution MS m/e 486.04060 (calcd for $C_{24}H_{16}F_2O_5S_2$, 486.04078).



1,1'-Oxybis[4-[(4-chlorophenyl)sulfonyl]benzene] (9)[41]. In an ice bath, under a nitrogen flow 1.5 g (4.27 mmol) of 4,4'-bis(4-chlorosulfonyl)diphenyl ether (**5**), 15 mL of chlorobenzene and 1.26 g (9.4 mmol) of aluminum chloride was stirred for 20 min. The resulting suspension was brown/orange. The ice bath was replaced with a heating mantle and the reaction vessel was fitted with a reflux condenser. Hydrogen chloride gas was liberated upon heating. After two days the mixture was poured into an ice/concentrated hydrochloric acid mixture and stirred for 15 min. The off-white layer was pipetted off and washed with water, dried over sodium sulfate and the excess solvent was removed. The product was recrystallized from 1,4-dioxane which gave 1.19 g; yield = 54%; mp 190-192°C; ^{1}H-NMR (DMSO-d_6) δ 8.02 (d, J=8.7 Hz, 4H), 7.97 (d, J=8.5 Hz, 4H), 7.70 (d, J=8.6 Hz,4H), 7.29 (d, J=8.8 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 159.5, 140.0, 138.7, 136.0, 130.3 (quadruple intensity), 129.9 (quadruple intensity), 129.3 (quadruple intensity), 119.9 (quadruple intensity); IR(KBr) 3094, 1577, 1489, 1323, 1242 (Ar-O-Ar), 1153 (R-SO_2-R), 1107 (Ar-Cl), 1010, 871, 760 cm^{-1}; MS (relative intensity) m/e 518 (100) peaks for m+2 and m+4 also present, 486 (23), 391 (18), 359 (28), 111 (44).

4,4'-[Sulfonylbis(1,4-phenyleneoxy)]bis[benzoic Acid] (12)[31]. To a flask equipped with a Dean Stark trap, nitrogen inlet tube and mechanical stirrer was added 300 mg (2.17 mmol) of p-hydroxybenzoic acid, 301 mg (2.17 mmol) of potassium carbonate, 835 mg (3.28 mmol) of 4,4'-difluorodiphenyl sulphone, 20 mL of N,N-dimethylacetamide and 10 mL of toluene. The temperature was increased to 135-145°C in order to azeotrope off the water/toluene. After 6 h the temperature was increased

to 160-165°C and refluxed overnight. After cooling to 50°C, 7 mL of acetone was added and the mixture was stirred for thirty minutes, then filtered, washed with acetone and refiltered. The pink to white solid obtained was dissolved in water, acidified with sulfuric acid, filtered, washed with water until neutral and dried in vacuo. The resulting white solid weighed 357 mg; yield = 72%; mp 302-306°C; (lit.[31] mp 306-308°C); ^{1}H-NMR (DMSO-d_6) δ 8.02 (d, J=8.8 Hz, 4H), 7.94 (d, J=8.6 Hz, 4H), 7.20 (d, J=8.8 Hz, 4H), 7.16 (d, J=8.6 Hz, 4H) the carboxylic acid proton was not observed in this sample; ^{13}C-NMR (DMSO-d_6) δ 166.6, 160.0, 157.3, 135.4, 131.2 (triple intensity), 129.6 (triple intensity), 129.1, 118.8 (triple intensity), 118.4 (triple intensity); IR (KBr) 3600-2400 (broad, carboxylic acid), 1689 (C=O), 1294 (R-SO_2-R), 1246 (Ar-O-Ar), 1152 (R-SO_2-R), 1107 cm^{-1}. MS (relative intensity) m/e 490 (100), 446 (87.6). Anal. Calcd for $C_{26}H_{18}O_8S$: C, 63.67; H, 3.70; S, 6.54. Found: C, 63.59; H, 3.65; S, 6.62.

