# SYNTHESIS OF POLYBENZIMIDAZOLES FROM MONOMERS CONTAINING FLEXIBLE LINKAGES

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# AN ABSTRACT OF THE THESIS OF

Dora J. Taylor Azmus for the degree of Master of Science in Chemistry presented on 13 May 1992.

Title: Synthesis of Polybenzimidazoles from Monomers Containing Flexible Linkages

Abstract approved: Richard W Thies
R. W. Thies

Polybenzimidazoles were synthesized from 3, 3', 4, 4'-tetraminobiphenyl (diaminobenzidine, or DAB) with orthoesters, carboxylic acid derivatives (an ester and an acid) and with m-benzenedialdehyde. The products were of low molecular weight, as evidenced by low inherent viscosity, except in the case of the dialdehyde plus DAB. The product of that system had inherent viscosities in the range of 0.7 dL/g, and formed strong, flexible films. Based on these results, a dialdehyde monomer was made from naphthalene disulfonyl dihalides and p-hydroxybenzaldehyde. In addition to the aldehyde end groups, this monomer contained internal sulfonate linkages, which were intended to increase the flexibility of the target polybenzimidazole which resulted when it was condensed with DAB. These polymerizations yielded poor polybenzimidazoles, probably due to lack of purity of the new dialdehyde monomer. Another type of monomer was also produced by condensing DAB with p-hydroxybenzaldehyde. The resultant bibenzimidazole unit with two phenolic end groups shows promise for use in nucleophilic aromatic substitution polymerizations.

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# Synthesis of Polybenzimidazoles from Monomers Containing Flexible Linkages

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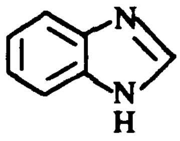
# Synthesis of Polybenzimidazoles from Monomers Containing Flexible Linkages

## INTRODUCTION

Polybenzimidazoles (PBIs) are a group of polymeric substances which contain the benzimidazole ring (shown in Figure 1) in the repeating unit.

**Figure 1.** Benzimidazole ring



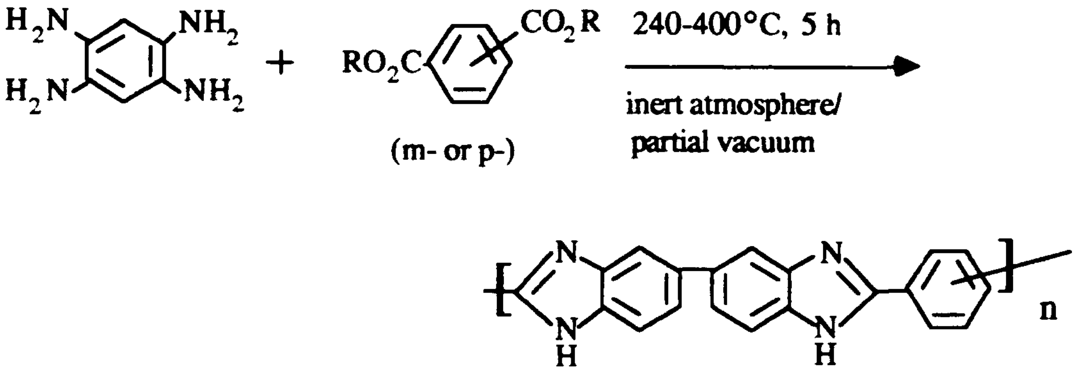
They are valued for their heat-resistance, with many potential applications, including aerospace and safety equipment. To date, their handling difficulties, low molecular weights and high price have limited their production and use.

### Early History of Polybenzimidazoles

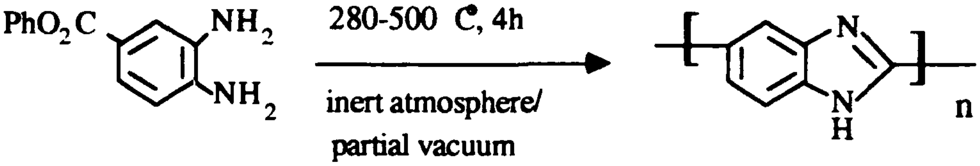
In 1960, Marvel synthesized the first all-aromatic polybenzimidazoles from aromatic diacids and tetramines, in a melt polycondensation process.[1] Note that this system (shown in Scheme 1) combined the polymerization and cyclization steps in a one-pot process, but the conditions were rather harsh.

**Scheme 1**

a. Using symmetrical monomers; R= H, Ph or Me



b. Using 3,4-diaminobenzoate

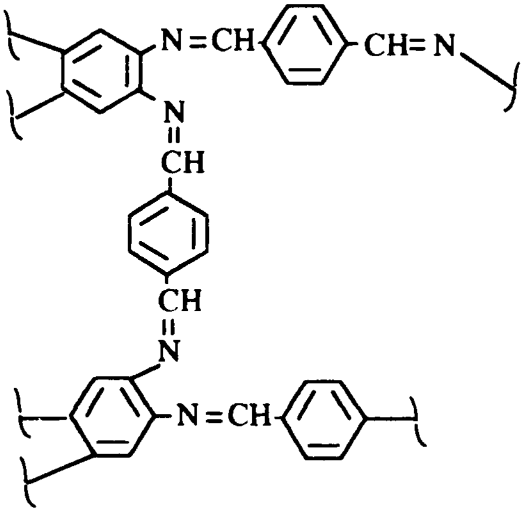


In 1964, PPA (polyphosphoric acid) was first used as solvent and condensing agent for the formation of PBIs from aromatic diacids and tetramines.[2] The temperature was lower (200 °C) but many monomers would not survive the strongly acidic conditions. Other drawbacks include undesired self-condensation of the tetramino monomers, and the frequent inability to completely remove the harsh solvent.[3]

In 1970, Higgins and Marvel published procedures for a solution polymerization of tetramines with the bisulfite adducts of dialdehydes, using polar aprotic solvents.[4]

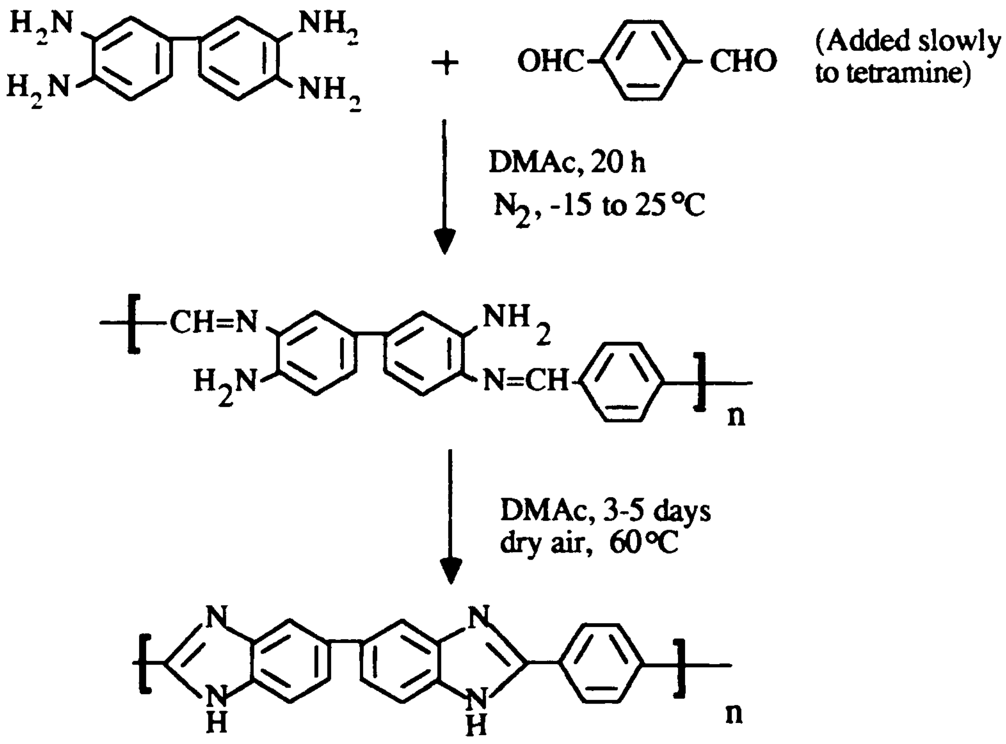
These polymerizations were run at the reflux temperatures of the solvents (165-200°C); and excessive crosslinking occurred when the unprotected dialdehydes were used. Uncontrolled cross-linking is a nuisance during processing, often rendering the product completely insoluble and unusable. In this case, the crosslinking was believed to be due to formation of aldehydine intermediates, as depicted in Figure 2. With this type of crosslinking, there is no free amino group available to easily close the benzimidazole ring, so the product often remains a polyimine.

**Figure 2.** Crosslinked aldehydine intermediate.



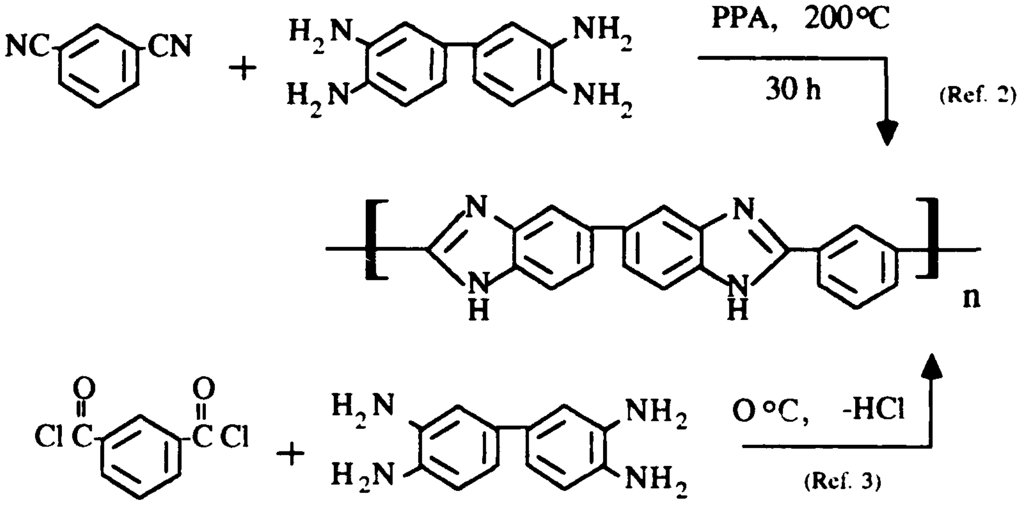
The aldehyde-amine condensation concept was extended further in a 1973 patent, which described several methods, including low-temperature polycondensations of aromatic tetramines with dialdehydes.[5] This system produced polymers of acceptable molecular weight, and provided clues to methods for limiting crosslinking, another problem especially troublesome for PBIs. Further refinements were made to this technique, which is summarized in Scheme 2.[6]

Scheme 2



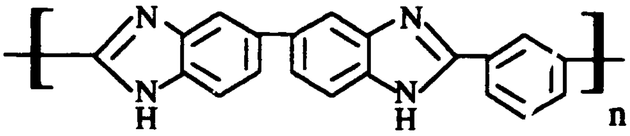
Several groups continued to pursue these compounds, developing milder polymerization conditions and various theories concerning the mechanisms of the reactions. In the 1960's and early 70's, PBIs were made by condensing various nitrogen-containing monomers (such as o-nitroanilines or tetramines) with nitriles, amides, carboxylic acids, aldehydes or acid chlorides.[2,4,7] Some examples are given in Scheme 3. Note that these reactions combine the polymerization and cyclization steps. Nitrogen compounds in higher oxidation states, such as o-dinitro aromatic compounds, have been used with various reducing agents to form benzimidazole monomers. However, there are no reports of benzimidazole-forming polymerizations using tetranitro components.

Scheme 3



Several years ago, Celanese developed methods for spinning a particular PBI (shown in Figure 3) into usable fibers, and began to market this under the tradename "polybenzimidazole". Thus far, the most important applications have been in protective clothing and heat-resistant paper products.

**Figure 3.** Celanese polybenzimidazole



IUPAC name: poly(2,5-benzimidazolediyl-5,2-benzimidazolediyl--1,3-phenylene).

## Properties of Polybenzimidazoles

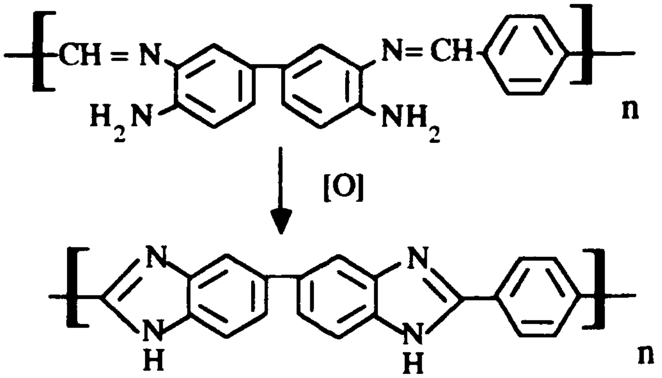
The presence of the benzimidazole ring conveys considerable heat resistance to polybenzimidazoles. PBIs have excellent heat-resistance for short-term exposure, retaining much of their structural integrity at temperatures of 600-650°C.[3] Long-term exposure, such as is encountered in thermogravimetry studies, causes loss of end groups at 350-400°C, and breakdown of aliphatic linkages at 400-600°C (under nitrogen).[1, 3] PBIs with aliphatic linkages become charred and brittle on long-term anaerobic exposure to temperatures of 900°C , but retain 80-90% of their weight.[3] This indicates that portions of the polymer do not degrade. Infrared and NMR spectroscopy confirm that the benzimidazole portions of polymer are still intact at these high temperatures.[1] Early calculations, using semi-empirical SCF-MO methods, estimate that the benzimidazole ring has a resonance stabilization of 129 kJ/mol. (C.f., 87 kJ/mol for pyridine and 83 kJ/mol for benzene, using the same method.)[8] This leads to the hope that the thermal properties could be further enhanced by eliminating the weaker portions of the repeating units. But even without such enhancement, this thermal resistance is far superior to that of aromatic polyamides (such as Kevlar or Nomex), which are also valued for high-temperature applications.[7]

It is generally accepted that heat stability of PBIs increases with molecular weight, as expected. But several more controversial conclusions have been drawn about trends in the thermal stability of PBIs. Substitution at the 1-nitrogen position has been claimed to enhance and to degrade thermal stability, as has the presence of ether and sulfone linkages.[3, 9] The presence of weak bonds in the repeating unit has been shown to decrease thermal stability of PBIs, but the definition of "weak" is open to question. Clearly, the presence of aliphatic carbon units diminishes thermal stability.[1] More doubtful is the 5-5' carbon-carbon bond of bibenzimidazole units. Several groups observed no difference in thermal stability of polybenzimidazoles (which do not have this carbon-carbon bond between the aromatic rings) and polybibenzimidazoles (which do).[3, 9] But in each case, other weak structural factors (such as methylene units) were present, making the conclusions ambiguous.

Solubility of PBIs is frequently a problem; the monomers or oligomers are often completely insoluble in the more common organic solvents. This has led to the routine use of expensive, polar aprotic solvents such as DMF (dimethyl formamide), DMSO (dimethyl sulfoxide), NMP (1-methyl-2-pyrrolidinone) and DMAc (N,N-dimethylacetamide). But even in these specialized solvents, as molecular weight increases, so does the likelihood that the polymer will "crash" out of solution. This often limits molecular weight, which in turn limits thermal stability.

One approach to the solubility problem has been to synthesize more soluble prepolymers, which can be altered to contain the benzimidazole unit (Scheme 4). Unfortunately, the prepolymers used thus far are usually polyazomethines, which are almost as insoluble and difficult to manage as are the PBIs they eventually become.[10]

Scheme 4



Concentration has also been adjusted, in attempts to overcome the solubility problems of PBIs. Decreasing the concentration of the polymerization mixture allows the polymer to stay in solution longer. However, polymerization kinetics suffer greatly as the reaction proceeds; very low concentrations decrease the frequency of polymer end groups encountering monomer.[11] Since high molecular weights are expected only very late in the reaction, the kinetic problem at lower concentration would essentially balance the benefit achieved by longer time in solution. Thus, the net gain from very low concentrations is that more expensive solvent is used, and molecular weight is essentially unchanged. Perhaps this could be overcome by further extending reaction times of the polymerization. However, since many methods already require 140-160 hours of reaction time, additional reaction time would be undesirable, and would severely limit commercial production.

The original melt polymerization method avoids the solubility problem altogether. However, some polymers made under these conditions show a large degree of cross-linking, making them insoluble in virtually all solvents after their initial synthesis.[1] The lack of workability in these cases makes the resulting polymer useless for many applications. Another problem with melt polycondensations is that the high temperatures required destroy (e.g., by decarboxylation) many of the monomers which one would like to incorporate into polybenzimidazoles. So the melt polymerization system is limited both in application and in the composition of the polymer itself.

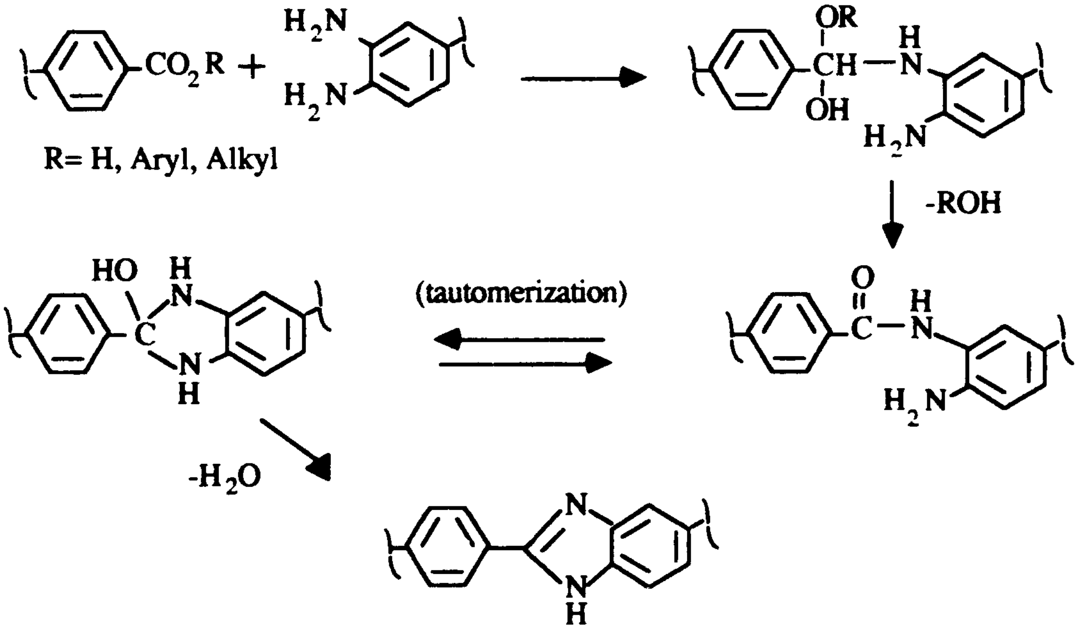
It is important to note that the limited solubility of PBIs, while a significant drawback during processing, makes the finished materials more durable and resistant to chemical degradation. One example of this is that the hydrolytic stability of Celanese PBI is superior to that of aromatic polyimides and polyamides.[11] This chemical resistance is potentially very useful in many applications.

