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INVESTIGATIONS OF POLYBENZIMIDAZOLE SYNTHESIS

FREDERICK L. HEDBERG

TECHNICAL REPORT AFML-TR-72-267

JUNE 1973

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AFML-TR-72-267

INVESTIGATIONS OF POLYBENZIMIDAZOLE SYNTHESIS

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "Synthesis of Novel Polymer Materials for High Temperature Resin Applications." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as Project Scientist.

This report covers work conducted from December 1970 to May 1972. The manuscript was released by the author in May 1972 for publication as a technical report.

This technical report has been reviewed and is approved.

R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

To investigate the suitability of a sample of 3,3',4,4'-tetraaminodiphenyl, from a new commercial source, for the synthesis of polybenzimidazoles (PBI), two standard procedures were used. The first procedure, melt phase reaction with diphenyl isophthalate, afforded a hydrated product of low viscosity. The second procedure, reaction with isophthaldehyde bis (bisulfite adduct), in refluxing N,N-dimethylacetamide, did not give meaningful results because of difficulties in purifying the bis (bisulfite adduct). A new method of PBI synthesis was then developed in which the tetraamine was reacted with diphenyl isophthalate in refluxing sulfolane. The product obtained by this method had a satisfactory inherent viscosity and showed no evidence of any appreciable cross-linking or hydration. The sample of tetraamine was therefore concluded to be of suitable quality for PBI synthesis. A critical comparison is given of the three synthetic methods used. The scope of the sulfolane solvent system for PBI-type syntheses was also explored by examining other tetraamine-diphenyl ester combinations. For cases where low reactivity of monomers or low solubility of products precluded the use of sulfolane, phyenyl sulfone proved to be a satisfactory alternative solvent.

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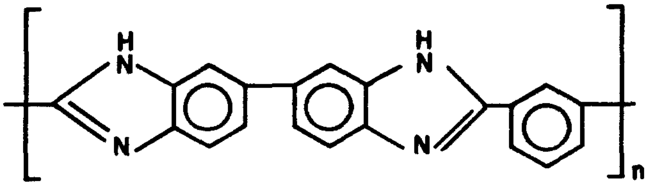
SECTION I

INTRODUCTION

Since the original synthesis of poly [2,2'-(m-phenylene)-5,5'-bibenzimidazole](PBI)(I) a number of methods have been reported for the preparation of this very thermally stable polymer. The four major methods are melt polymerization at atmospheric pressure (Reference 2a) melt polymerization under high vacuum (Reference 2b), solution polymerization is polyphosphoric acid (Reference 3) and solution polymerization in N,N-dimethylacetamide (DMAc) (Reference 4). All of these methods employ, as monomers, derivatives of 3,3',4,4'-tetraaminodiphenyl (II) and isophthalic acid or isophthalaldehyde. The most expensive monomer is, currently, the tetraamine. One goal of this research investigation was to determine the quality of a sample of II supplied by the Upjohn Company as a potential new low-cost commercial source.



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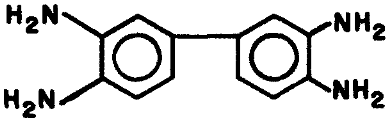

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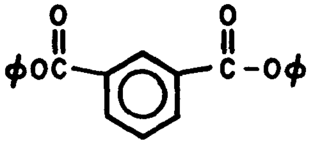
Of the four methods for synthesis of I mentioned above, the two most promising appeared to be the melt polymerization at atmospheric pressure and the solution polymerization in DMAc. The former is a two-step process using a mixture of II and diphenyl isophthalate (III), and is the common commercial method for synthesis of I. The latter is a considerably simpler procedure, but uses the more expensive isophthalaldehyde bis (bisulfite adduct) (IV) as the comonomer with II. These two methods were, therefore, used initially with the sample of II to be tested. In addition to the experimental examination of monomer II, the present investigation also afforded the opportunity to critique the two methods of synthesis used, as well as to compare with the new synthetic method derived during the course of this research.



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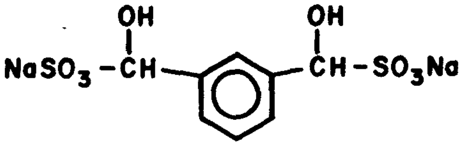

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SECTION II

RESULTS AND DISCUSSION

A. Melt Phase Polymerization

The first step in the reaction of II and III in the melt phase under nitrogen was effected by heating slowly to a bath temperature of 295-305°C. During this process, a white sublimate formed in the upper part of the reaction flask and the lower part of the outlet tube, and remained there during the rest of the reaction period. While the majority of the sublimate was undoubtedly phenol, it is possible that a portion may have been monomeric material. Such a loss of monomer (aided under these conditions by both the nitrogen flow and the "steam distillation" effect of the evolved water) may have contributed to the low viscosity of the final product (of Table 1).

The second step in the polymerization consisted of grinding the prepolymer from the first step and heating it to 390°C. The disadvantages in this operation are the difficulty in effecting complete removal of air absorbed on the prepolymer surface before heating, and the difficulty (also applicable to the first step) in maintaining even heating of the solid material, complicated more by the cooling effect of the nitrogen flow. De-aeration of the solid reactant mixture in both steps was accomplished by stirring the solid under a brisk stream of nitrogen, but for thorough de-aeration it is undoubtedly more desirable to use the recommended procedure of repeated evacuation and nitrogen flushing.

Some crosslinking resulting in H_2SO_4-insoluble product has been reported (Reference 2b) for this reaction. All of the product obtained in our reaction was soluble in H_2SO_4, due, undoubtedly, to the low viscosity obtained. Precipitation of the H_2SO_4 solution of polymer with water and drying to constant weight at 160°C in vacuo afforded a 112% yield, apparently due to hydrate formation as, in spite of the low viscosity obtained, the product was almost completely insoluble in DMAc. Whether the hydrate formation occurred during the second step of the reaction or during the subsequent precipitation operation was not determined.