Alternate method for the preparation of 4,4'-[Sulfonylbis(1,4-phenyleneoxy)]bisbenzoic Acid (12). To a flask equipped with a Dean Stark trap, nitrogen outlet tube and magnetic stirrer was added 1.0 g (6.57 mmol) methyl p-hydroxybenzoate, 0.908 g (6.52 mmol) potassium carbonate, in 20 mL N,N-dimethylacetamide and 10 mL toluene. To the resulting solution was added 0.920 g (3.62 mmol) of 4,4'-difluorodiphenylsulphone.The temperature was increased to 135-145°C in order to azeotrope off the water/toluene. After 6 h the temperature was increased to 160-165°C and refluxed for 84 h. After cooling to 50°C, 500 mL of acetone was added and the mixture was stirred for one hour, filtered, washed with acetone for one hour and refiltered. The white solid

obtained was dissolved in water, acidified with sulfuric acid and stirred at 50°C for 30 min, filtered, washed with water until neutral and dried in vacuo. The resulting tan solid was recrystallized from dioxane to give 0.78 g; yield = 44 %. Characterization data same as above.

4,4'-[[1,1'-Biphenyl]-4,4'-diylbis(sulfonyl-1,4-phenyleneoxy)]bis [benzoic Acid] (13). To a flask equipped with a Dean Stark trap, nitrogen inlet tube, heating mantle and magnetic stirrer was added 37.77 g (0.248 mol) of methyl p-hydroxybenzoate, 34.28 g (0.248 mol) of potassium carbonate, 30.23 g (0.062 mol) of 4,4'-bis(4-chlorophenyl sulfonyl) biphenyl (**7**), 475 mL N,N-dimethylacetamide and 250 mL toluene. The temperature was increased to 135-145°C in order to azeotrope off the water/toluene. After 6 h the temperature was increased to 160-165°C and refluxed for 84 h. After cooling to 50°C, 500 mL of acetone was added and the mixture was stirred for 30 min, then filtered, washed with acetone and refiltered. The white to tan solid obtained was dissolved in water, acidified with sulfuric acid, filtered, washed with water until neutral and dried in vacuo. The resulting white solid was stirred in EtOAc and filtered to remove residual unreacted starting material. After drying overnight in vacuo to remove solvents 35.7 g of a white to coral solid was obtained; yield = 81%; mp <400°C decomposes at 322°C. ^{1}H-NMR (DMSO-d_6) δ 12.95 (s, broad), 8.06 (d,J=8.2 Hz, 4H), 8.03 (d, J=8.6 Hz, 4H), 7.98 (d, J=8.7 Hz, 4H), 7.94 (d, J=8.5 Hz, 4H), 7.24 (d, J= 8.8 Hz, 4H), 7.19 (d, J=8.8 Hz, 4H); ^{13}C-NMR (DMSO-d_6) δ 166.5, 160.3, 158.5, 143.1, 141.3, 135.5, 131.8, 130.2 (double intensity), 128.6 (double intensity), 128.0 (double intensity), 127.1 (double intensity), 119.4 (double intensity), 119.1 (double intensity); IR (KBr) 3071, (broad, carboxylic acid), 1689, (C=O),

1585, 1489, 1423, 1319, 1246 (Ar-O-Ar), 1153 (R-SO_2-R), 875, 763 cm^{-1} ; FAB 707.0, 688.9; Anal. Calcd for $C_{38}H_{26}O_{10}S_2$: C, 64.58; H, 3.70; S, 9.07. Found C, 65.94; H, 3.41; S, 7.39.