## Proposed Mechanisms of Polybenzimidazole Synthesis

### Polar, aprotic solvents; diacid derivatives plus tetramines

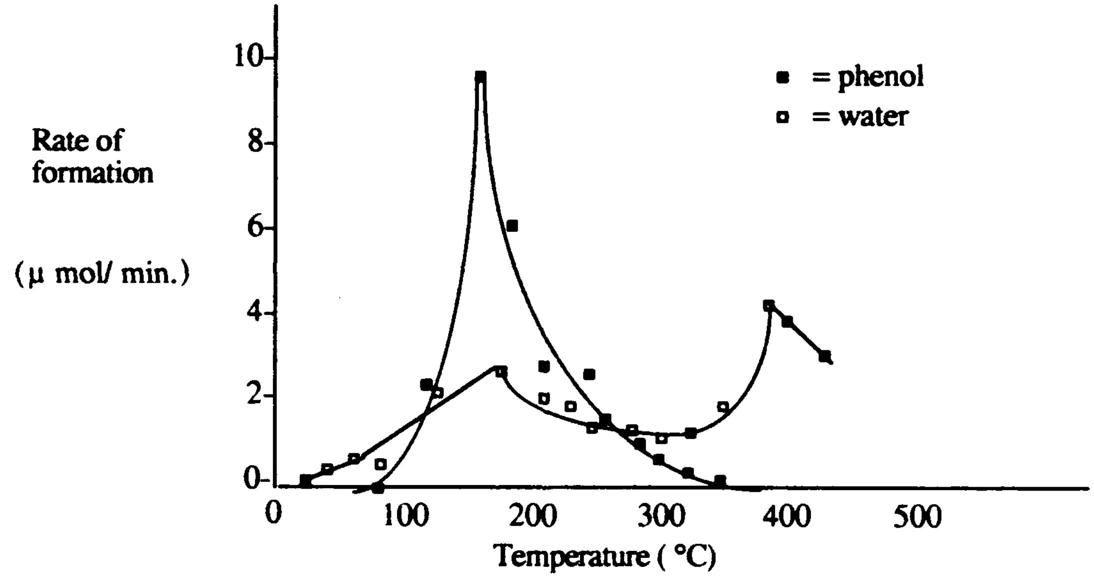
Two possible mechanisms have been proposed for this reaction system. The first is depicted in Scheme 5, an amidation followed by dehydration.

**Scheme 5**



The mechanism shown in Scheme 5 is supported by Gray's kinetic study of a melt polymerization of an aromatic tetramine with an aromatic diphenylester.[12] His group, using gas chromatography, followed the rate of appearance of water and phenol. Their findings suggest that phenol is generated before water. Analysis of their isolated intermediate suggested a partially hydrated structure, and the pattern of water evolution implied that the water was bonded covalently rather than electrostatically. At 400 °C, the product cyclized completely to the expected PBI. Some of the data from their study is presented in Figure 4.

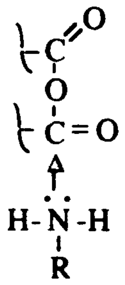
**Figure 4.** Data from Gray's kinetic studies of PBI formation



Mass spectroscopy study of phenol and water evolution.[12]
Note that the rates are nearly equal at 260 °C, and that water continues to form long after phenol formation has ceased. (Temperature was raised 10 °C/min throughout the experiment.)

Trends observed in polyamide synthesis in solution cast doubt on this being the major route from diacids to PBIs. Namely, aromatic amines do not normally condense with carboxylic acids to form amides, because the aromatic ring decreases the electron density of the amine nitrogens.[11] The reaction does occur, but the temperatures often required to drive this reaction cause undesired side-reactions, such as transamination and crosslinking. It is important that the systems described were monoacids, not diacids. Alkyl dicarboxylic acids do form amides, when condensed with amines in acidic solution with oxidizing agents present.[13,14] Higuchi proposed an acid anhydride intermediate, shown in Figure 5, in which the second carboxyl group facilitates the nucleophilic attack by the amine.

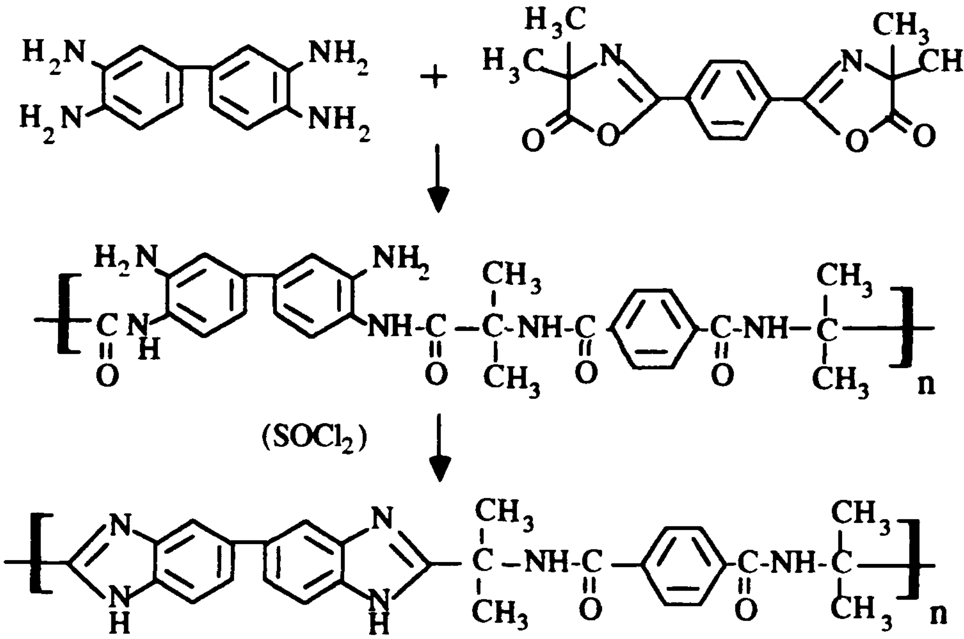
**Figure 5.** Proposed acid anhydride intermediate in conversion of diacids to amides



At fairly high concentrations, one might envision aromatic diacids being close enough to form the acid anhydride intermediate postulated in the alkyl diacid to amide pathway. If the nucleophilic-enhancement effect of this intermediate is enough to overcome the dampening effect of the aromatic amine, amides could be formed in aromatic systems. In fact, Yang, et al found that aromatic diacids will form amides with aromatic amines at 100 °C in a polymeric system.[15]

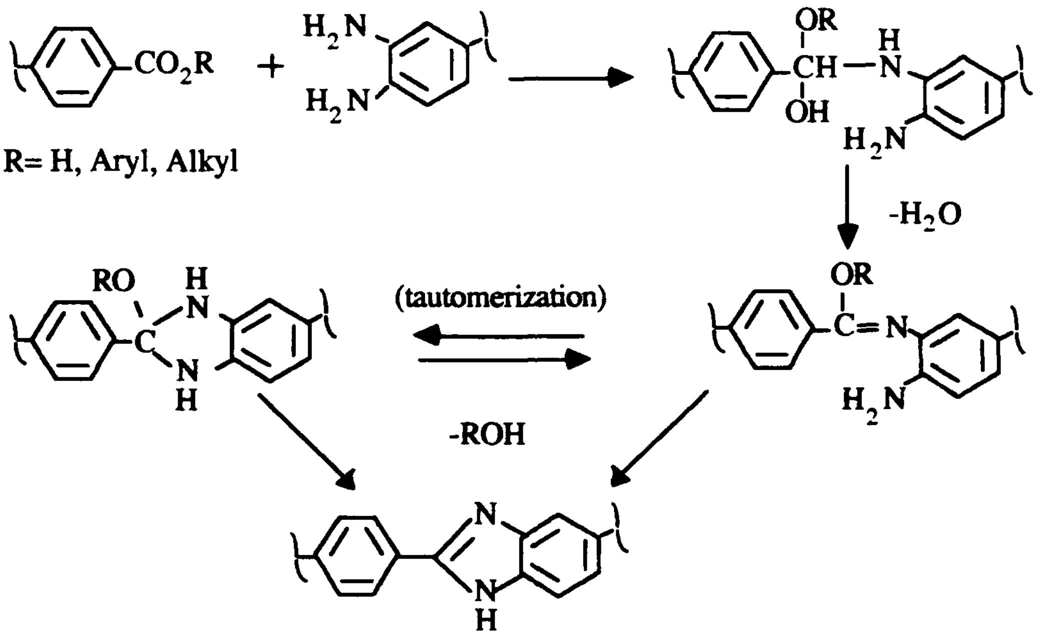
Polyamides can also be formed at low temperatures from the more active diacid dichlorides with diamines,[11] and from bisazlactones with diamines,[16,17] thus avoiding many of the side-reactions. One group has used bisazlactones to generate polyamides (their synthesis is shown in Scheme 6). Treating the polyamides with dehydrating agents confirmed that polybenzimidazoles are formed. This is convincing evidence that the latter portion of the mechanism shown in Scheme 5 is a viable pathway to polybenzimidazole, if the polyamide is formed.

Scheme 6



Wrasidlo and Levine conducted a previous kinetic study that supported a second possible mechanism, which is presented in Scheme 7.[18] In this proposed mechanism, the dehydration occurs first, followed by the loss of an alcohol.

Scheme 7

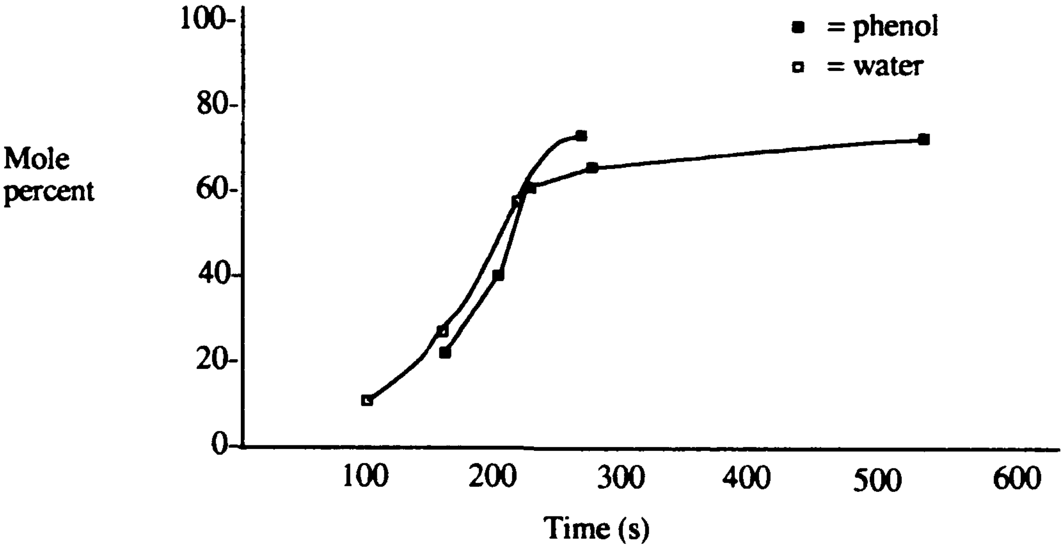


Wrasidlo and Levine used gas chromatography to monitor water formation and ultraviolet spectroscopy to measure formation of phenol. Their polymerization used the same monomers as Gray's study, but the design of their experiments are less certain than that of Gray. Specifically:

a) Studying water formation (by gas chromatography), Wrasidlo and Levine broke the reaction tubes under anhydrous methanol. The idea is that any gases generated during the reaction would escape into the methanol, which was then injected into the chromatography column. Since methanol is very hygroscopic, it might have contained enough water to affect the results of such an exact quantitative study. They did not report their method of drying the methanol, and their experimental procedures did not mention the extent of their precautions to exclude water during the workup. Gray's gas chromatography study involved pulling the volatile materials (with suction) directly from the reaction vessel into the chromatograph. This version, while running at a reduced pressure, eliminates the possibility of wet solvent affecting the results.

b) Studying phenol formation. Wrasidlo and Levine broke their reaction tubes under (into) distilled water, and measured the phenol content by ultraviolet spectroscopy. Gray used gas chromatography, as for the water study. But his results were also confirmed by an experiment in which both water and phenol were measured during a reaction, run on the mass spectrometer. One other element of Wrasidlo and Levine's experimental design is also less than satisfactory: the relatively low temperature. It was shown in several subsequent studies that cyclization is often incomplete at 260-300 °C.[3] This means that Wrasidlo and Levine might have been studying only part of the polymerization. Their data are shown in Figure 6.

**Figure 6.** Data from Wrasidlo and Levine's kinetic study of PBI formation.



Data from ultraviolet spectroscopy, in methanol (water) and from gas chromatography, in water (phenol).[18]
Experiment was run at 260 °C.

In spite of these experimental uncertainties, the mechanism proposed by Wrasidlo and Levine has been generally accepted as the major route to PBIs from diacids and tetramines. This is probably because the first benzimidazoles were made from azomethines, implying that they must be an intermediate in benzimidazole synthesis from other systems, as well.[19] Another likely factor is the analogy drawn to polymerizations of dialdehydes with tetramines (discussed in the next section of this paper), in which azomethine intermediates have been isolated. The validity of such analogies is questionable, since the monomers are in different oxidation states and the reaction conditions are very different in the two systems. It is significant that both kinetic studies were done on melt polymerizations; care must be used in extrapolating these results to solution polycondensations. To date, there have been no similar studies for these reactions in polar, aprotic solvent.

Another difficulty is that these reactions were run with aromatic esters, not acids. Clearly these systems are different. But using acids in this type of kinetic study would not have been useful, since both steps would give off water. It would have been impossible to distinguish between the steps.

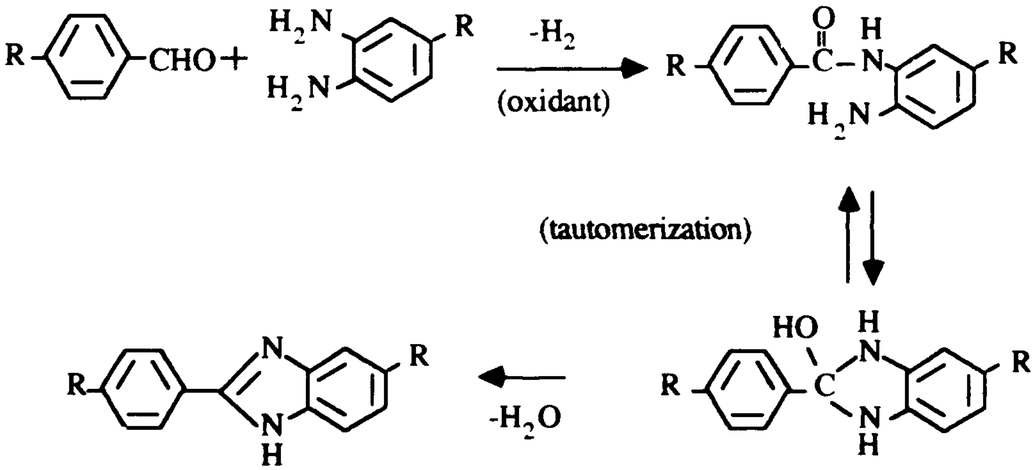
In model (nonpolymeric) systems, ortho-amino azomethines gave off hydrogen peroxide when cyclized to benzimidazole in the presence of air. The cyclization will also proceed in the absence of air and other oxidants, but in these cases, hydrogen gas is evolved.[20] While this has not been proven to occur in polymeric systems, it is generally accepted that this system is a good model for similar polymerizations. The finding that different byproducts result under different reaction conditions supports the idea that more than one route is occurring in these polymerization systems, depending on the specific conditions employed.

In short, because of all of the experimental uncertainties and system variables described above, it is genuinely impossible to know which mechanism is correct, without further study. Understanding the mechanism is important in choosing reaction temperature (to ensure the polymer is completely cyclized) and to know if the reaction steps are reversible. But in one respect, the question of mechanism has less bearing on the choice of conditions for diacids than for diesters. With the diacids, both steps will generate water; conditions which favor removal of water should encourage these polycondensations.

## Polar, aprotic solvents; dialdehydes plus tetramines

There have been no similar kinetic studies of the polymerizations of dialdehydes and tetramines. Two mechanisms have been proposed for this reaction system, both are similar to those given for diacid compounds. A major component of the proposed first mechanism shown in Scheme 8 is the presence of an amide intermediate.

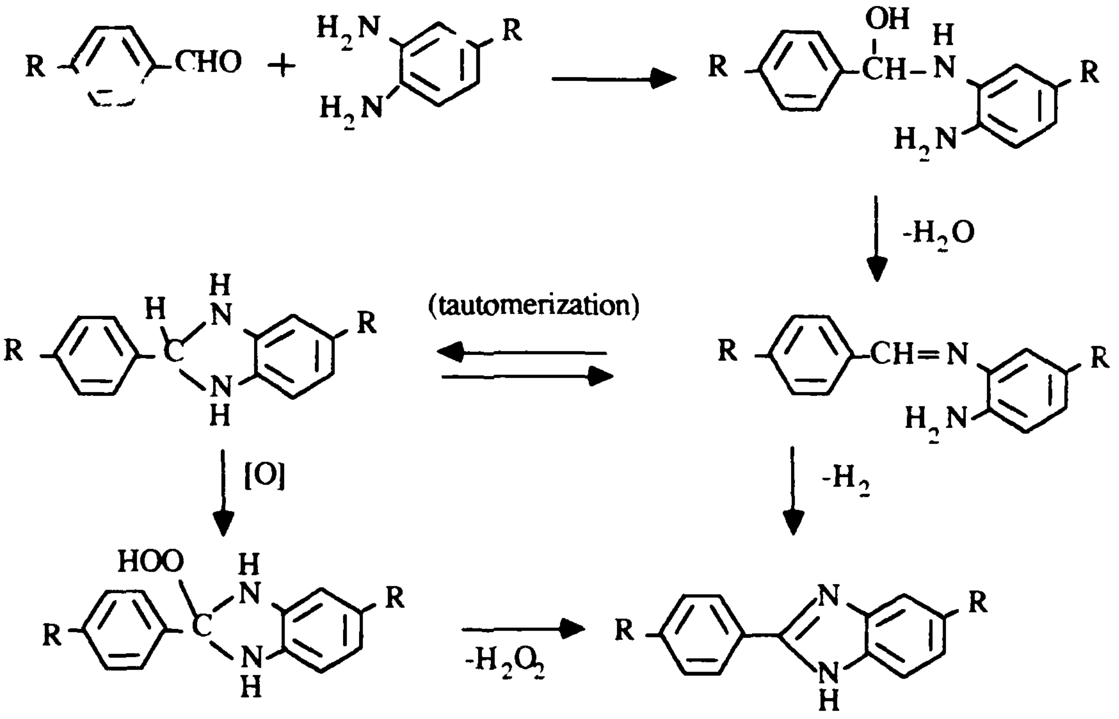
**Scheme 8**



One would not normally expect aldehydes plus amines to react to form amides. However this is known to occur in the presence of oxidants, such as nickel.[21, 22] Dialdehyde/tetramine polymerization systems often do include oxidants, such as iron trichloride with oxygen gas or air. So, while these particular combinations have not been specifically studied, the results from these nonpolymeric model systems suggest that it is possible to form polyamides from dialdehydes and tetramines under commonly employed conditions. Once polyamide is formed, dehydration should yield PBI. The bisazlactone example, shown in Scheme 6, would support the polyamide to polybenzimidazole conversion in the dialdehyde system, as well as the diacid system.

The second proposed mechanism includes an azomethine intermediate, and is shown in Scheme 9.

Scheme 9



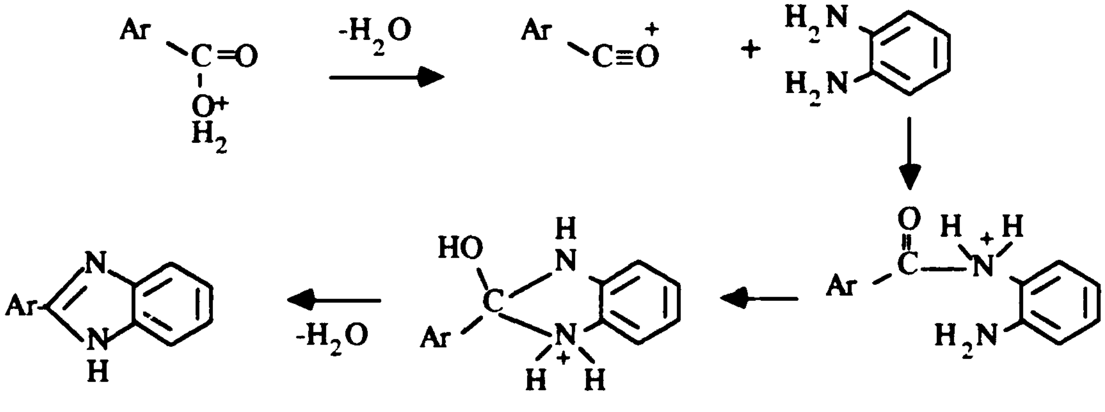
Several groups have isolated polyazomethine intermediates in similar solution polymerizations, strengthening the case for this mechanism.[22,23,24]

As with the diacid systems, it is likely that more than one reaction mechanism operates, depending upon variables in the reaction conditions which are not yet understood.

Acidic solvent; diacids plus tetramines

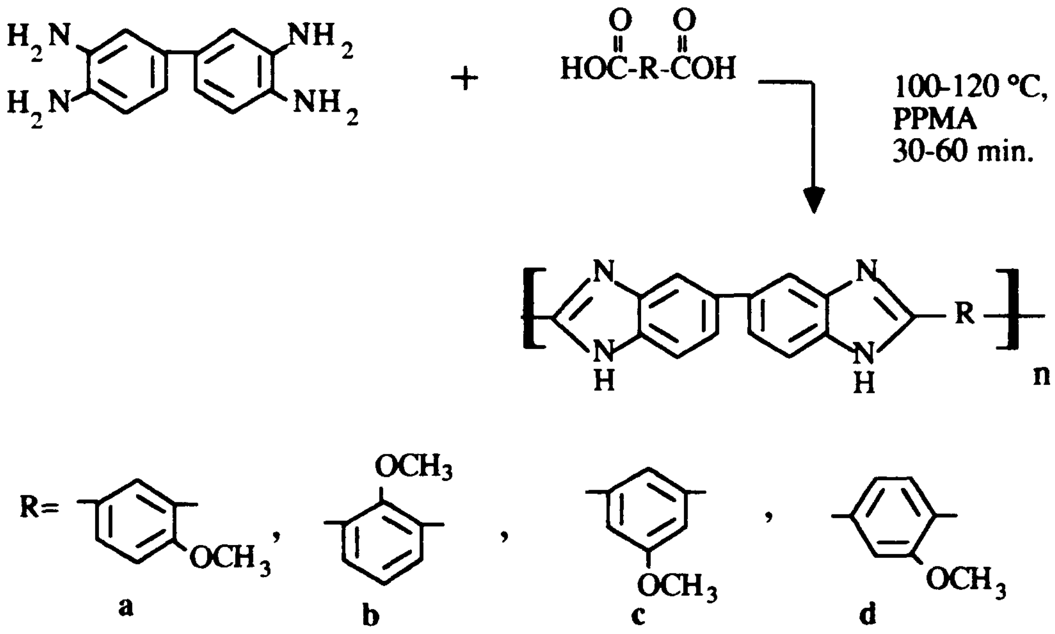
Recently, it has become routine to run PBI syntheses in PPA (polyphosphoric acid) to overcome solubility problems. Ueda and others have had success using the solvent PPMA (phosphorous pentoxide-methanesulfonic acid in a 1:10 weight ratio).[25,26] It is unlikely that the intermediates proposed for polar, aprotic solvents could withstand the strongly acidic solvent. When these monomers are condensed in PPMA, yet another mechanism can be pictured, which is shown in Scheme 10.

Scheme 10



Ueda's work with these systems points to acylium ion formation as the rate-determining step. His group found that the reactions would not occur with ortho- and para-substituted dicarboxylic acids, presumably because the acylium ion intermediate would be destabilized by electron-withdrawing substituents in these positions. They next undertook PBI synthesis using methoxyphthalic acids, postulating that the electron-donating methoxy group would stabilize the acylium ion. Their experimental system is summarized in Scheme 11.

**Scheme 11**



These researchers found that the isomers in which the methoxy substituent was meta to one or both of the carboxylic acid groups (c and d) gave significantly lower yields than the systems in which the substituent was ortho or para to both acid groups (a and b).[25] This result gave additional support to the theory of an acylium ion intermediate in the acid-catalyzed system.

## Experimental Factors that Influence Polymerizations

### Effects of water content on polymerization systems

Many polymerizations are extremely sensitive to the presence of small amounts of water. Water is often produced as polymer is formed, in equimolar amounts, so starting with dry solvents is not enough. Water must usually be removed during the course of the reaction so that its concentration does not rise. Figure 6 illustrates the extremely low limit of water concentration which must be maintained for a typical polymerization system.[11]

**Figure 7.** Effect of water on a step-polymerization. For a reaction in which one mole of water is generated per mole of repeating unit formed:

$$K = \frac{p[H_2O]}{[M_o]\,(1-p)^2}$$

$$p = \frac{K - K^{1/2}}{K - 1}$$

$$[H_2O]_{eq} = \frac{K\,[M_o]}{\bar{X}_n(\bar{X}_n - 1)}$$

$p$ = fraction of reaction

$[M]_o$ = initial concentration of monomer units

$\bar{X}_n$ = Degree of polymerization $= \frac{1}{1-p}$

Choosing K= 100 (see note), water concentration must be kept to the following limit in order to reach a degree of polymerization of 200.

$$[H_2O] = \frac{100\ (0.04\ \text{mol/L})}{200\ (199)} = 1 \times 10^{-4}\ \text{mol/L}$$

NOTE: $K_{eq}$ values for polymers in commercial production are typically in the range of 1 (polyesters) to 300 (polyamides). $K_{eq}$ values for polybenzimidazole reaction systems have not been determined.

One practical effect of this phenomenon is that solvents must be specially dried immediately before their use in polymerizations. Even solvents certified by their manufacturers to be anhydrous (such as "gold label") contained enough water to inhibit polymerization in the systems we studied. Various water removal methods have been used, including molecular sieves and azeotroping. The latter method is often complicated by the need to maintain low temperatures (to prevent crosslinking, discussed later).

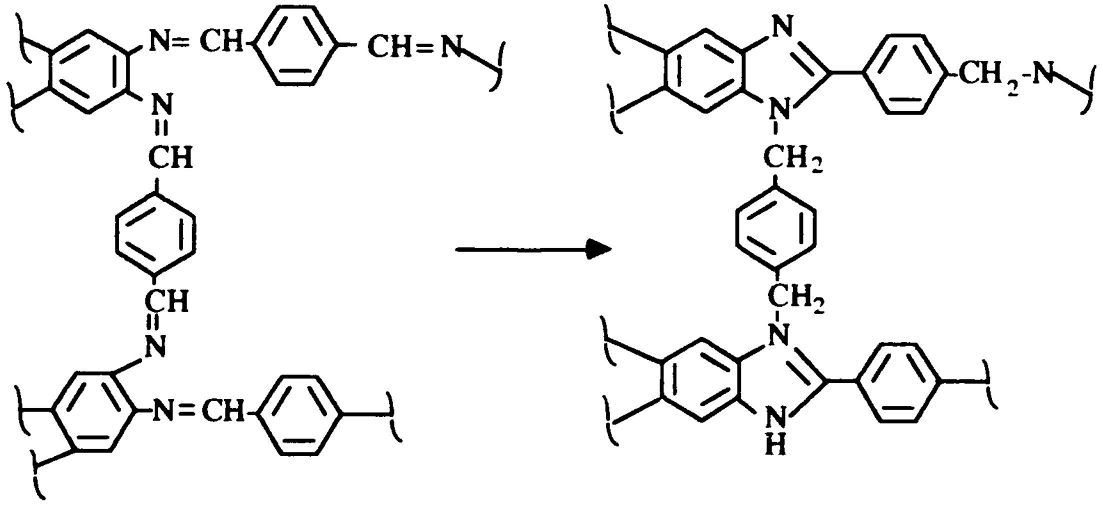
## Effects of single-sided monomers on polymerization systems

Another feature in polymerization systems, which must always be kept in mind, is the effect of "single-sided" monomers. In most other reactions, these defective starting materials would simply limit yield. But in polymerizations, mono-dentate monomers limit chain length, which can completely change the bulk properties of the product. Since the benzimidazole ring is so thermodynamically stable, the ring-closure is viewed as essentially irreversible. Once a single-sided monomer is added to the chain, and the ring is closed, that polymer chain cannot undergo any further reaction at that end. If this happens early in the polymerization, or if enough defective monomers are present, all of the polymer chains could be "capped" at a very low molecular weight.

## Effects of crosslinking on polymerization systems

Crosslinking is another factor which must be considered in choosing experimental conditions, especially with polybenzimidazoles. Ideally, both amino groups from the diamino/tetramino monomer will react with the same carbon atom in the carbonyl monomer, and a benzimidazole will result from these polymerizations. But since the ring closure has a fairly high activation energy, there is the potential for the reaction intermediates to equilibrate and for the growing polymer molecule to move and react with other free amino groups prior to ring closure. In some cases, this leads to formation of the aldehydine structure shown earlier (in Figure 2). This structure can remain, with uncyclized portions scattered throughout the finished polymer. Or the branch points can cyclize to N-substituted benzimidazoles, as shown in Figure 8. In either case, the polymer is crosslinked in three dimensions and the polymer is unworkable. Thus, the question is not only whether the thermodynamics of the system will drive the cyclization, but how quickly and efficiently the cyclization occurs. Several different approaches have been used to try to minimize crosslinking, in favor of linear polymers with high molecular weights.

**Figure 8.** Crosslinked PBIs from aldehydines



Using N-substituted amines is one such technique.[11] The rationale is that one side of the intermediate chain would be sterically blocked, thus favoring the reaction with the nearest amino group (the one ortho to the initial reaction site). Also, the presence of pendant groups on the amino nitrogens tends to anchor the growing polymer chain, limiting accessability to other reactive sites by restricting chain movement. Unfortunately, the substitution also tends to retard the reaction with the preferred nitrogen, raising the energy requirements for all reactions in the system. Another major limitation of this approach is that the substituted amines are more difficult to make and more expensive than their unsubstituted analogs. This would be especially troublesome in large-scale commercial production.

Another approach to limiting crosslinking is the slow addition of the dialdehyde monomers during PBI synthesis, to maintain a large excess of the amine. The aim is to keep the free aldehyde concentration so low that the ring closes before another carbonyl group can react with the same diamino monomer. This has been done at low temperature, to complement the effect of low concentration with the kinetic effects with reduced chain movement.[3] This has also been successful at higher temperatures (100-150 °C, with air). In the high temperature system, the energy and oxidant needed for ring closure is immediately available, and the ring is irreversibly formed before the ortho-amino group encounters any other reactive sites. The key points are to limit the availability of aldehyde monomers at any given moment, and to restrict the amount of equilibration that can occur before the benzimidazole ring is formed.

## Measurement of Polymer Molecular Weight

There are several methods to determine the molecular weight of polymers, including ebulliometry, gel permeation chromatography, ultracentrifugation, and others. Perhaps the easiest way to gauge the polymer size is to measure the inherent viscosity of a dilute polymer solution. This technique will not provide an actual number, without additional data from other studies of the particular system, but it will indicate if the polymer chain is growing. And correlations between the inherent viscosity and the physical properties of the polymer are simple to obtain by observing the types of films which result from solutions of varying viscosities. Thus, inherent viscosity measurement is a relatively simple way to monitor the course of the reaction, and to determine if the polymer has reached suitable length for the particular application planned.

In polymer literature, it is customary to report inherent viscosity measured at 0.5 g/dL at 25-30°C; this allows some coarse comparisons between reaction systems. Inherent viscosity is measured by timing the movement of the polymer solution through a viscometer, and comparing it to the time required for solvent to travel the same path. Using the formula detailed in Figure 9 gives the inherent viscosity.

**Figure 9.** Inherent viscosity measurement of a dilute polymer solution

$$\frac{t_{\text{sample}}}{t_{\text{solvent}}} = \eta_{\text{rel}}$$

t = time through viscometer, in s

$$\eta_{\text{inh}} = \frac{\ln(\eta_{\text{rel}})}{c}$$

c= concentration, in g/dL

Convention in polymer literature[11] is for $\eta_{\text{inh}}$ to be measured at 0.5 g/dL, at 25-30 °C

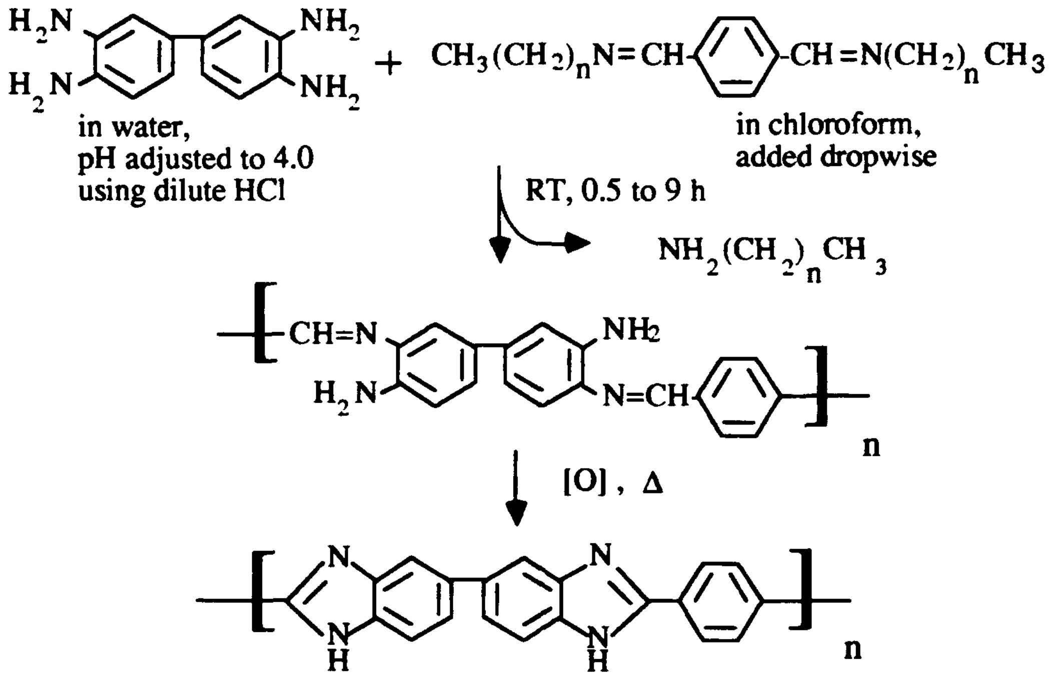
## Recent developments in PBI synthesis

A recent approach to polybenzimidazoles, mentioned earlier for its importance in clarifying mechanistic models, was that of condensing an aromatic tetramine with a bisazlactone.[16,17] (This approach was shown as Scheme 6.) The resulting poly(amide-benzimidazole)s were of low molecular weights (inherent viscosities of 0.10 to 0.12 dL/g). Films were brittle and decomposed at temperatures considerably lower than expected for polybenzimidazoles. Proton and carbon NMR studies indicated incomplete cyclization in the polymer. It was unclear whether the poor thermal properties were due to the low molecular weight, the decreased amount of cyclization, or the introduction of amide linkages in the polymer backbone.

Many of the same researchers reported that longer reaction time, and the introduction of dehydrating agents (such as thionyl chloride) increased the degree of cyclization. [17] However, when phosphorous pentoxide was used, the reaction produced intractible oils which were impossible to analyze. Even with successful cyclization, the molecular weights remained low. Thermal stability data were not given. Still, the fact that the amide cyclized to the benzimidazole ring in dehydrating agents does support the viability of the mechanisms depicted in Schemes 5 and 8. And treatment of other ortho-amino polyamides with thionyl chloride and heat, or perhaps air or other oxidants, could provide another route to PBIs.

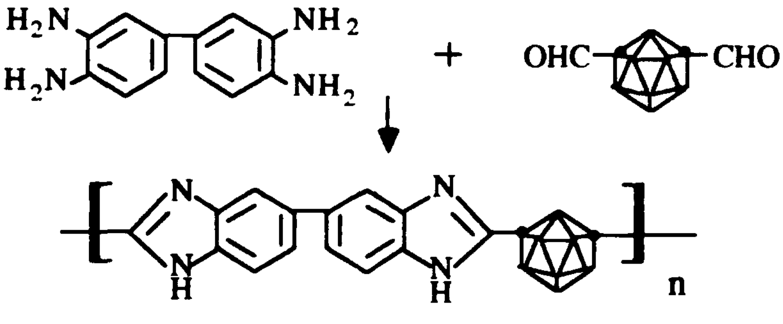
Ueda's group has recently studied different synthetic methods for PBI synthesis; namely, intrafacial polymerization of tetramines in acid and aldimines. This system, which is shown in Scheme 12, produces ultra-thin films. These films can be studied more easily than the thick films cast from solution condensation products. If greater strength is needed, the films can be layered on a solid support. These thin films also hold great promise for use in electonic and optical applications.[28]

**Scheme 12**



Neuse, Loonat and Rabilloud have obtained an unusual PBI, one formed from a tetramine and a large carborane dialdehyde (illustrated in Scheme 13).[27]

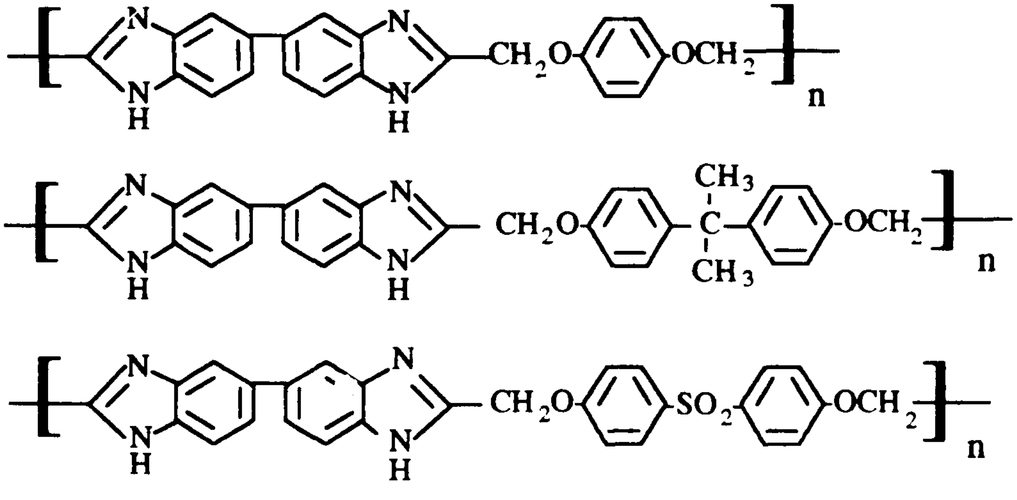
**Scheme 13**



The product was of very low molecular weight (inherent viscosity was 0.08 dL/g). Another complication was the apparent cleavage of the C-C bond between the 2-carbon of the benzimidazole ring and the carborane cage. This places a limit on both the reaction temperature and the reaction time. The explanation given for this bond cleavage highlights both the electron-deficient nature of the carborane cluster (which withdraws electrons from the benzimidazole ring), and the steric requirements of the carborane cage (which also destabilizes the bond in question). Despite the low molecular weights, the products obtained were stable to about 500 °C.