4,4'-[Oxybis (1,4-phenylenesulfonyl-1,4-phenyleneoxy)] bis[benzoic Acid] (14). To a flask equipped with a Dean Stark trap, nitrogen inlet tube, heating mantle and magnetic stirrer was added 7.77 g (0.051 mol) of methyl 4-hydroxybenzoate, 7.09 g (0.051 mol) of potassium carbonate, 5.03 g (0.013 mol) of 1,1'-oxybis[4-[(4-fluoro phenyl)sulfonyl]benzene] (**8**), 100 mL N,N-dimethylacetamide and 50 mL toluene. The temperature was increased to 135-145°C in order to azeotrope off the water/toluene. After 6 h the temperature was increased to 160-165°C and refluxed for 84 h. After cooling to 50°C, 500 mL of acetone was added and the mixture was stirred for 30 min, then filtered, washed with acetone and refiltered. The white to tan solid obtained was dissolved in water, acidified with sulfuric acid, filtered, washed with water until neutral and dried in vacuo. After drying overnight 7.27 g of a white to coral solid was obtained; mp >400°C decomposes at 288°C. ^{1}H-NMR (DMSO-d_6) δ 7.99 (d,J=2.3 Hz, 4H), 7.97 (d, J=2.4 Hz, 4H), 7.87 (d, J=2.1 Hz, 4H), 7.22 (d, J=8.6 Hz, 4H), 7.17 (d, J=8.6 Hz, 4H), 6.99 (d, J=8.6 Hz, 4H) the carboxylic acid proton was not observed in this sample; ^{13}C-NMR (DMSO-d_6) δ 166.5, 163.0, 160.1, 158.5, 136.2, 132.5, 132.1 (double intensity), 131.6 (double intensity), 130.3 (double intensity), 129.7, 129.5, 127.0, 120.5, 119.6 (double intensity), 119.3 (double intensity),114.1(double intensity); IR (KBr) 3071-2775, (broad, carboxylic acid), 1689, (C=O), 1585, 1489, 1423, 1305, 1223 (Ar-O-Ar), 1153 (R-SO_2-R), 875 cm^{-1}.

Attempted synthesis of 4,4'-(1,3-Phenylenebisoxy) bis[benzoic Acid] (15)[32]. 1,3-Diphenoxybenzene 1.0 g (5.87 mmol) was dissolved in 1.04 mL (14.5 mmol) of acetyl chloride, and 10 mL of dichloromethane under nitrogen. In another clean dry flask at 0°C (ice bath), 3.25 g (24.4 mmol) of aluminum chloride, was stirred in 10 mL of dichloromethane. The diphenoxybenzene solution was added dropwise to the aluminum chloride suspension and an orange to yellow suspension resulted. The ice bath was replaced with a heating mantle, the reaction vessel was fitted with a reflux condenser and the solution was refluxed for 12 h. The resulting brown residue was allowed to cool and stirred with an excess of cold 10% hydrochloric acid. The suspension became light yellow. The mixture was extracted with chloroform and concentrated in vacuo. The resulting brown syrup was not purified and a ^{1}H-NMR and ^{13}C-NMR of the crude product indicated that the desired product had not been formed. ^{1}H-NMR (DMSO-d_6) δ 8.02 (d, J=2.0Hz), 7.93 (d, J=3.9), 7.21 (d, J=8.7 Hz), 7.14 (d, J= 8.7Hz), 7.04 (d, J=2.2Hz), 7.01 (d, J=2.4Hz), 6.78 (d, J= 2.3Hz), 2.50 (s), 2.54 (s), (The proton spectrum lacks the proton at δ 7.16 that would be expected for the meta-proton on the central aromatic ring.); ^{13}C-NMR (DMSO-d_6) δ196.5, 196.4, 196.0, 160.2, 160.1, 159.1, 155.6, 132.9, 132.8, 132.3, 130.8 (quadruple intensity), 126.3, 118.8 (double intensity), 117.4 (double intensity), 115.0, 111.1, 30.7, 26.6; IR (KBr) 2920, 1678 (C=0), 1589 (Ar-O), 1485, 1263 (C-O-C), 1223, 1165, 983, 960. The oxidation to the diacid was not carried out because it was clear that bis[4,4'-acetyl]-1,3-diphenoxybenzene had not formed cleanly.

5,5-Dimethyl-2-(4-hydroxyphenyl)-1,3-dioxalane (16)[34]. To a clean dry 3-neck flask equipped with a magnetic stirrer, thermometer, Dean Stark trap, nitrogen inlet and an addition funnel was added 2.35 g (0.019 mol) of 4-hydroxybenzaldehyde, 2.00 g (0.019 mol) of 2,2 dimethyl-1,3 propanediol and 200 mL of toluene. This was stirred and heated to reflux (105°C). A mixture of 4.09 g of p-toluene sulfonic acid monohydrate in 100 mL was placed in the addition funnel and slowly added to the reaction flask as the water evolved during the reaction was azeotroped off into the Dean Stark trap. The solution was amber after 1 h and stirring was continued at reflux for 2 h. The p-toluene sulfonic acid monohydrate was not totally soluble in the cool toluene so an excess was added. The amber solution was cooled to 70°C and half of the toluene was removed using rotary evaporation. The remaining solution was washed with 2X 50 mL of 5% sodium hydrogen carbonate. The organic phase was dried over magnesium sulfate and the remaining solvent was removed by rotary evaporation and vacuum. The crude product contained a small amount of starting material and was purified using flash chromatography (50% EtOAc:50% Hexane) which gave 914 mg; yield = 79%; mp 124-128°C; ^{1}H-NMR (DMSO-d_6) δ 9.46 (s, 1H), 7.22 (d, J=8.5 Hz, 2H), 6.72 (d, J=8.5 Hz, 2H), 5.28 (s, 1H), 3.63 (d, J=10.5 Hz, 2H), 3.56 (d, J=10.7 Hz, 2H),1.18 (s, 3H), 0.74 (s, 3H); ^{13}C-NMR (DMSO-d_6) δ 157.5, 129.5, 127.4 (double intensity), 114.6 (double intensity), 100.9, 76.5 (double intensity), 29.7, 22.7, 21.4; IR (KBr) 3302 broad (O-H), 2951, 2866 (C-H), 1616, 1601, 1523, 1450, 1223 (C-O), 1081, 833 (C-O-C); MS (relative intensity) m/e 207 (50), 191 (9), 121 (100); Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; O, 23.05. Found: C, 69.35; H, 7.86; O, 22.79.

4,4'-[Sulfonylbis(1,4-phenyleneoxy-1,4-phenylene)]bis-2-(5,5-dimethyl-1,3-dioxalane (17). To a flask equipped with a Dean Stark trap, nitrogen inlet tube and mechanical stirrer was added 25.0 g (0.12 mol) of acetal **(16)**, 24.0 g (0.18 mol) of potassium carbonate, 17.2 g (0.06 mol) of 4,4' dichlorodiphenyl sulphone, 425 mL of N,N-dimethylacetamide and 210 mL of toluene. The temperature was increased to 135-145°C in order to azeotrope off the water/toluene. After 6 h the temperature was increased to 155-165°C and refluxed overnight. The resulting product solution was used to form the dialdehyde **(18)**. As a result of flash chromatography used in attempts to purify the dialdehyde **(14)**, a sample of the pure diacetal was obtained as a 70 mg sample of yellow crystalls; mp 156-158°C; ^{1}H-NMR (DMSO-d_6) δ 7.92 (d, J=8.9 Hz, 4H), 7.50 (d, J=8.6 Hz, 4H) 7.13 (d, J= 2.6 Hz, 4H), 7.10 (d, J= 2.8 Hz, 4H), 5.43 (s, 2H), 3.65 (d, J= 10.5 Hz, 4H), 3.62 (d, J= 10.5 Hz, 4H), 1.18 (s, 6H), 0.75 (s, 6H); ^{13}C-NMR (DMSO-d_6) δ 154.6, 145.2, 135.6, 135.2, 129.8, 128.3, 119.8, 117.9, 100.1, 76.5, 29.8, 22.7, 21.3; IR (KBr) 2951, 1585, 1489, 1305,1242 (Ar-O-Ar), 1153 (R-SO_2-R), 1107, 856 (C-O-C) cm^{-1}. MS (relative intensity) m/e 630 (100), 543 (72), 457 (61); high-resolution MS m/e 630.2284 (calcd for $C_{36}H_{38}O_8S$, 630.2288).