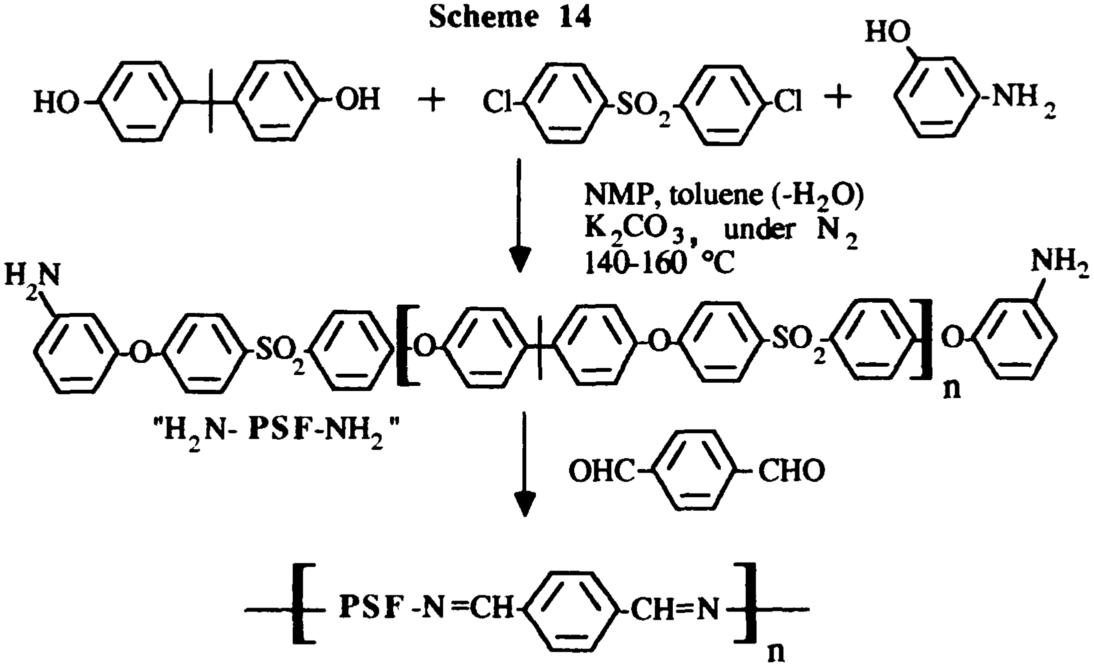
To overcome the problem of chain stiffness, several researchers have tried to insert various "hinge groups", such as amide, ether or sulfone linkages, into the polymer backbone. Recently, Scariah introduced methylene, methyloxy, isopropylidene and sulfone linkages on the polymer backbone. Some of these polymers are shown in Figure 10.[9]

**Figure 10.** PBIs with flexible linkages in the polymer backbone.



Others have introduced sulfone and sulfonic ester linkages into other polymer systems, such as the one shown in Scheme 14.[10]

Scheme 14



This system differs from Scariah's in that it is a block polymerization. In this type of system, two oligomers of differing polymer type are made, and then linked together by their endgroups. This group made poly(azomethine-sulfone)s, but the idea of flexibilizing sulfone linkages is very similar to the sulfone systems used in our current research.

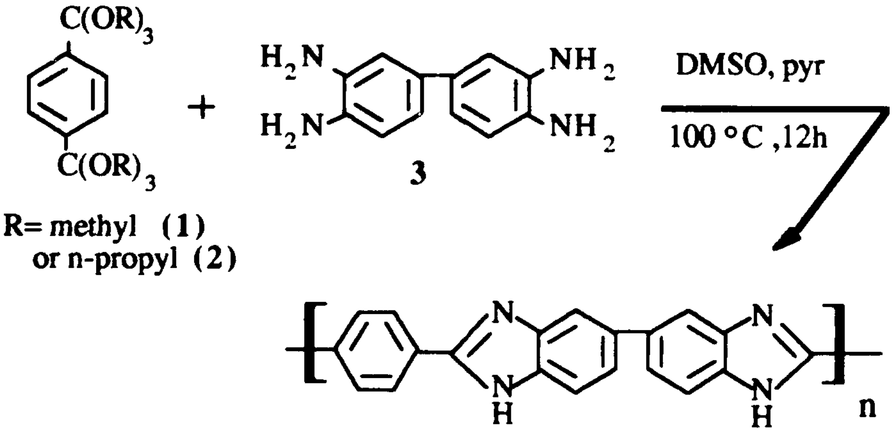
# RESULTS AND DISCUSSION

There were four basic approaches to polybenzimidazole synthesis used in this research. The first was to use highly reactive ortho esters with tetramines. The second was to carry out polymerization and oxidative ring formation concurrently in a single reaction. The third was to make polymeric azomethines, which would then be oxidized to PBI. The fourth was to make monomers which already contained the benzimidazole or bibenzimidazole unit, and then link them with other monomers in a nucleophilic polymerization.

## Polycondensation of Orthoesters with Tetramines

Two ortho esters (**1** and **2**) were chosen for study in the first approach. Their highly reactive nature enhances the single step polymerization, relative to such a polymerization using diesters. The polymerization scheme follows.[29]

**Scheme 15**



R= methyl (1)
or n-propyl (2)

4

All polymerizations attempted with ortho esters gave products of extremely low molecular weight (see Table 1), probably due to the questionable purity of these monomers. The first three runs suggested that additional reaction time might improve molecular weight, but this was not the case. Essentially, the limited amount of research conducted with these monomers confirmed earlier reports that ortho esters were very difficult to purify.[29] These purification difficulties and the very limited shelf life of the ortho esters led us to abandon this line of research.

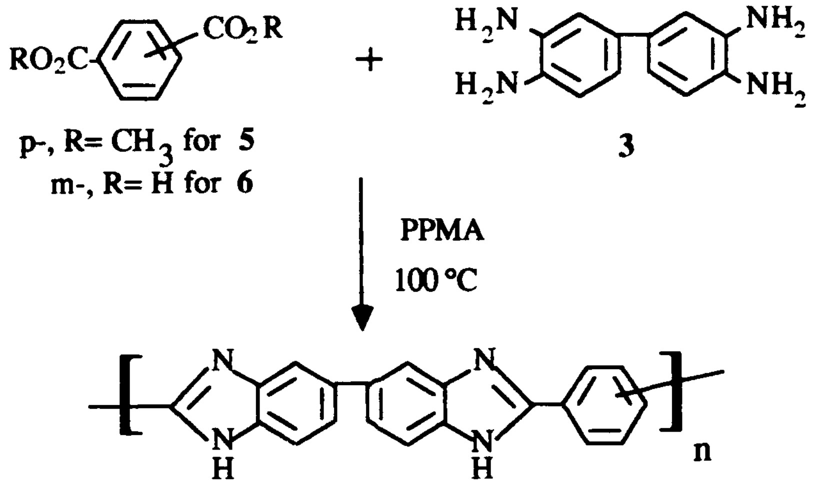
Table 1. PBI synthesis from ortho esters plus tetramines in DMSO/pyridine.

| | System | Temp. | Time | $\eta$ (inh) |
|---|---|---|---|---|
| 1 | 1+3 | 100 °C | 12 h | 0.09 dL/g |
| 2 | 2+3 | 100 °C | 12 h | 0.08 |
| 3 | 2+3 | 85 °C | 12 h | 0.04 |
| 4 | 2+3 | 100 °C | 20 h | 0.07 |

## Carboxylic Acid Derivatives in Acidic Solvent

A second approach was run with diacids (or diesters) and tetramines in the specialized solvent, PPMA (phosphorous pentoxide-methanesulfonic acid). This system had been developed by Ueda, et al, who stated that meta-substituted diacids polymerized effectively in this set of conditions, while para-substituted diacids did not.[25, 26] To test this, we chose DMT, dimethyl terephthalate (5) and isophthalic acid (6) with 3,3',4,4'-tetraminobiphenyl (DAB, 3), as shown in Scheme 16.

**Scheme 16**



The results, which are summarized in Table 2, indicated that these systems were indeed very different.

Table 2. Dicarboxylic acid derivatives plus tetramine to PBI (in PPMA)

| | Reactants[a] | Amt PPMA | t (rxn) | $\eta$ (inh) |
|---|---|---|---|---|
| 1 | 5+3 | 6 mL | 20 h | 0.43 dL/g |
| 2 | 5+3 | 6 mL | 23 h | 0.41 |
| 3 | 5+3 | 7 mL | 72 h | insol. |
| 4 | 5+3 | 6 mL | 24 h | 0.19 [a] |
| 5 | 5+3 | 6 mL | 24 h | 0.15 [a] |
| 6 | 5+3 | 6 mL | 24 h | insol. |
| 7 | 6+3 | 6 mL | 1 h | insol. |

a. One mmol each of 5 and 3 were used, but these reactions were run under a partial vacuum, apparently causing the loss of some DMT due to sublimation.

As Table 2 shows, mediocre viscosities were obtained with the para-substituted diester (5). Methanol was removed by suction during two reaction trials, in an attempt to drive the equilibrium to the right, but it appeared that 5 was removed as well (by sublimation). Viscosity was not improved by increasing the reaction time; in fact the products of the longer trials became insoluble. Since the benzimidazole ring formation is essentially irreversible, the formation of insoluble (crosslinked) polymer implies that some intermediate has a lifetime long enough to undergo equilibration, or that additional side-reactions can occur.

The meta-substituted diacid monomer (6) came out of solution in roughly one hour. Attempts to redissolve the material were unsuccessful, even after 72 h of sonication in warm DMSO.

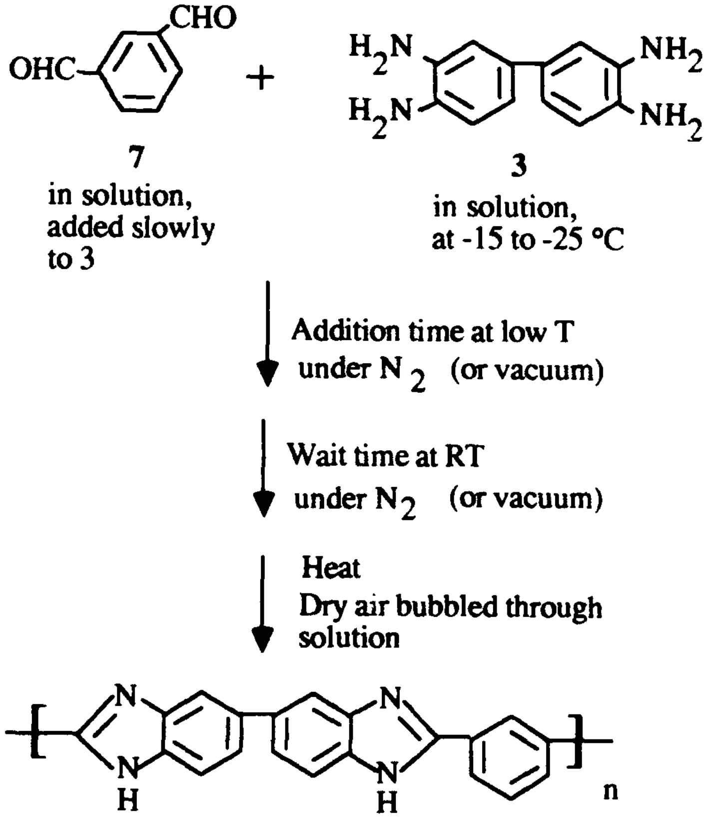
These reaction systems were chosen to compare with the results obtained in similar systems by Ueda, and to test his statement that unsubstituted diacids and diesters could not be used for PPMA polymerizations.[25] These results were consistent with this statement; the resulting viscosities of the unsubstituted system were significantly lower than those formed with Ueda's substituted reactants. In fact, the unsubstituted systems gave results equivalent to the weakest electron-donating monomer used by Ueda. There are experimental differences which may prevent strict comparison, such as the different solvents used for viscosity measurements and the differing reaction times. But the results generally confirm Ueda's hypothesis that the intermediate in polymerizations of carboxylic acid derivatives in PPMA may be an acylium ion, which is not sufficiently stabilized to run well in systems which lack electron donating substituents.

## Two-Stage Polymerizations

### Model reactions

Scheme 17 illustrates the model compound polymerizations for the third (polymerization-oxidation) approach. The monomers used were isophthaldehyde (m-benzenedicarboxaldehyde, 7) and DAB (3). This system was chosen to take advantage of the facile benzimidazole-forming reactions of dialdehydes and tetramines.[27]

Scheme 17



8

The major benefit of this method is to minimize the solubility problems encountered with polybenzimidazoles, at least during the initial polymerization of the azomethine. However, the oxidation step has been shown to be more difficult as the polymer grows.[3] The more strenuous conditions required to carry out the cyclization of the polymer tend to increase crosslinking. This proved to be one of the major difficulties with this method, and was especially troublesome when higher concentrations were used. In the cases where all of the solvent was completely lost (due to evaporation) before it could be replenished, the product was completely insoluble in DMAc. The procedures used for the model polymerizations were chosen to minimize crosslinking at normal concentrations. A dilute solution of the dialdehyde was added slowly to the tetraamine, which was maintained at -15 °C. The rationale for this approach was that limiting the available dialdehyde would minimize formation of the aldehydine polymer (of the type shown in Figure 2). One factor which has not been completely controlled is the equilibration that occurs during the wait time and second stage of the reaction. During this time, aldehyde end groups could become available again, and cause the aldehydine-type crosslinking. The most certain way to prevent this is to ensure that the benzimidazole ring has completely closed during the first step, but this would be impossible under the low-temperature conditions. The reaction conditions depend on the likelihood of the favorable equilibrium of the first step overwhelming the effects of any undesired equilibration during the rest of the reaction. The results of these, and several other, polymerizations are shown in Table 3.

Table 3. Model compounds: isophthaldehyde (7) plus tetramine (3)[a]

| | Solvent | t (add) | t (wait) | t (rxn) | T (rxn) | Cond's | $\eta$ (inh) |
|---|---|---|---|---|---|---|---|
| 1 | dry DMAc | 2 h | 0 h | 133 h | 60 °C | $N_2$ / air[a] | 0.99 dL/g |
| 2 | dry DMAc | 2 h | 0 h | 120 h [b] | 60 °C | $N_2$ / air | 0.86 |
| 3 | dry DMAc | 2 h | 0 h | 145 h | 60 °C | $N_2$ / air | 0.72 |
| 4 | dry DMAc | 2 h | 20 h | 120 h | 60 °C | $N_2$ / air | 0.71 |
| 5 | DMAc | 2 h | 21 h | 49 h [c] | 60 °C | $N_2$ / air | 0.61 |
| 6 | DMAc | 2 h | 20 h | 0 h [d] | 25 °C | $N_2$ / air | 0.15 |
| 7 | DMAc | 3 h | 21 h | 14 h [e] | 60 °C | vacuum | lost solv. |
| 8 | dry DMAc | 2 h | 0 h | 36 h [f] | 60 °C | vacuum | lost solv. |

a. Flow rate of air was 175-200 mL/min. Air was dried by passing through two tubes of fresh Drierite.
b. Inherent viscosity began to decrease after 120 h (it was 0.6 dL/g after 144 h).
c. Inherent viscosity began to decrease after 49 h (it was 0.56 dL/g after 96 h).
d. Sample taken 3 h after aldehyde addition was complete was soluble. Sample taken when heat and air were added was insoluble in DMAc, in spite of extended sonication.
e. At t=0 (before air was added) inherent viscosity was 0.26 dL/g. After solvent loss, product was insoluble in DMAc, even with extended sonication.
f. Inherent viscosity of recovered product was 0.41 dL/g.

As expected, the water content of the solvent has a significant effect on the degree of polymerization. When the solvent was used without the final drying over calcium hydride, the inherent viscosity peaked at 0.61 dL/g. Even in the polymerizations with dry solvent, which produced good polymer (inherent viscosity greater than 0.7 dL/ g), the effect of water content was apparent. The first three reactions in the table were carried out sequentially, using the same batch of dry solvent. The first polymerization was run immediately after the solvent was dried, and the third was run six weeks later.

Since all other experimental factors were the same, the decrease in inherent viscosity was probably due to the solvent absorbing water from the atmosphere during storage.

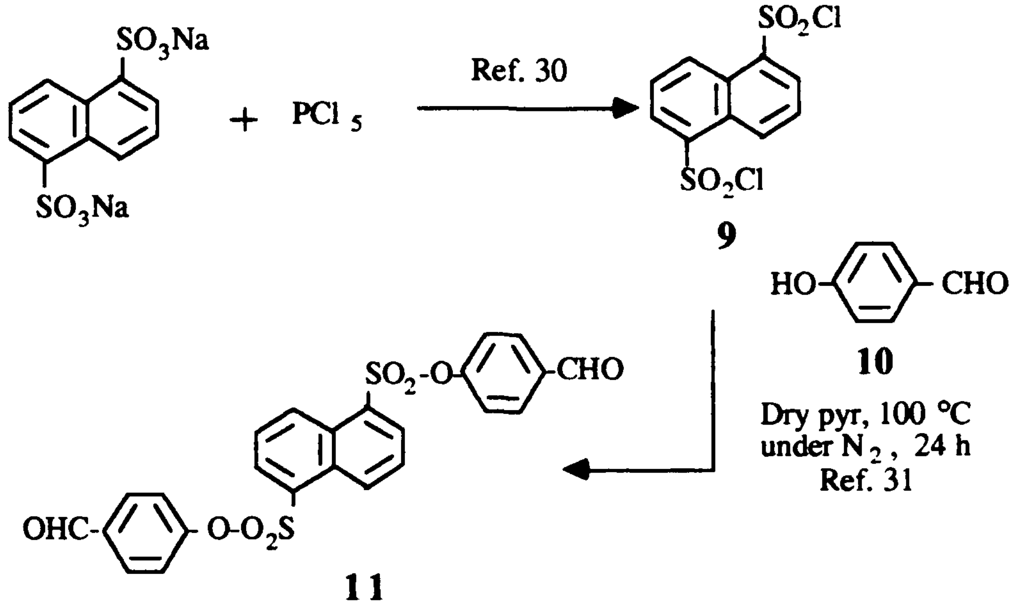
These model compound polymerizations confirmed that inherent viscosity is an reasonable measure of polymer quality, correlating well to the properties of the polymer films produced. Polymers with an inherent viscosity of more than 0.7 dL/g gave strong, flexible films which could be creased. Even very dilute solutions (5 mg/mL) gave films which were easily peeled from the plate after curing. They were strong and fairly resistant to tearing, but once a tear was started, it was easy to extend. The polymers with inherent viscosities less than 0.7 dL/g gave extremely weak, brittle films which could not be removed from the plate in one piece.

It was very important to actually isolate the product and dry it prior to the viscosity measurements. Because of solvent loss (due to evaporation during the air addition), the concentration varied considerably throughout the second stage of the reaction. Attempts to estimate and/or to replenish solvent to a known level were unsuccessful. Because of the small scale of the reaction, these attempts were too imprecise.

## Dialdehyde-sulfonate monomers with tetramines

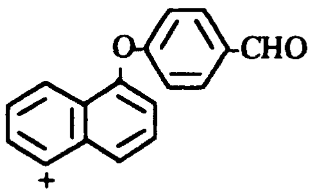
Since the trends seen with the model polymerizations were consistent with our expectations, the results were encouraging enough to warrant trying these methods with several new monomer systems which contained sulfonyl flexibilizing linkages. To introduce sulfonic ester linkages, a dialdehyde containing this group (**11**) was condensed with DAB (**3**). Since this sulfonic ester-dialdehyde is not readily available, it was first necessary to make it; the synthetic scheme is shown in Scheme 18.[30, 31]

**Scheme 18**



The product of this reaction system was very difficult to characterize, and insoluble in most solvents normally used for polymerizations. The IR spectrum gave inconclusive results. The NMR spectrum showed signals with the expected chemical shifts, but the integrations were consistent with a mixture of the desired product, monoadduct and starting material. The mass spectrum showed a parent peak at M/Z = 496, which was consistent with the formation of some desired product. Mass spectroscopy also showed a very large peak at M/Z = 247; one possible structure that fits this peak is given in Figure 11.