4,4'-[Sulfonylbis(1,4-phenyleneoxy)] bis[benzaldehyde] (18). The diacetal (**17**) was stirred in 200 mL of acetone in a 500 mL round bottom flask equipped with a magnetic stirrer. To the resulting solution 250 mL of 4M HCl was added dropwise and the reaction mixture was stirred for 24 h at room temperature. The acetone and a large portion of the water was removed by rotary evaporation. Upon cooling a yellow to white solid was observed in the reaction vessel. The yellow solution was filtered using a

Buchner funnel and the isolated solid was dried in vacuo. After drying overnight 5.0 g of a white to yellow solid was obtained. Recrystallization from 1,4-dioxane gave the desired product. ^{1}H-NMR (DMSO-d_6) δ 9.96 (s, 2H), 8.01 (d, J=8.9 Hz, 4H), 7.98 (d, J= 8.6 Hz, 4H), 7.28 (d, J= 8.6 Hz, 8H); ^{13}C-NMR (DMSO-d_6) δ 192.0, 160.2, 106.0, 136.6, 132.9 (double intensity), 130.4 (double intensity), 119.9 (double intensity), 119.8 (double intensity); IR (KBr) 3416, 3130 (C-H,doublet), 1697 (C=O), 1581, 1487, 1300,1246 (Ar-O-Ar), 1149 (R-SO_2-R), 1105, 877 (C-O-C) cm^{-1}; high-resolution MS m/e 458.08231 (calcd for $C_{26}H_{18}O_6S$, 458.082).

Synthesis of Polymers

Poly ([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,4-phenyleneoxy-1,4-phenylene) (19)[14]. In a clean dry flask under nitrogen was added 198 mg (0.50 mmol) of 3,3'-diaminobenzidine tetrahydrochloride dihydrate and 5.8 g of polyphosphoric acid. The solution was heated at 120°C with stirring for 1 h and bubbles of hydrochloric acid were eliminated. To this flask 140 mg (0.50 mmol) of 4,4'-oxybis[benzoic acid] **(2)** was added and the temperature was increased to 160°C. After 36 h the reaction mixture was viscous and the hot polymer solution was stirred into dilute sodium bicarbonate, filtered, washed with water and refluxed in water for 2 h. The polymer was then filtered, washed with water and dried in vacuo at 160°C for 36 h. The resulting polymer was orange brown and weighed 215 mg; yield = 64%; mp >400°C; η_{inh}= 0.25 dL/g in DMAc; UV in DMAc (2.5 x10^{-5}M) 346 nm, 290 nm; IR(KBr) 3438 broad, 1653, 1453, 1458, 1270 cm^{-1}.

Poly([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,3-phenylene) (20)[25]. In a clean dry flask under nitrogen was added 214 mg (1.00 mmol) of 3,3'-diaminobenzidine and 5 mL of polyphosphoric acid. The solution was heated at 140°C with stirring for 1 h. To this flask 166 mg (1.00 mmol) of isophthalic acid was added and the temperature was increased to 160°C. After 24 h the reaction mixture was viscous and the hot polymer solution was stirred into dilute sodium bicarbonate, filtered, washed with water and refluxed in water for 2 h. The polymer was then filtered, washed with water and dried in vacuo at 160°C for 36 h. The resulting polymer was brown and weighed 379 mg; yield = 98%; mp >400°C; η_{inh}= 1.16 dL/g in DMAc/4%LiCl; IR(KBr) 3194 broad, 1626, 1558, 1442, 1408, 1270, 796 cm^{-1}.

Poly ([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (21). In a clean dry flask under nitrogen was added 83 mg (0.39 mmol) of 3,3'-diaminobenzidine and 2 mL of phosphorus pentoxide/methane sulfonic acid. The solution was heated at 120°C with stirring for one hour. To this flask 190 mg (0.39 mmol) of 4,4'-[sulfonylbis(4-phenyleneoxy)]dibenzoic acid **(12)** was added and the temperature was increased to 140°C. After 1.5 h the reaction mixture was extremely viscous and was thinned by adding 2 mL of methane sulfonic acid. The hot polymer solution was stirred into aqueous 10% sodium hydroxide, filtered, washed with water and refluxed in water overnight. The polymer was then filtered, washed with water and dried in vacuo at 160°C for 36 h which gave 234 mg; yield = 86%; mp>400°C; η_{inh}= 1.62 dL/g in DMAc/4% LiCl; UV in DMAc (2.5 x

10^{-5}M) 336 nm, 268 nm; IR(KBr) 3428 broad, 1653, 1558, 1506, 1456, 669 cm^{-1}.