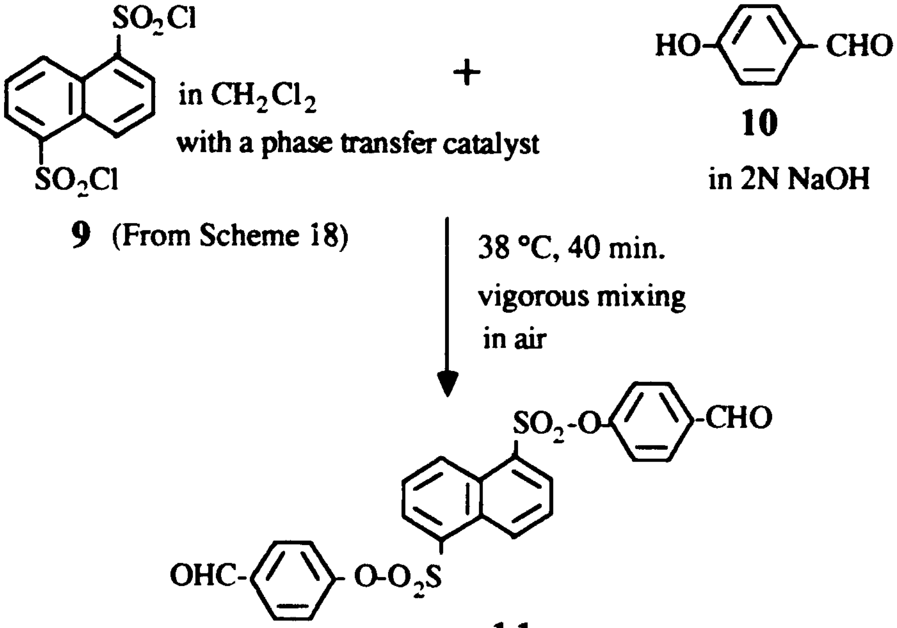
**Figure 11.** Proposed structure of peak at M/Z = 247. (Possible side-reaction for Scheme 18, monomer 11)



This peak was completely unexpected and inconsistent with the structure of **11**, and suggested that desulfonation might have occurred in the spectrometer. Some of these inconsistencies are explained by the solubility differences of the crude products (NMR and mass spectroscopy were run in different solvents). However, the most likely conclusion from all of the spectral data is that **11** was actually a mixture of starting materials, di- and monoadduct. Various separation trechniques were tried to isolate **11**, without success.

Since the desired product could not be isolated or identified, a different synthetic route (shown in Scheme 19) was attempted. This synthesis yielded a large amount of material which was minimally soluble in standard solvents and difficult to characterize. Mass spectroscopy confirmed that some product was formed (there was a peak at m/z = 496). The proton NMR spectrum was also consistent with the formation of some product, but the material was not isolated.

**Scheme 19**



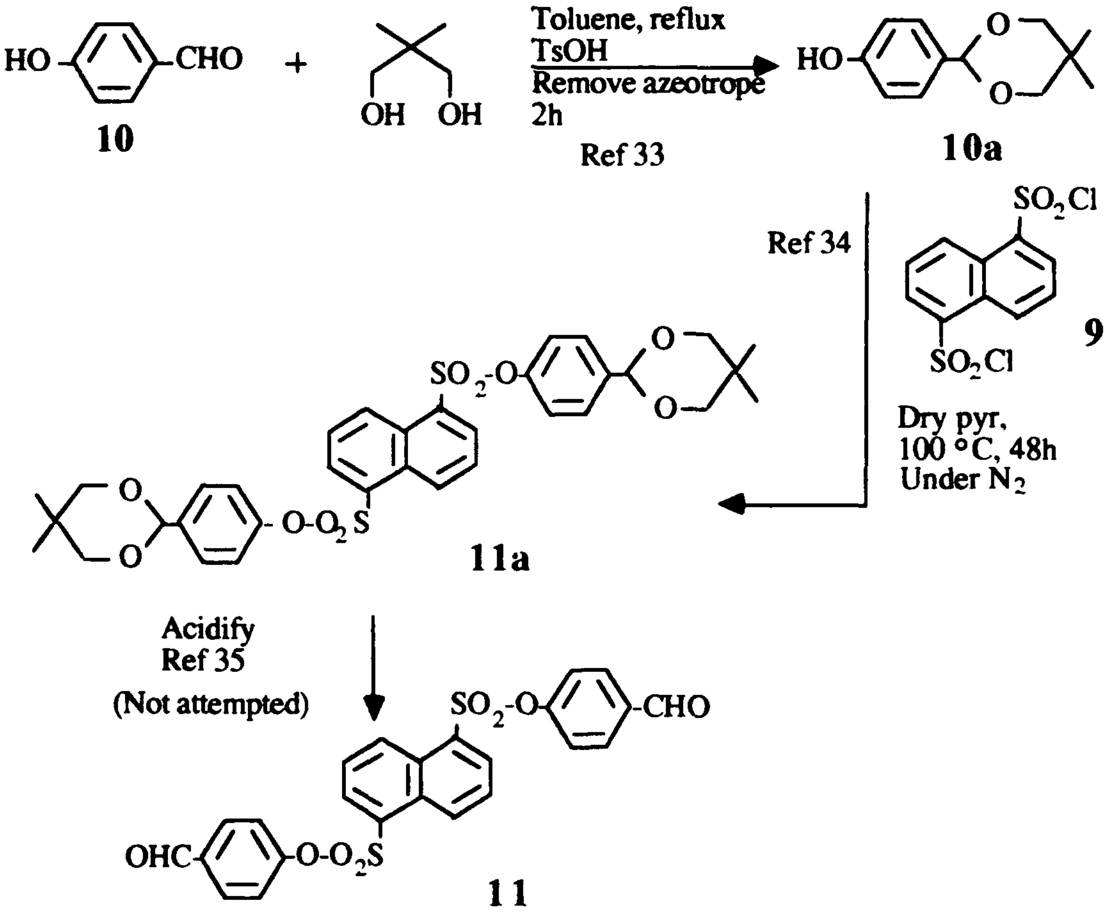
**9** (From Scheme 18)

**10**

**11**

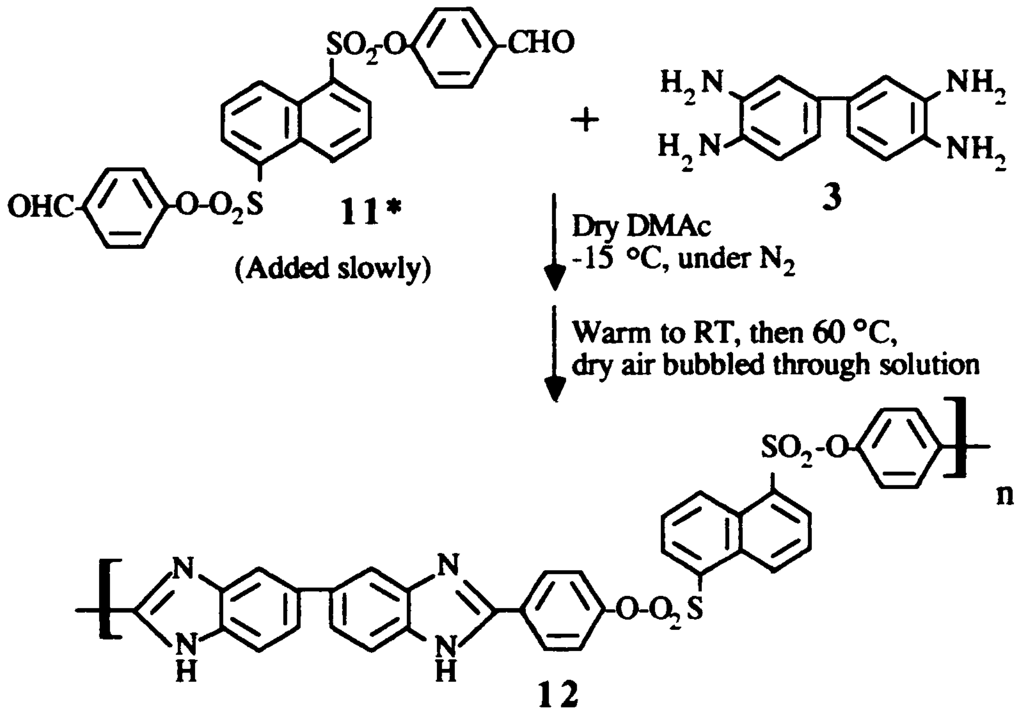
A third method (depicted in Scheme 20) was attempted, using the acetal instead of the aldehyde. This synthetic scheme was not successful in early attempts, because **10a** was formed in very low yield and could not be purified, and this method was also abandoned. Later work by Cook [32] yielded **10a** in reasonable purity, using a revised synthetic method. The second and third steps of Scheme 20 were not attempted with pure **10a**.

**Scheme 20**



The polymerization of **11** (the product of reactions shown in Scheme 18; structure and purity are uncertain) with **3** is depicted in Scheme 21. The results of these polymerizations follow in Table 4.

**Scheme 21**



*Purity and structure uncertain

Conditions were varied somewhat from those of the model polymerizations, in order to test the systems' similarities. This system showed greater sensitivity than the model reactions to water content of the solvent. When DMAc was meticulously predried, the inherent viscosity of the resulting polymer increased roughly four-fold. Even with this special predrying, the polymer did not reach adequate size to be of use. Films were

Films were attempted from several samples, with viscosities of less than 0.6 dL/g; the films could not be removed from the preparation plate by any of the usual methods. The "films" scraped off of the plate with a razor blade, yielding an extremely brittle solid.

Table 4. Polymerization of **11** with **3**.

| | Solvent | t (add) | t (wait) | t (rxn) | T (rxn) | % solids | η (inh) |
|---|---|---|---|---|---|---|---|
| 1 | DMAc | 2.5 h | 0 h | 25 h | 25 °C | 2.7 | 0.09 dL/g |
| 2 | DMAc | 3.5 h | 0 h | 78 h | 60 °C | 2.3 | 0.15 |
| 3 | DMAc | 2 h | 15 h | 48 h | 60 °C | 3.4 | 0.11 |
| 4 | DMAc | 2 h | 21 h | 120 h [a] | 60 °C | 2.5 | lost solv |
| 5 | DMAc | 2 h | 21 h | 65 h [b] | 60 °C | 1.9 | 0.14 |
| 6 | dry DMAc | 2 h | 0 h | 24 h [c] | 60 °C | 3.6 | lost solv |
| 7 | dry DMAc | 1 h | 0 h | 3 h [d] | 60 °C | 2.8 | 0.45 |
| 8 | DMSO | 1 h | 0 h | 24 h | 110 °C | 4.3 | 0.21 |
| 9 | DMF | 2.5 h | 0 h | 2 h [e] | 60 °C | 3.3 | 0.19 |
| 10 | NMP | 3 h | 0 h | 24 h | 60 °C | 8.9 | 0.55 |
| 11 | NMP | 2 h | 0 h | 24 h [f] | 60 °C | 7.1 | lost solv |
| 12 | dry NMP | 1 h | 20 h | 120 h [g] | 60 °C | 2.8 | 0.2 |
| 13 | dry NMP | 1 h | 20 h | 120 h [h] | 60 °C | 2.8 | 0.19 |

a. Inherent viscosity of recovered product was 0.19 dL/g.

b. Inherent viscosity began to decrease after 65 h (was 0.01 dL/g after 113 h). Molecular sieve was added near end of wait time.

c. Inherent viscosity before air/heat was 0.09 dL/g. Product after solvent loss was insoluble.

d. Inherent viscosity began to decrease after 3 h (was 0.30 dL/g after 7 h)

e. Inherent viscosity began to decrease after 2 h (was 0.15 dL/g after 20 h)

f. Applied vacuum at 1-hour intervals during first 5 hours and last 4 hours of reaction.

g. Molecular sieve was added near end of wait time.

h. Run with $FeCl_3$. Molecular sieve was added 2 h prior to the addition of $FeCl_3$, heat and air.

Several entries indicate "solvent loss" as a problem. In all of the DMAc polymerizations, the solvent evaporated throughout the second stage (60°C, with air bubbling through the solution). Often, simply replacing the lost volume with dry DMAc allowed the polymerization to continue. In a few cases, solvent was lost so quickly that the polymer precipitated before more solvent was added. New solvent sometimes redissolved the polymer, and the reaction could continue. However, even when the solvent could be replaced, this problem caused the constant fluctuation of reaction concentration.

At first glance, NMP seemed to be a better solvent than DMAc, yielding polymers with viscosities of 0.55 dL/g without rigorous predrying. However, this hypothesis was tested by running a polymerization in dry NMP, and the results were much lower than expected (entries 10 and 12 of Table 4). A closer look at the experimental variables indicated that the concentration of the reaction system might have been the true cause of the higher viscosity of the earlier NMP run (entry 10). This reaction was run at 9% solids, whereas entry 12 was run at 2.8%. However, concentrations and addition rates of dialdehyde were not constant, because **11** was insoluble or minimally soluble in all solvents. In each case, **11** was added as a slurry, and the air-exclusion system did not allow resuspension of the material as it settled. Thus, addition rate and concentration were uncontrolled variables. The impact of this on the reaction systems cannot be evaluated. (Note: all DMAc and DMSO trials were run at 2-3 % solids.)

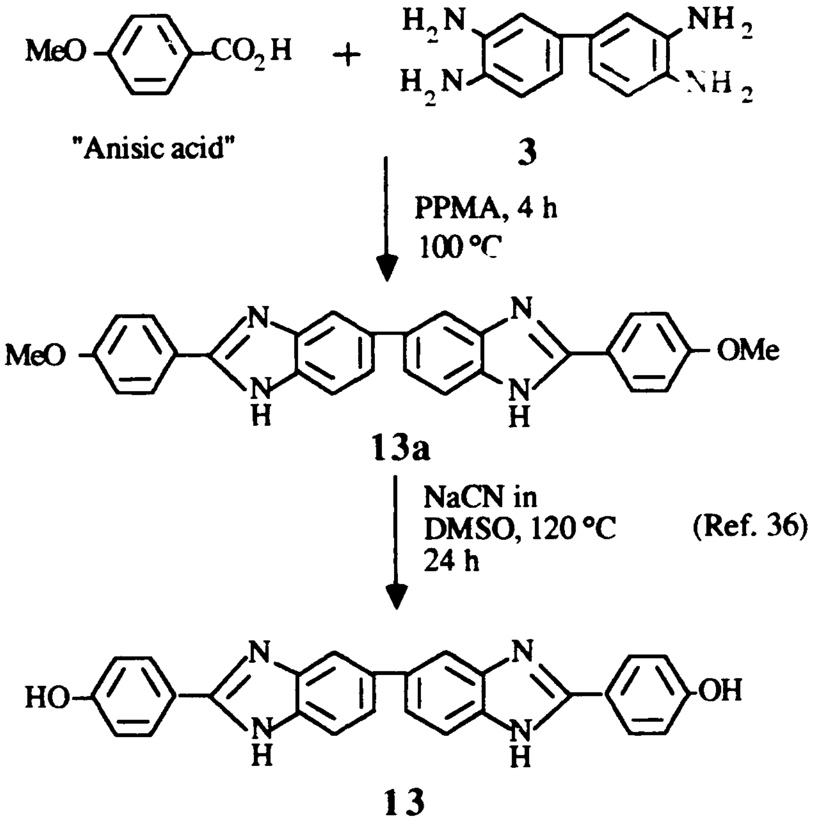
Another significant difference is the use of ferric chloride for one of the polymerizations in NMP (entry 13). A crucial factor in the use of this catalytic oxidation agent is the removal of the water previously formed, prior to introduction of the iron reagent. Otherwise, the water competes with polymer for the available oxidant. During the first stage, the temperature had to remain low (-15 to 25°C), to minimize cross-linking. Therefore, azeotropic removal of water was not feasible. For the ironcatalyzed ring closure reactions, freshly activated 3A molecular sieves were added to the reaction mixture for the last 2 hours of the "wait time." Earlier addition might drive the reaction even further, by the continuous removal of water as it is formed. But this gain must be weighed against the potential of physically impeding the movement of the growing polymer chains. It is unclear whether this physical obstruction or the low concentration was the major factor contributing to the poor results of the ferric chloride trial, or if the water removal was insufficient.

The most likely handicap to this polymerization is the possibility that **11** was impure. The impurity of **11** would affect the ratio of **11** to **3**, and could explain the generally poor results of this polymerization system.

## Premade Bibenzimidazole Monomers

The target monomer was 2,2'-bis(p-hydroxyphenyl)5,5'-bibenzimidazole (**13**). The first synthetic route used the methyl ether, which was then cleaved to the dihydroxy compound before the polymerization (see Scheme 22). In this case, the dihydroxy compound would be protected while the material was in the strongly acidic solvent, and deprotection would take place under neutral conditions.[36]

Scheme 22

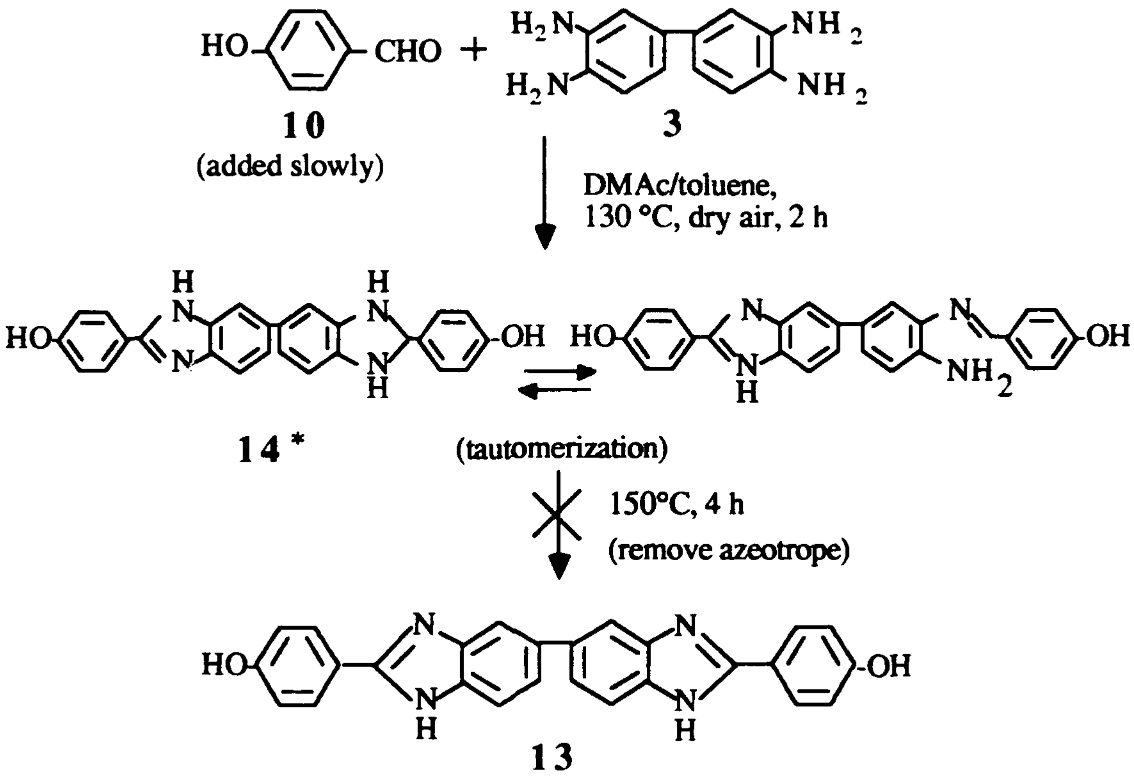


Several problems arose while attempting the chemistry shown in Scheme 22. The product could not be completely separated from solvent (methane sulfonic acid). This was evidenced by the weight of isolated, dried "product", which was equivalent to a quantitative yield plus solvent residue. The majority of the material generated in the first step remained sulfonated through several vigorous water washes and recrystallization attempts. Infrared spectroscopy also supported this conclusion, showing strong sulfur-oxygen absorptions in the 1400-1300 cm $^{-1}$ region. An NMR spectrum was not obtained, since the product was completely insoluble in standard polymer solvents, and in concentrated acids and bases.