Poly ([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl [1,1'-biphenyl]-4,4'-diylsulfonyl-1,4-phenyleneoxy-1,4-phenylene) (22). In a clean dry flask under nitrogen was added 93.5 mg (0.44 mmol) of 3,3'-diaminobenzidine, 214 mg (0.31 mmol) of 4,4'- [(1,1'-biphenyl]-4,4'-diylbis (sulfonyl-4,1-phenyleneoxy)] bis[benzoic acid] **(13)** and 2 mL of phosphorus pentoxide/methane sulfonic acid. The solution was heated at 70°C with stirring for 30 min and the temperature was then increased to 100°C for 2 h. The resulting brown/black polymer was very viscous.The hot polymer solution was stirred into water and the resulting solids were ground with a mortar and pestle and refluxed in water overnight. The polymer was then filtered, washed with water and dried in vacuo at 150°C for 36 h which gave 300 mg; yield = 97.5%; mp>400°C; η_{inh}= 0.84 dL/g in DMAc; UV in DMAc (10 x 10^{-5}M) 334 nm, 296 nm; IR(KBr) 3437, 1585, 1489, 1250, 1153, 1107 cm^{-1}.

Poly ([5,5'-bi-1H-benzimidazole]-2,2'-diyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (23). In a clean dry flask under nitrogen was added 214 mg (1.00 mmol) of 3,3'-diaminobenzidine, 722 mg (1.00 mmol) of 4,4'- [oxybis(4,1-phenylenesulfonyl-4,1-phenyleneoxy)] bis[benzoic acid] **(14)** and 2 mL of phosphorus pentoxide/methane sulfonic acid. The solution was heated at 110°C with stirring for 1 h and the temperature was then increased to 140°C for 2.5 h. The resulting brown/black polymer was very viscous.The hot polymer solution was

stirred into water and the resulting solids were ground with a mortar and pestle and refluxed in water overnight. The polymer was then filtered, washed with water and dried in vacuo at 160°C for 48 h which gave 930 mg; yield = 99%; mp>400°C; η_{inh} = 0.20 dL/g in DMAc; UV in DMAc (7 x 10^{-5}M) 336 nm, 296 nm, 284 nm; IR(KBr) 3450 broad, 3050, 2990, 1610, 1585, 1460, 1210, 1075, 770 cm^{-1}.

REFERENCES

1. Neuse, E.W. *Adv. Polym. Sci.* **1982**, *47*, 2.

2. Kourtides, D. A.; Parker, J. A. *Polym. Eng. Sci.*, **1975**,*15*, 415.

3. Helminiak, T. E.; Benner, C. L.; Gibbs, W. E. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **1990**, *31*, 291.

4. Scariah, K. J.; Krishnamurthy, V. N.; Rao, K. V. C. *J. Polym. Sci., Polym. Chem Ed.*, **1987**, *25*, 2675.

5. Dudgeon, C. D.; Vogl, O. *J. Polym. Sci., Polym. Chem Ed.*, **1978**, *16*, 1831.

6. Levine, H. H. *Encycl. Polym. Sci. Tech.*, **1969**, *11*, 188.

7. Heliniak, T. E.; Benner, C. L.; Gibbs, W. E.; Kojima, T.; Yokota, R.; Kochi, M.; Kambe, H *J. Polym. Sci., Polym. Phys. Ed.*, **1980**, *18*, 1673.

8. Odian, G. *Principles of Polymerization, 2nd Ed.*; Pergamon Press: New York, **1989**.

9. Higgins, J.; Marvel, C. S. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **1970**, *8*, 171.

10. Cotter, R. J.; Matzner, M. *Ring-Forming Polymerizations, Pt. B, Vol. 1, Heterocyclic Rings,* Academic Press, New York, **1972**, 163.