Another problem arose during routine workup of the first step. When base was slowly added to the product in PPMA, to neutralize excess acid in the reaction mixture, a large volume of foam was generated (100 mL of reaction mixture produced 200 mL of foam). The foam eventually collapsed, yielding a small amount of the product, but its development severely hindered the workup. The second step was attempted with the small amount of **13a** that was isolated. That step appeared to proceed with high yield, but the final product retained the sulfur-oxygen absorptions on IR. The overall yield for the entire reaction sequence shown in Scheme 22 was estimated to be considerably less than 10% (the yield could not be calculated exactly, due to the presence of an unquantifiable amount of the sulfur-containing material). The difficulties encountered in the first step, the low yield of the system and incorporation of solvent with the product led us to abandon this approach.

The next approach (shown in Scheme 23) yielded a mixed intermediate. The first step of this reaction scheme is somewhat similar to the conditions of dialdehyde-tetramine polymerizations described in a patent by D'Alelio.[5] The method differs from the patent in that the solvent is a mixture of lower polarity, and that the synthesis is tailored for monomer preparation, rather than for polymerization.

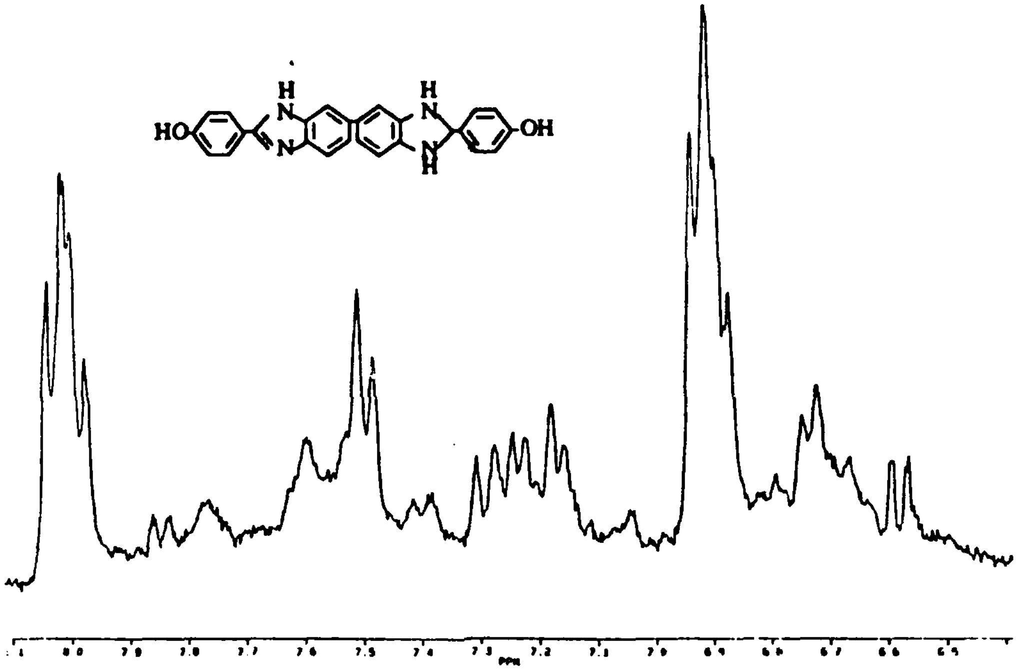
**Scheme 23**



* 14 probably also contains the bis-diazomethine (no rings closed) and its tautomer, and a small amount of 13

Proton NMR confirmed that the product was not the desired bibenzimidazole; the spectrum contained extra peaks in the δ 7.8 - 6.4 region (the aromatic region of this spectrum is given as Figure 12). The bibenzimidazole would be expected to show a singlet and two doublets in this region. The mixed structure (14) best fits the NMR data, and is consistent with the observation that aromatization of the second ring of a bibenzimidazole does not occur under these conditions (i.e., without an oxidative metal catalyst at these lower temperatures).[24, 37]

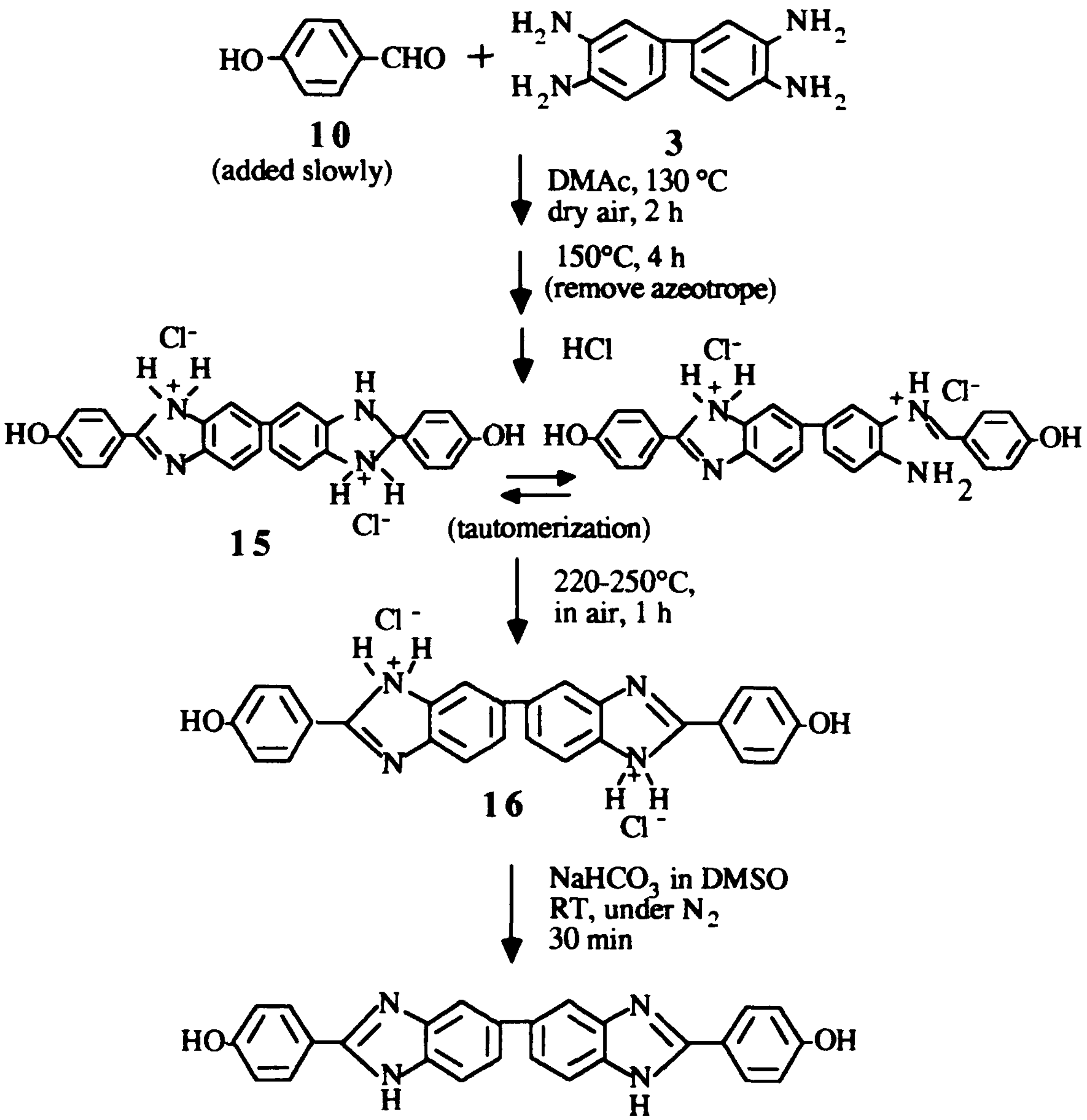
**Figure 12.** Aromatic region, proton NMR of 14.



In the course of this synthetic route, several difficulties were encountered in handling the crude product. The product binds (seemingly irreversibly) to filter paper, making collection by filtration difficult at best. In another trial, the product was precipitated and allowed to settle overnight, before the supernatant was decanted. The product requires a long time to settle, and additional time was required for drying under vacuum after the reaction solvent/supernatant was partially removed (by decanting). The isolated product has an annoying tendency to cling to glass; apparently 14 is very sensitive to static electricity. It also clung tenaciously to the polar portion of the reaction solvent (DMAc), which appeared on NMR even after 3 successive recrystallizations from acetone, ethanol and ether, and vacuum drying cycles. Large amounts of the recrystallization solvents were required, due to the extreme reluctance of 14 to dissolve in anything but boiling DMSO or DMAc.

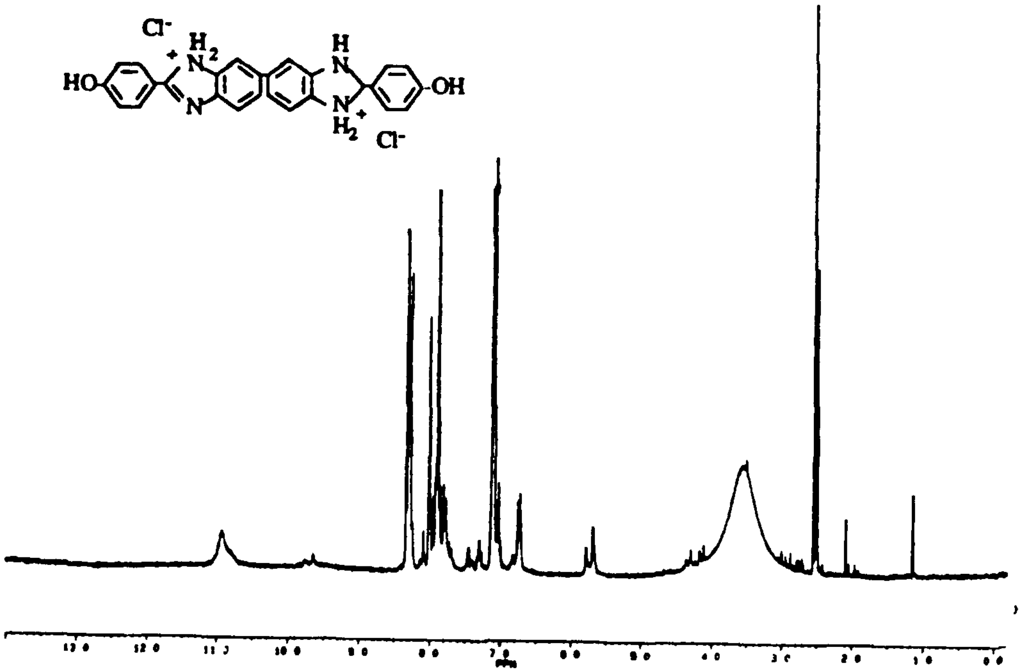
Most of these difficulties were overcome by working with the dihydrochloride **15**, rather than the free benzimidazoline **14**. Scheme 24 shows this reaction system, which produced the desired bibenzimidazole monomer (**13**).

Scheme 24



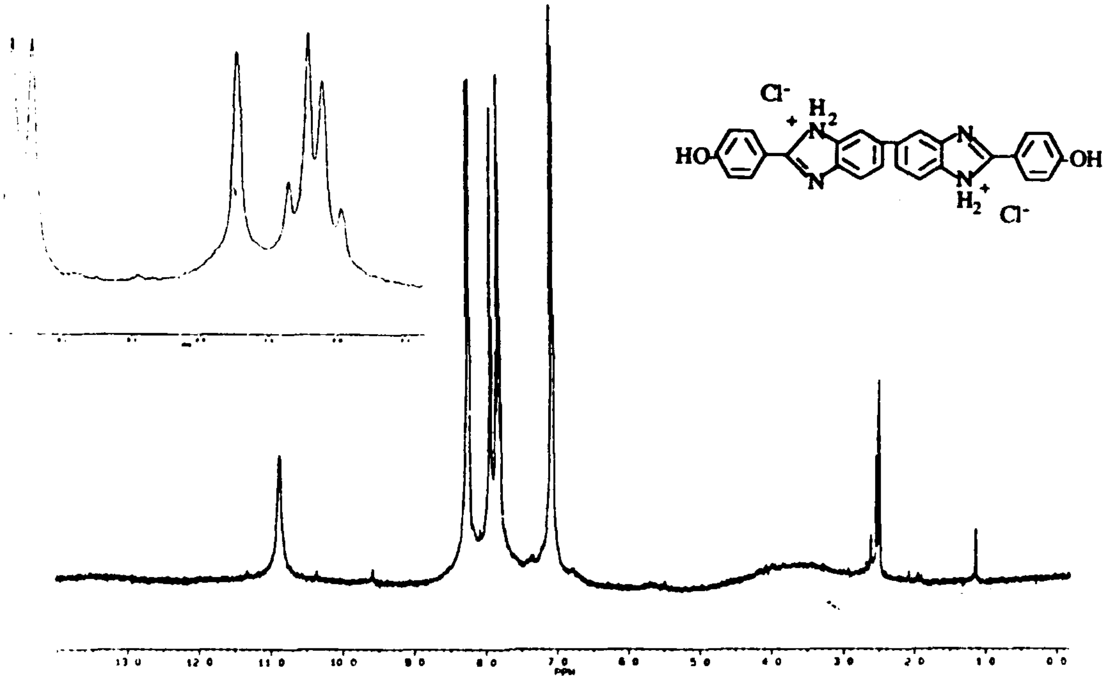
The dihydrochloride, like the free benzimidazoline, was slow to precipitate, but the processing was greatly simplified because filtration could be used with **15**. It was not as sensitive as **14** to static charges, but was soluble only in standard polymer solvents (like DMSO). The dihydrochloride was very finely divided (as is the free benzimidazoline), making loss to drafts a constant concern. Both intermediates (**15** and **16**) were isolated and analyzed. It is significant that the second benzimidazole ring was not completely formed under the conditions of the first step. This was evidenced by the extra signals in the aromatic region of proton NMR of **15**, which is given as Figure 13.

**Figure 13.** Proton NMR of **15**.



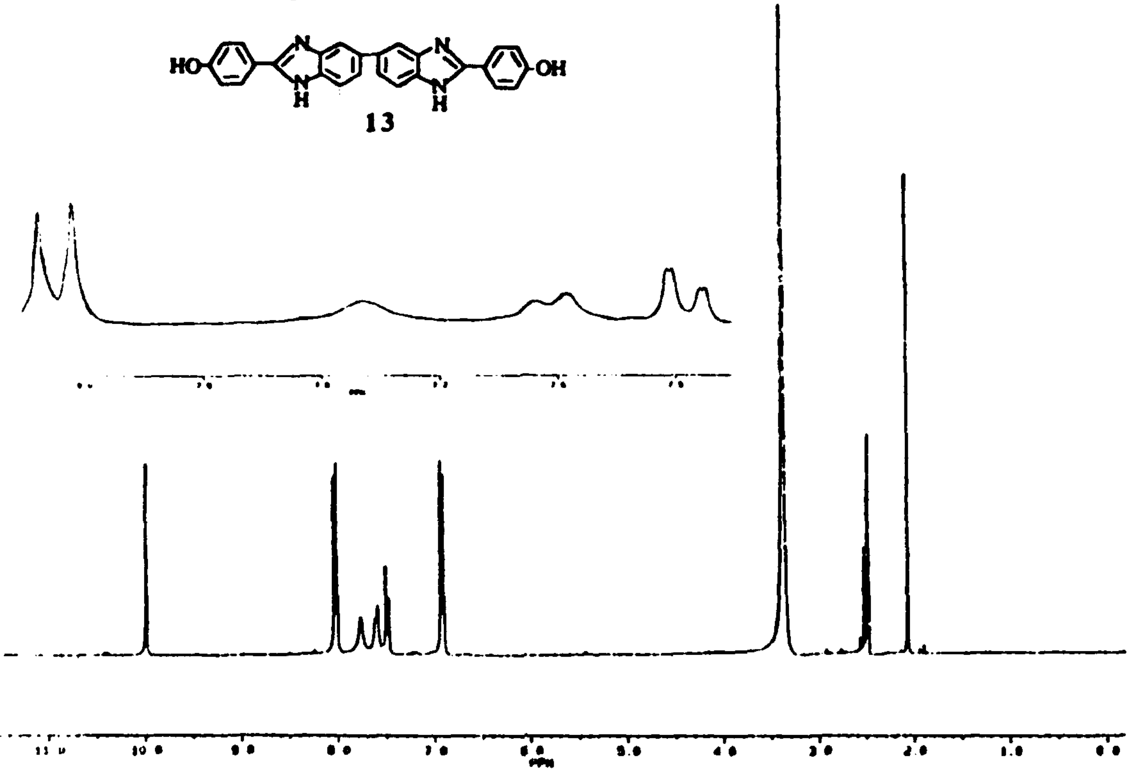
Higher temperatures, in the presence of air, caused the aromatization of the second ring to occur quickly and quantitatively. This conversion was easily followed by observing the color change which occurred; the intermediate went from brick-red (15) to brown (16). The structure of 16 was confirmed by proton NMR (given as Figure 14); the broad multiplets in the aromatic region of 15 were replaced by a very clear singlet and two doublets.

Figure 14. Proton NMR of 16.



The hydrochloride 16 was easily converted to the free benzimidazole 13 with a weak base, under very mild conditions. The proton NMR (shown in Figure 15) was consistent with the desired structure.

Figure 15. Proton NMR of 13.

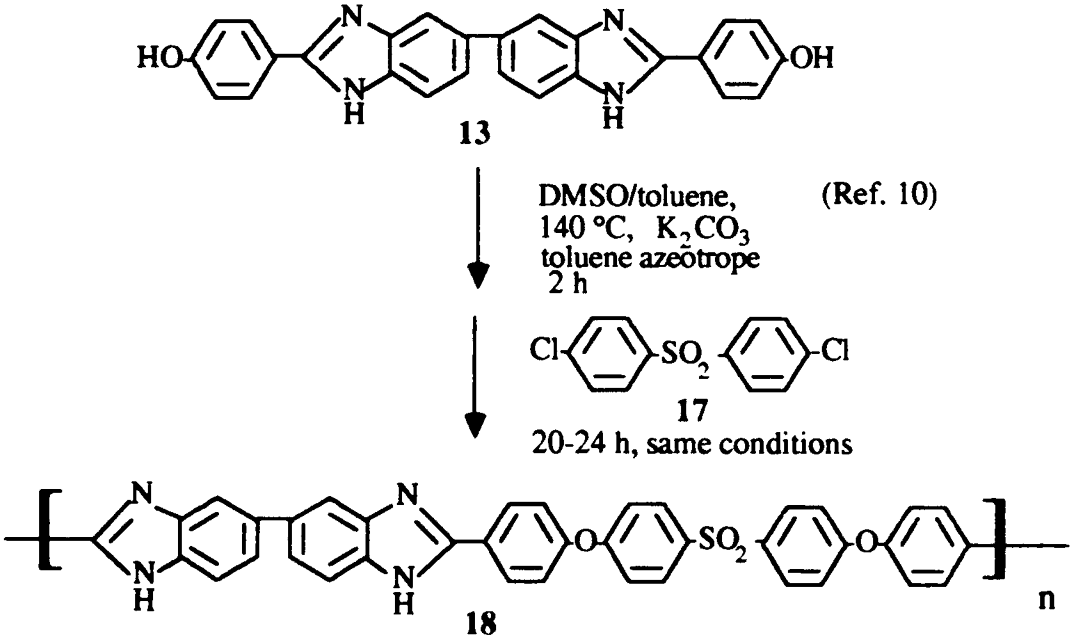


As expected, the aromatic signals of the free bibenzimidazole appeared further upfield than those of the dihydrochloride. The product (13) did not exhibit the sensitivity to static or the strong affinity for solvent shown by the free benzimidazole/ benzimidazoline intermediate (14). It was unaffected by prolonged exposure to strongly acidic conditions, and was soluble in warm DMSO.

If this model were extended to similar polymerization systems, it implies that the first benzimidazole-forming step goes easily, and formation of subsequent rings requires a much higher energy input. It also suggests that many "polybenzimidazoles" may actually contain more benzimidazoline/ azomethine structures than previously believed. Efforts to keep the reaction systems free of water would drive the first step (formation of the benzimidazoline/ azomethine), but would have no influence on the second step (closing the benzimidazole ring). Hence, the emphasis in ring-forming polymerization systems should shift to include raising reaction temperatures, to ensure quick closure of the benzimidazole ring. In polymerizations using premade bibenzimidazole monomers, the benzimidazole rings are closed before the polymerization step, so the length of the polymer chain depends less on water-excluding precautions than on other experimental factors. The extreme care needed for successful model ring-closing polymerization systems would not be as necessary with premade benzimidazole monomer; this would greatly simplify these polymerizations. Ensuring complete formation of all desired benzimidazole structures already present in the monomers used would allow the subsequent polymerization system to be designed with fewer critical variables, water exclusion being but one of several factors to maximize the equilibrium shift toward polymer formation.

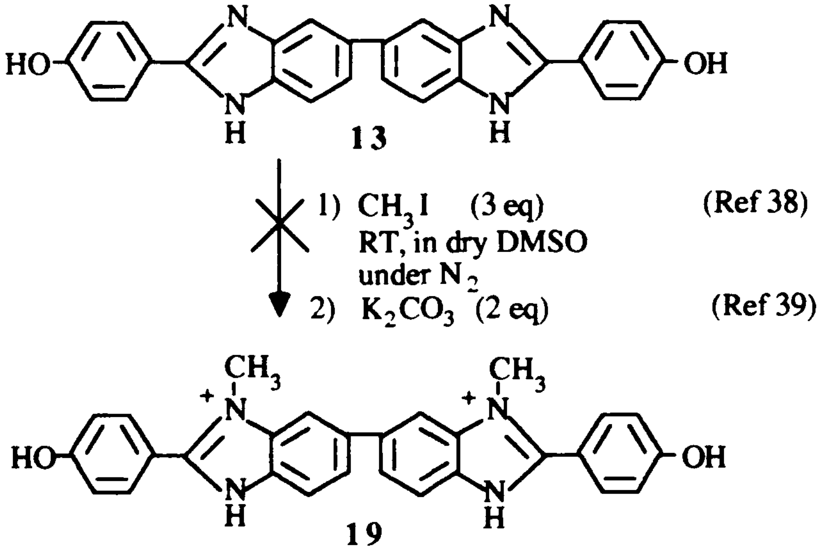
Once **13** was obtained, it was subjected to the polymerization conditions shown in Scheme 25. This system provided disappointing results (inherent viscosities of **18** were on the order of 0.2-0.4 dL/g)

**Scheme 25**



Prolonged reaction times produced completely insoluble products. This was attributed to crosslinking via nucleophilic interactions of the benzimidazole nitrogens. One attempt was made to methylate (i.e., block) these sites, as is depicted in Scheme 26. The benzimidazole ring was not stable to these conditions, and began to degrade within an hour of the start of the reaction. The proton NMR spectrum of a sample taken 45 minutes after the reaction start time showed the aromatic signals were clear and consistent with the bibenzimidazole structure of **13**. It also confirmed that little or no methylation had occurred. A sample taken 4 h into the reaction showed aromatic signals more consistent with the structure of **14** (the ring(s) appeared to begin breaking apart). We were also concerned that methylation of the hydroxy groups might occur, rather than the methylation of the benzimidazole nitrogens. This possibility was not evaluated, because the presumed breakup of the benzimidazole ring clouded the results.

**Scheme 26**



During the time these approaches were under investigation, another group found that the fluorinated analog of **17** readily polymerizes with **13** under conditions identical to those shown in Scheme 25.[40] They used different starting materials to arrive at **13**, and did not report NMR or mass spectroscopy data. Because of this, it is not possible to determine if their product is identical to mine, or varies in some important way (such as having the benzimidazole nitrogens blocked by one of the components of the reaction mixture). It could also be that the presence of the more reactive difluorinated compound may be enough to drive the polymerization.

# EXPERIMENTAL SECTION

## General Procedures

Spectral measurements utilized Perkin-Elmer 727B and 621, and Nicolet 510P (FT) infrared, Hewlett Packard 8452 UV, Bruker 300 or 400MHz NMR, and CDC mass spectrometer instruments. All reactions were conducted under nitrogen gas, which was dried by passing through two tubes of fresh Drierite, unless otherwise stated. Mixing was done with a magnetic stirrer for most reactions.

## Preparation of Solvents

Dry DMAc (N,N-dimethylacetamide): Aldrich anhydrous DMAc was refluxed over calcium hydride for 2-12 h, under a slow stream of dry nitrogen gas, then distilled onto newly activated 4A molecular sieves.

Dry toluene: Baker reagent grade toluene was dried for at least 24h over newly activated 4A molecular sieve.

Dry methanol: Aldrich anhydrous methanol was refluxed over magnesium turnings for 3 h, under a slow stream of dry nitrogen gas, then distilled directly into the pre-dried reaction flask which contained freshly activated 3A molecular sieve.[41]

Dry benzene: Baker reagent grade benzene was washed with concentrated sulfuric acid until it was no longer discolored. It was then distilled onto freshly activated 4A molecular sieves.[42]

Dry pyridine: Aldrich reagent grade pyridine was distilled under a blanket of dry nitrogen gas, from barium oxide into a pre-dried round bottom flask containing fresh barium oxide.

Dry NMP (N-methyl pyrrolidinone): Aldrich reagent grade NMP was refluxed over calcium hydride for 4 h, under a slow steam of dry nitrogen gas, then distilled onto newly activated 3A molecular sieve.

PPMA (phosphorous pentoxide-methanesulfonic acid) [43]: Phosphorous pentoxide (4.4g, granular) was added to 44g (30 mL) Aldrich reagent grade methanesulfonic acid. The mixture was heated, under dry nitrogen gas, at 80-90 °C until the phosphorous pentoxide was dissolved (3-4 h). Crystals often formed after several days of standing; these redissolved quickly when the solvent was heated to 40 °C.

Non-dried solvents were from the same sources as the dried solvents, but did not undergo the additional drying procedures.

## Synthesis of Monomers

### Ortho esters

**1,4-Bis(trimethoxymethyl)benzene (1).**[29] p-Bistrichloromethyl benzene (34.6 g) and 0.663 mol freshly prepared sodium methoxide (from 15.25 g sodium lump and 300 mL dry MeOH, mixed at room temperature until metal was dissolved) were added to a Parr pressure reactor. A stream of dry nitrogen gas was passed through the reaction vessel during the addition of the reagents. The mixture was heated to 180 °C, where it remained for 5h. The heat source was then removed, and the sealed reactor was allowed to cool overnight.

The solid was removed by filtration and washed with chloroform. The chloroform extracts were condensed on a rotary evaporator, yielding a fluffy, white solid, which was recrystallized from petroleum ether. A total of 68 g of purified product was collected (a yield of 69%). Proton NMR ($CDCl_3$): δ 7.65 (s, 4H), 3.15 (s, 18H).

Alternative procedure: This reaction was also run, with the same reagents as above, in a 1 L three-neck flask for 7 days at 65 °C. The work-up was unchanged, and yields were essentially the same for both procedures.

**1,4-Bis(tri-n-propoxymethyl)benzene (2).**[29] Freshly distilled, dry benzene (115 mL) was added to a dry 1 L round-bottomed flask containing 4A molecular sieves. Then 7.0 g of 1 and 65 mL dry 1-propanol were added. The mixture was allowed to reflux for 20 h. The mixture was filtered, and most of the solvent was removed on a rotary evaporator, under high vacuum. The product was a clear, colorless, slightly viscous liquid, which was further separated on a 45-cm spinning band column (10:1 drop ratio). Bp (at 2 torr) was 182 °C (lit.[29] 124-126 °C at 0.001 torr). NMR($CDCl_3$) δ 7.5 (s, 4 H), 3.2 (m, 12 H), 1.5 (m, 12 H), 0.85 (t, 18 H). Sample hydrolyzed during attempts to obtain an IR spectrum.

Tetramine

**3, 3', 4, 4'-Tetraaminobiphenyl (3)**; alternatively called "diaminobenzidine," 99+%, was used as received from Aldrich. The mp (175-177 °C) and proton NMR spectum confirmed the lack of impurities.

Diacids/diesters

**1,4-Bis(methylcarboxy)benzene (5)**; alternative name is dimethyl terephthalate. Deionized water (200 mL) was added to 10 g of **1**, and the mixture was allowed to stand overnight at room temperature. The ester was collected and recrystallized from petroleum ether. Mp 140-142 °C (lit. mp[44] 139.5 °C).

**1,3-Benzene Dicarboxylic Acid (6)**; alternative name isophthalic acid, was used as received from Aldrich. Mp (341-343 °C) agreed with literature values. [45]

Dialdehydes

**1,3-Benzenedicarboxaldehyde (7)**; alternative name is isophthaldehyde, was used as received from Aldrich. Mp (88-90 °C) agreed with literature values. [46]

**1,5-Naphthalenedisulfonyl Dichloride (9)**. This procedure is a variation of that described by Caesar.[30] The disodium salt of 1,5-naphthalene disulfonic acid (13.9 g, 0.04 mol) was placed in a 1 L three-neck flask. Phosphorous pentachloride (20.4 g, 0.1 mol) was added, and the flask was capped and vigorously shaken until the color and texture of the mixture appeared uniform. The flask was equipped with a reflux condenser and a drying tube filled with fresh Drierite. (Air was present; nitrogen gas was not used.) This temperature was maintained for 1 h. The condenser and drying tube were removed for roughly 30 seconds every 10 minutes, to allow mechanical stirring of the reaction mixture. As the reaction progressed, a clear, colorless liquid was observed in the condenser, and the previously powdered mixture became a thick paste.

The reaction flask was removed from the oil bath and placed on a Kugelrohr apparatus. The temperature was brought to 110 °C, and suction was gradually applied, to remove liquid $POCl_3$. The resulting dry cake was pulverized in a mortar, and transferred to an Erlenmeyer flask. The crude product was mixed with 75 mL deionized water and 200 mL chloroform, and heated (with vigorous stirring) until the solid was almost completely dissolved. The hot mixture was transferred to a separatory funnel, and the organic layer was collected. Roughly three-quarters of the chloroform was boiled off, and the remaining liquid was cooled overnight in a sealed container. Pale yellow crystals (14.5 g) were collected (61% yield of 9). Mp 183-186 °C (lit. mp[30] 183 °C).

**Naphthalene-1,5-bis(sulfoneoxy-1,4-phenylene carboxaldehyde) (11);** Procedure 1 (Scheme 18): A portion of 9 (3.18 g, 10 mmol) was dissolved in 20 mL dry pyridine. An equimolar portion of 4-hydroxybenzaldehyde (**10**, from Aldrich) was added, and the mixture was heated to 100 °C and held there for 1 h. The reaction mixture was cooled to 5 °C, and the precipitate was collected by filtration. This beige solid was quickly washed with 20 mL deionized water at room temperature (to remove pyridinium hydrochloride). The resulting beige power was washed with hot chloroform, which absorbed much of the yellow-brown color from the material. The product was dried at 50 °C, under vacuum, for 18 hours. The product consisted of 0.69 g (14% overall yield for this synthesis) of pale beige crystals, presumed to be **11**. Mp 224-226 °C (sealed tube, low pressure). The product was insoluble in the normal range of NMR solvents. MS *m/e* (relative intensity) 63 (10), 64(10), 65(48),121 (60), 122(21), 126 (100), 127(29), 247 (70), 248(13), 310(14), 374(23), 496(1).

Procedure 2 (Scheme 19)[47]: A portion of **9** (3.18 g, 10 mmol) was dissolved in 15 mL warm (37 °C) dichloromethane containing 0.05 g of benzyltriethylammonium chloride (a phase transfer catalyst). In a separate container, 3.05 g (25 mmol) of **10** was added to 25 mL of a slightly warm 2 N aqueous sodium hydroxide solution. The two mixtures were combined and mixed vigorously at 38 °C (in the presence of air) for 40 minutes. During the reaction, the two layers formed a stiff, foamy emulsion. The reaction mixture was washed with chloroform (3 X 50 mL), and the emulsion disappeared. The organic washes were added slowly to acetone and the fine, light beige precipitate was collected by filtration and dried overnight over Drierite. The crude yield was 79%. The product decomposed at 225-228 °C. It was minimally soluble in chloroform after drying. Proton NMR($d_6$-DMSO): $\delta$ 9.9 (s, 2H), 9.2 (d, 2H, J= 8.7 Hz), 8.3 (d, 2H, J= 7.3 Hz), 7.8 (dd, 6H, J= 8.3 and 8.7 Hz), 7.2 (solvent), 7.1 (d, 4H, J= 8.5 Hz). MS: m/e (relative intensity) 65(11), 121(29), 126(100), 127(28), 218(10), 225(14), 247(60), 288(13), 311(17), 375(22), 496(7).

Procedure 3 (Scheme 20): Preparation of acetal (**10a**).[33] A 1.22 g portion of **10** and 4-5 grains of p-toluene-sulfonic acid monohydrate were added to 150 mL of dry toluene. The mixture was heated to reflux, and 1.14 g (a 10% excess) of predried 3, 3,-dimethyl propane diol was added. (The diol had been dried at 65 °C, low pressure, for several hours.) Water-toluene azeotrope was collected in a Dean-Stark trap as the reaction progressed. The reaction was allowed to continue until azeotrope no longer appeared (a total of 7 h). The reaction mixture was cooled, and 125 mL of ethyl acetate was added to it. The mixture was washed with deionized water (2 X 50 mL) and dried over sodium sulfate. The solvent was removed on a rotary evaporator, and the resulting beige solid was recrystallized from ethyl acetate. The recrystallized crude product crystals were crushed and washed with ethyl acetate until no additional color was lost to the solvent. The final product was a colorless crystalline solid, mp was 134-136 °C. Overall yield was 20%.

Attempt to form **11** via **10a**.[34] A 5 mmol portion of **9** and 10 mmol of **10a** were added to 25mL of dry pyridine. The mixture was heated to 100 °C and allowed to react for 1-48 h (varying times did not affect product). The reaction mixture was cooled, and 1.82 g (55%yield) of fine white precipitate was collected by filtration and placed in a dessicator overnight. Proton NMR ($D_2O$, sample tube was base-washed) $\delta$ 8.6 (d, 2H, J= 8.7 Hz), 8.5 (d, 4H, J= 5.6 Hz), 8.3 (dd, 2H, J= 8.4 and 7.6 Hz), 8.0 (d, 2H, J= 7.3 Hz), 7.8 (dd, 4H, J= 6.9 and 7.0 Hz), 7.5 (t, 2H, J= 8.0 Hz). The product was not analyzed further, due to the lack of methyl signals.

## Bibenzimidazoles

**Bis-2,2'-(p-hydroxyphenyl)-5,5'-bibenzimidazole (13)**; Procedure 1 (Scheme 22): A 0.304 g (2 mmol) portion of anisic acid (p-methoxybenzoic acid) was added to 0.214 g (1 mmol) of **3** in 6 mL PPMA. The mixture was heated to 130 °C, for 3 h. The solution was then added to 100 mL deionized water and neutralized with potassium carbonate, during which a large volume of foam (approximately 300 mL) was generated. The foam slowly collapsed, and then the precipitate was filtered and washed with boiling water (100 mL X 3). The beige solid was dried for 18 h at room temperature, in air. The product decomposed at 275 °C, in a sealed tube. The product was insoluble in standard NMR solvents at room temperature (it was minimally soluble in hot DMSO). Based on the weight of the product (equivalent to 110% yield), it was postulated that the solvent was present in the crude product.

Cleaving the methoxy groups to hydroxy groups.[36, 48] A 0.30 g portion of the crude product was added, with 0.335 g (6.7 mmol) of sodium cyanide (an estimated 10 times excess), to 8 mL of DMSO. The mixture was heated to 160 °C, and kept at that temperature for 24 h. The reaction mixture was cooled and added to 150 mL ice water. This was acidified with HCl, and the resulting brown gel was collected by filtration (filtration was extremely slow; the gel seemed to hold the liquid and/or clog the filter paper). The brown gel was washed with deionized water, refiltered, and dried at high vacuum for 16 h. The dried product was a fibrous brown solid, which was insoluble in standard solvents. The sample seemed to contain a large amount of filter paper, and was not subjected to further analysis.

**Bis-2,2'-(p-hydroxyphenyl)-5,5'-bibenzimidazole (13):** Procedure 2 (Scheme 23): A 10 mmol portion of **3** was heated to 130 °C in 15 mL of a dry DMAc/dry toluene mixture (70:30) . A solution of **10** (20 mmol in 15 mL dry DMAc) was added over a period of 2 h. Dry air was bubbled through the reaction mixture during the dialdehyde addition time. The mixture was then heated to 150 °C to facilitate removal of the azeotrope, which was collected in a Dean-Stark trap. After an additional 4 h of reaction time, azeotrope appearance stopped. The reaction mixture was cooled and added dropwise to 300 mL of toluene. A bright yellow precipitate formed, which formed dark brown, tarry lumps as it settled in the container. The tarry solid was redissolved in 300 mL warm acetone. Approximately 2/3 of the acetone was boiled off, without any precipitation. The remaining 100 mL of crude product/acetone mixture was condensed to a volume of 20 mL on a rotary evaporator, at which point, tarry brown precipitate reappeared. The tarry precipitate was heated in a vacuum oven at 100 °C for 30 minutes. The dried product (**14**) was ground in a mortar and pestle, the result was 2.7 g of a red-brown powder (65% yield, based on molecular weight of desired product). NMR ($d_6$-DMSO) δ 9.9 (m), 7.9 (m), 7.8 - 7.1(m), 6.9 (m), 6.8 - 6.4 (m); (aromatic region shown as Figure 11). Integrations were not obtained, due to the difficulty in distinguishing aromatic signals.

**Bis-2,2'-(p-hydroxyphenyl)-5,5'-bibenzimidazole dihydrochloride (16)**; (Scheme 24): Twenty mmol (4.28 g) of **3** was heated to 130 °C in 30 mL dry toluene/dry DMSO (2:1). Dry air was bubbled through the mixture, and 4.88 g (40 mmol) of **10** (in 20 mL of the same solvent) was added dropwise to the hot tetramine solution, over a period of two hours. The temperature of the mixture was raised to 150°C, and was maintained there for 4 hours. Water was removed during the reaction by collection in a Dean-Stark trap. As reaction volume decreased, an additional 10 mL of dry toluene was added to the flask. The extremely dark, clear reaction mixture was acidified with HCl, cooled to room temperature and diluted in 200 mL acidic water. The metallic pink-brown precipitate was collected and washed with hot acetone-HCl (100:1). The red-brown solid (**15**) was recovered by filtration and dried at room temperature for 14-18 h under vacuum. This material (**15**) had a mp of more than 400 °C. NMR ($d_6$-DMSO) δ 10.8-10.7 (s), 8.4-8.2 (m), 8.1-7.6 (m), 7.4-7.2 (m), 7.1-6.9 (m), 6.8-6.6 (m), 4.5-2.8 (broad s); (shown as Figure 12; as with procedure 2, integrations were not reliable). This material was ground in a mortar and heated for one hour at 220 °C, in the presence of air. During the heating, the material lost its red tint, and became light brown. A total of 6 g (a yield of approximately 60% of **16** was obtained. (Mp: 390 °C, decomposed). Proton NMR ($d_6$-DMSO; integrations were not reliable) δ 10.9 (s), 8.25 (d, J=8.5 8.5Hz), 7.95 (s), 7.9 - 7.75 (dd, J= 8.45, 5.96 Hz), broad hump at 4.5 - 2.8 (HCl); (shown as Figure 13). Carbon NMR ( $d_6$-DMSO) δ 162, 149, 137, 132, 131, 130, 124, 116, 114, 113, 111 (given below as Figure 16). IR: broad signal from

3700 - 2200 , 7743, 7563, 7484, 7448, 7370, 7274, 7230, 6514, 2845, 1610, 1469, 12β4, 1182, 841,806, 692, 358, 351 cm $^{-1}$ (given below as Figure 17). FAB/MS (in 3-nitrobenzyl alcohol) $M^{+}+1 = 419$ ($C_{26}H_{18}N_4O_2$).