11. Ueda, M.; Sugita, H.; Sato, M. *J. Polym. Sci., Polym. Chem Ed.*, **1986**, *24*, 1019.

12. Tsur, Y.; Levine, H. H.; Levy, M. *J. Polym. Sci., Polym. Chem Ed.*, **1974**,*12*, 1515.

13. Iwakura, Y.; Keikichi, U.; Yoshio, I. *J. Polym. Sci., Polym. Chem Ed.*, **1964**, *2*, 583.

14. Ueda, M.; Sato, M.; Mochizuki, A. *Macromolecules*, **1985**,*18*, 2723.

15. D'Alelio, G. F. US Pat. 3763107, **1963**.

16. Azmus, D. M.S. Thesis, Oregon State University, Oregon,**1992.**

17. Korshak, V. V.; Rusanov, A. L.; Tugushi, D. S.; Cherkasova, G. M. *Macromolecules*, **1972**, *5*, 807.

18. Milford, G. N. US Pat. 4394500,**1983**.

19. Brock, T.; Sherrington, D. C. *Polymer*, **1992**, *33* (8), 1773.

20. Izyneev, A. A.; Varga, J.; Mazurevskaya, S. P.; Novak, I. S.;Mazurevsky, V. P.; Mognonov, D. M.; Radnaeva, L. D. *Acta Polymerica*, **1991**, *42*, 128.

21. Kane, J. J.; Tomlinson, R. C. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **1990**, *31*, 709.

22. Odian, G. *Polymer Synthesis*. American Chemical Society: Washington, D. C., **1975**.

23. Wasidlo, W.; Levine, H. H. *J. Polym. Sci., Polym. Chem Ed.*, **1964**, *2*, 4795.

24. Gray, D. N.; Shulman, G. P.; Conley, R. T. *Macromol. Sci. (Chem.)*, **1967**, *A1* (3), 395.

25. Ueda, M.; Sugita, H. *J. Polym. Sci., Polym. Chem Ed.*, **1989**, *27*, 2815.

26. Gilman, N. W. *Chem. Commun.*, **1971**, 733.

27. Coville, N. J.; Neuse, E. W. *J. Org. Chem.*, **1977**, *42*, 3485.

28. Smith, J. G.; Connell, J. W.; Hergenrother, P. M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **1991**, *32*, 193.

29. Neuse, E. W.; Loonat, M. S. *Macromolecules*, **1986**, *19*, 481.

30. Mulvaney, J. E.; Figueroa, F. R.; Wu, S. J. *J. Polym. Sci., Polym. Chem Ed.*, **1986**, *27*, 618.

31. Idage, S. B.; Idage, B. B.; Shinde, B. M.; Vernekar, S. P. *J. Polym. Sci., Polym. Chem Ed.*, **1989**, *27*, 583.

32. Evers, R. C.; Arnold, F. E.; Helminiak, T. E. *Macromolecules*, **1981**, *14*, 925.

33. Davies, D. G.; Derenberg, M.; Hodge, P. *J. Chem. Soc. (C),* **1971**, 455.

34. Meskens, F. A. J. *Synthesis*, **1981**, 501.

35. Perrin, D. D.; Armarego, W.; Perrin, D. R. *Purification of Laboratory Chemicals, 2nd Ed.*; Pergamon Press: New York, **1989**.

36. Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.,* **1973**, *38*, 4071.

37. *Catalog Handbook of Fine Chemicals*; Aldrich Chemical Company: Milwaukee, WI, **1990**.

38. Litter, M. I.; Marvel, C. S. *J. Polym. Sci., Polym. Chem Ed.,* **1985**, *23*, 2205.

39. Levine, R.; Stephens, J. R. *J. Amer. Chem. Soc.*, **1950**,*72*, 1642.

40. Marvel, C. S.; Caesar, P. D. *J. Amer. Chem. Soc.*, **1951**, *73*, 1097.

41. Balanda, P. B.; Cummings, D.; Mohanty, D. K. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.,* **1990**, *31*, 671.