Figure 16. Carbon NMR of 16.

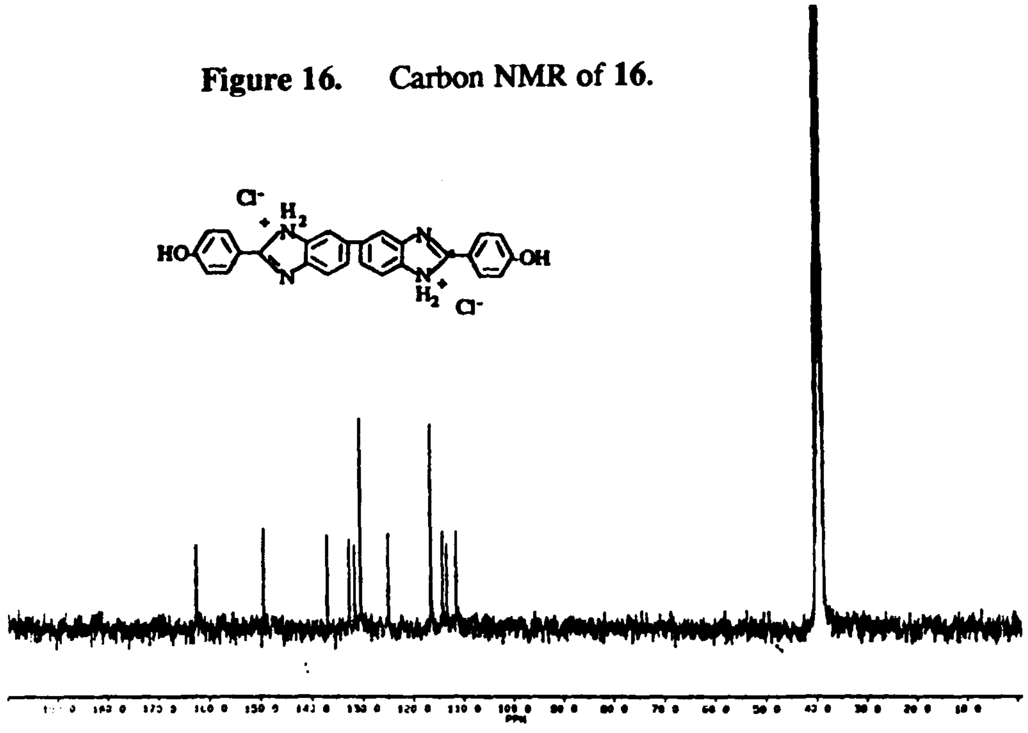
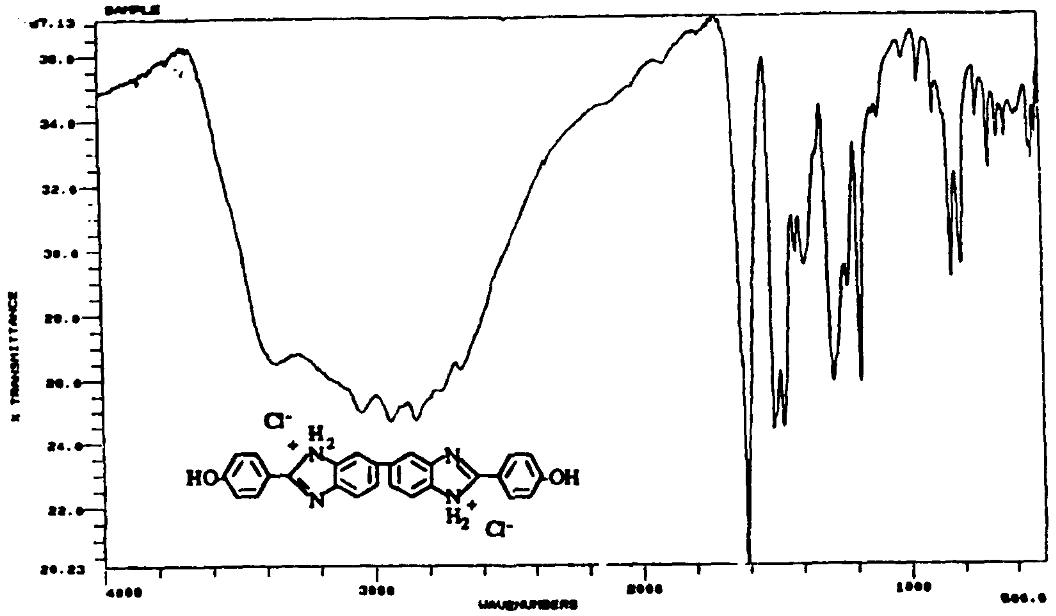


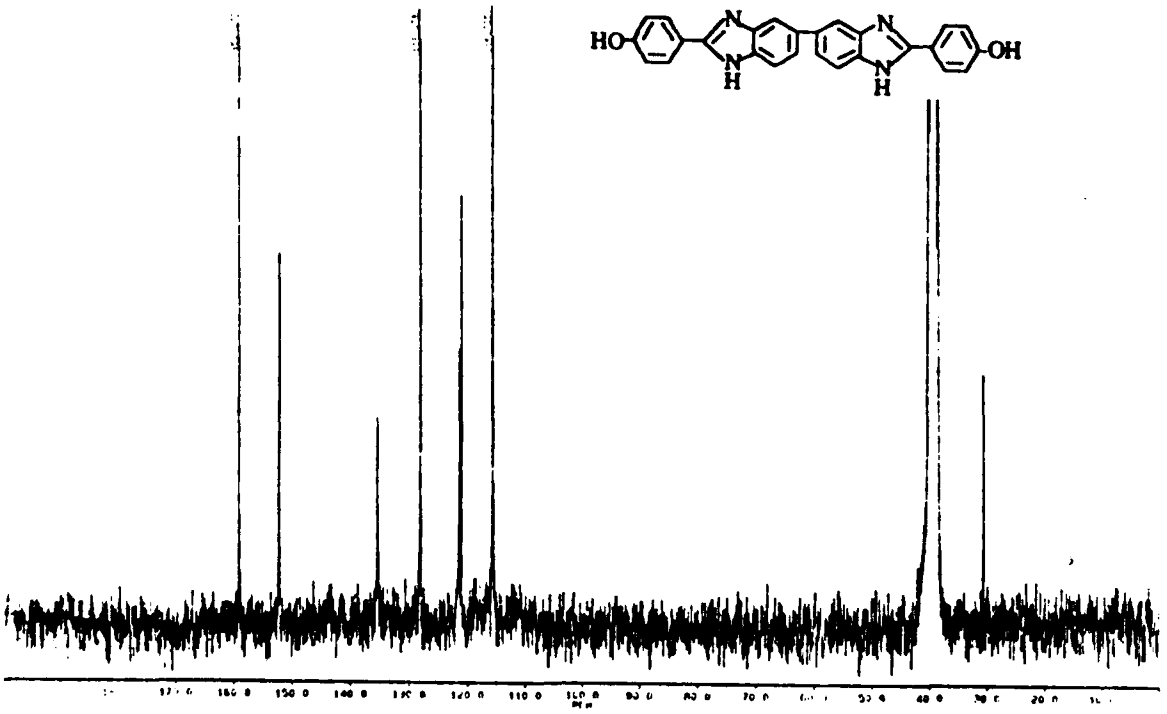
Figure 17. IR spectrum of 16.



### Bis-2,2'-(p-hydroxyphenyl)-5,5'-bibenzimidazole (13)

(Procedure 3, Scheme 24, continued) The product from the procedure just described (16) was redissolved in dry DMSO, under nitrogen, and 2.5 equivalents of sodium bicarbonate were slowly added. This mixture was stirred, under nitrogen, for 30 minutes at room temperature. The reaction mixture was added to deionized water, and immediately filtered. The resulting precipitate (13) was dried at 80 °C, under vacuum, for 2 h. Material appeared to begin decomposition at 260 °C. Proton NMR ($d_6$-DMSO) δ 10.0 (s, 1.6 H); 8.0 (d, 4 H, J= 8.6 Hz); 7.76 (s, 2 H); 7.6 (d, 2H, J= 7.9 Hz); 7.5 (d, 2 H, J= 8.5Hz); 6.9 (d, 4 H, J= 8.6 Hz); (shown as Figure 14). Carbon NMR ($d_6$-DMSO) δ 159, 152, 136, 128, 122, 121, 115, 114, 40 (DMSO), 30 (spectrum given below as Figure 18).

Figure 18. Carbon NMR of 13.



Attempted methylation of **13**: To a dry 50 ml, 3-neck round bottom flask were added 10 mL dry DMSO, 0.838 g (2 mmol) of **16** and 5 equivalents sodium bicarbonate. The mixture was stirred at room temperature for 30 min, yielding **13** in solution. To this was added 0.4 mL (6 mmol) of freshly distilled methyl iodide (from Aldrich). The mixture was stirred at room temperature for 6 h.[38] Then 4 equivalents of potassium carbonate were added and the mixture was maintained under the same conditions for 14 h.[38, 39] The reaction mixture was added to deionized water. The precipitate was collected and dried under vacuum at 60 °C for 2 h. An aliquot was removed after 45 min of reaction and subjected to the same workup that the bulk reaction mixture later underwent. Proton NMR (d6-DMSO): $\delta$ 10.07 (s, 1H), 8.0 (d, 4H, J= 8.6 Hz), 7.78 (s, 2H), 7.6 (s, 2H), 7.5 (s, 2H), 6.93 (d, 4H, J= 8.6 Hz). At that point, little or no methylation had occurred. Spectra of an aliquot taken at 3 h appeared to show the breakup of the benzimidazole ring(s). Proton NMR at 3 h (d6-DMSO): d 10.25 (broad), 8.1 (broad), 7.9-7.5 (broad), 6.9 (broad).

## Polymerizations

### Ortho esters plus tetramine

(Scheme 15): A 100 mL 3-neck round bottom flask was dried at 110 °C for 6 h. The flask was equipped with a mechanical stirrer. A 0.67g (2.3 mmol) portion of ortho ester (**1** or **2**) and 0.5 g (2.3 mmol) of **3** were added to 33 mL of a 10:1 solution of dry DMSO:dry pyridine. The mixture was stirred at room temperature for 15 min, and then placed in an oil bath (100 °C) and maintained under these conditions for 12 h. The flask was removed from the oil bath and cooled to room temperature. The reaction mixture was added dropwise to 75 mL acetone. No precipitate formed in any trial of this chemistry, so product (4)was judged to be of very low inherent viscosity.

Dicarboxylic acid derivatives plus tetramine

(Scheme 16): A 25 mL 3-neck flask was predried and equipped with a reflux consenser. Freshly prepared PPMA (6 mL) was warmed slightly, in a different flask, and transferred to the reaction vessel by syringe. To this was added 0.19g (1 mmol) of dicarboxylic acid derivative (5 or 6) and 0.214 g (1 mmol) of 3. The extremely dark-colored mixture was heated to 100 °C and stirred for 12-20 h. The reaction mixture was removed from the heat and added dropwise to 50 mL of deionized water. Precipitate was collected by filtration, washed several times with deionized water, and dried in a vacuum oven at 60 °C for 6-14 h. Aliquots were removed periodically during the reaction times, and subjected to the same workup that the bulk reaction mixture would later undergo. In all cases, the product resembled a gel and was generally dark orange-brown before drying (dark brown-black after drying). The samples were redissolved in DMAc, producing an orange-brown solution, for inherent viscosity measurements. In several trials, the product was insoluble in DMAC or other standard solvents (sulfuric acid, acetone, DMSO, formic acid), despite sonication for over 48 h. Inherent viscosity results were given in Table 2.

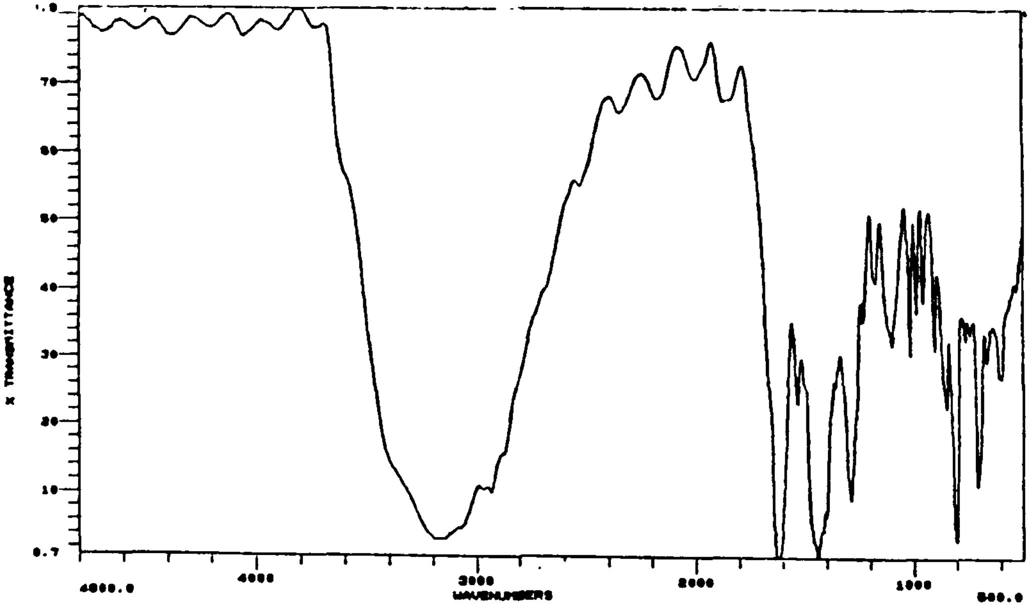
Dialdehydes plus tetramine

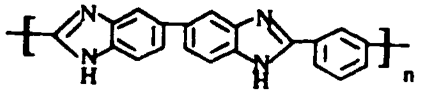
(Scheme 17): A small 3-neck round bottom flask was predried and equipped with a predried dropping funnel. To the round-bottom flask was added 0.214g (1 mmol) of 3 and 5 mL dry DMAc (forming a very pale pink solution), and the apparatus was placed in a dry ice/carbon tetrachloride bath (-15 °C). Meanwhile, 0.0.134 g (1 mmol) of 7 was added to 15 mL dry DMAc in a predried vial, and the resulting mixture was placed in a dropping funnel. The pale yellow solution containing 7 was added in very small portions over 2-3 h, while the reaction mixture was vigorously stirred and maintained at -15 °C. The reaction mixture became a very clear, intense yellow color as 7 was added. After the addition of 7 was complete, the reaction mixture was allowed to come to room temperature and remained there for 0-21 h. The dropping funnel was replaced by a septum and thermometer. Upon warming to room temperature, the reaction mixture became a clear, dark orange. After the "wait time" the temperature was raised by an oil bath, and dry air was bubbled through the solution at approximately 200 mL/min. The air was passed through two drying tubes containing Drierite and introduced into the solution. The solution became orange-brown as the reaction progressed. Throughout the reaction, aliquots were taken and added to deionized water. The resulting precipitate (8) was collected, washed with more water and dried in a vacuum oven for 12-24 h, at 60 °C. The samples were redissolved in DMAc (producing solutions ranging from orange-brown to yellow), and the inherent viscosity was measured. The volume of the reaction was kept constant by replacing the volume of the aliquots taken with dry DMAc. Upon completion of the total reaction time, the remaining bulk of the reaction mixture was added to deionized water. The resulting precipitate was collected, washed with water and dried in the same fashion as the aliquots described above. Samples were generally brown to orange-brown prior to drying, and dark brown after drying.

Samples exhibiting inherent viscosities in the order of 0.7 dL/g or above were fibrous, both before and after drying. Results were given in Table 3.

Film preparation: Product polymer was redissolved in DMAc (concentrations ranging from 0.5 g/mL to 1 g/mL). The solutions were placed on a glass plate and heated to 60 °C, in air, and held there for 2-3 h. Polymer with $\eta_{inh}$ of 0.7 dL/g or higher peeled from the plate spontaneously during the drying process, and were easily removed. Samples with lower viscosities were removed by placing the slide in water and/or acetone; if this were unsuccessful, attempts were made to peel the "film" from the plate with a razor blade. Films were dried further in a vacuum oven at 100 °C, and stored in a dessicator or low-humidity cabinet. Color did not relate directly to the quality of the films (good films were clear pale brown, yellow or golden). Sample films were subjected to IR analysis: 3700-2500, 2366, 2197, 2025, 1888, 1743, 1558, 1450, 1336, 1242, 1184, 1111, 1030, 1005, 972, 929, 858, 839, 771, 723, 675, 607 cm $^{-1}$ (given below as Figure 19).

**Figure 19.** IR spectrum of film made from **8**.





## Disulfonate dialdehydes plus tetramine

(Scheme 21): A solution of 3 (1 mmol, 0.214 g) in various solvents listed in Table 4 was cooled to approximately -15 °C by a carbon tetrachloride/ dry ice bath. An equimolar amount of **11** (0.496 g, 1 mmol), in the same solvent, was slowly added to the tetramine solution via an equalized pressure dropping funnel. At the end of the addition time, the solution was allowed to come to room temperature (the "wait time"). Then the dropping funnel was replaced by a reflux condenser, and the nitrogen inlet was replaced by an air inlet (with a long, large-bore needle. The solution was heated (to the temperature given as "T (rxn)" in Table 4) and dry air was bubbled through it for the duration of the "t (rxn)." Conditions such as length of addition times, concentration, and wait or reaction times were varied. Specific conditions were given in Table 4. Periodically, aliquots were taken from the reaction vessel, and precipitated in deionized water. The product (**12**) was collected and dried at 100 °C for 18-24 h, then redissolved in DMAc for inherent viscosity measurements. When inherent viscosity began to decrease (or stop increasing), the bulk of the reaction mixture was subjected to the same workup as the aliquots. Molecular sieves (3A), when used, were freshly activated.

## Nucleophilic aromatic substitution with bibenzimidazole monomers

(Scheme 26): A predried 3-neck flask was equipped with a Dean-Stark trap and a reflux condenser. To this was added 1 mmol of **13** in 15 mL of a 2:1 mixture of dry DMSO/dry toluene (some runs were done in dry DMAc). This was heated slightly (60 °C) to dissolve the monomer, and then 2-4 equivalents of potassium carbonate (other runs were done with potassium hydroxide) were added. Within 15 minutes of base addition, the reaction mixture changed to a clear red-purple color, and a white precipitate formed at the bottom of the flask. The temperature was raised to 135 °C, and 1 mmol of **17** (obtained from Aldrich) was added. Aliquots were removed periodically, and worked up as described below (for the bulk of the reaction mixture) to check inherent viscosity. The volume was kept constant by replacing the aliquots with dry solvent. The reaction mixture was cooled, added to deionized water, and neutralized with hydrochloric acid. The precipitate (**18**) was collected by filtration, washed several times with water, and dried in a vacuum oven (100 °C for 2-10 h). Inherent viscosities were on the order of 0.1- 0.3 dL/g. The reaction was allowed to run up to 4 days, with little increase in inherent viscosity. Films were not attempted, due to the low quality of the product.

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