In general, the melt phase reaction was found to be very tedious and time-consuming.

B. Solution Polymerization in DMAc

The solution polymerization of II and IV to polybenzimidazole should actually be considered as a two-step process, since IV is not available commercially, but must be prepared beforehand from isophthalaldehyde and sodium bisulfite. The polymerization step is quite simple, consisting of refluxing II and IV in DMAc, followed by precipitation with water. The inherent viscosities obtained in two separate runs, however, were rather low (cf. Table I).

To determine the reason for the low viscosities, a closer look at the purity of the IV used was taken. The isophthalaldehyde used for making IV was obtained from a freshly opened bottle, but one of indeterminate age, and, even after recrystallization, had a light brown color and a somewhat low melting point. The conversion of this material to IV afforded a colorless bisulfite addition product which was assumed to be pure. Upon reconversion of IV back to isophthalaldehyde by acidification, a light brown colored material with a low melting point was obtained, indicating that the impurity was carried over into the bisulfite addition product.

It was thus impossible to determine the purity of II when the IV used as comonomer was itself impure. While the isophthalaldehyde could probably be purified by a process such as sublimation, it apparently, like most aldehydes, tends to decompose upon standing. Aside from economic considerations, the tendency toward decomposition of isophthalaldehyde together with the necessity to convert it to IV imply that any process for synthesis of polybenzimidazole starting from IV will be less desirable than a process which uses the more stable III.

C. Polymerization in Sulfolane

Rather than repeat the tedious melt polymerization described in Part A, or attempt further to purify the isophthalaldehyde necessary for the polymerization process described in Part B, a new method for synthesis of polybenzimidazole was developed which combined the convenience of using III as a monomer with the ease of a solution polymerization. The reaction of II and III in refluxing sulfolane (tetrahydrothiophene-1,1-dioxide) afforded excellent yields of polymer. The reaction was carried out with concentrations of monomer leading to both solutions and suspensions of polymer with good viscosities obtained in either case (cf. Table 1). The solution viscosity appeared to be time-dependent, but more runs will be necessary to determine the optimum time for attaining a maximum viscosity, as well as to determine the maximum concentration permissible.

In spite of the high viscosity, all of the PBI obtained from this reaction was soluble in DMAc, indicating the absence of either appreciable crosslinking or hydration. It can be concluded at this point that the sample of II from the Upjohn Company is of sufficient quality for polymer synthesis.

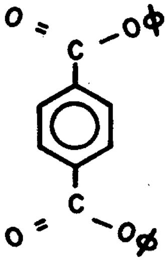
The advantage of the above-described synthesis of PBI in sulfolane over the synthesis in DMAc, described in Part B, is the greater accessibility and stability of III versus IV. Some of the advantages of the sulfolane polymerization over the melt-phase reaction, described in Part A, are: (1) one step vs two steps; (2) no attention to temperature control necessary; (3) solvation of transition states by polar sulfonyl group of solvent to lower energy of activation; this, in turn, permits much lower reaction temperature, with less consequent chance of cross-linking; (4) constant mixing possible throughout course of reaction, permitting reactive end-groups to find one another more easily; in solid state reaction, endgroups may be trapped in positions where they can only cross-link; (5) the byproducts, water and phenol, are driven out of the reaction by the boiling sulfolane, whereas they can be trapped in the solid; (6) the solution of monomers in sulfolane is easier to de-aerate than the mixture of solids.

TABLE I

YIELDS AND VISCOSITIES OF I

Type of Polymerization	Yield	Viscosity (solvent)
melt	112%	0.28 (H_2SO_4)
DMAc solution (1)	65%	0.14 (HCOOH) 0.21 (H_2SO_4)
DMAc solution (2)	93%	0.14 (H_2SO_4)
sulfolane solution (3.5 hrs. reflux)	9%	0.024 (H_2SO_4)
sulfolane solution (17 hrs. reflux)	85%	0.43 (H_2SO_4)
sulfolane suspension (72 hrs. reflux)	99%	0.69 (DMAc)

To determine the general utility of sulfolane for the synthesis of PBI polymers, a variety of other tetraamine-diester combinations were reacted together in sulfolane. Reaction occurred between II and diphenyl terephthalate (V), as evidenced by water and phenol evolution, but the resultant poly[2,2'-(p-phenylene)-5,5'-bibenzimidazole] (VI) (Reference 1) came out of solution as a sticky gel which adhered to the walls of the reaction vessel and scorched to an insoluble, infusible, dark brown solid during the heating period. The use of 2% lithium chloride to increase solubility gave no improvement in results. The use of sulfolane for polymerization of this system, therefore, appears to be impractical for concentrations other than possibly very dilute solutions.



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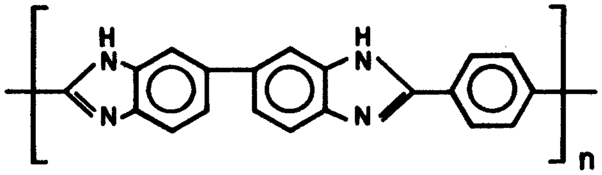

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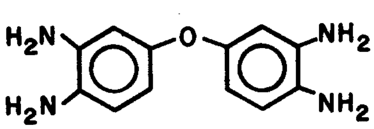
A much better method of synthesis of VI was found to be polymerization of II and V in refluxing phenyl sulfone. The polymeric product came out of solution during the course of this reaction as a yellow solid which was completely soluble in sulfuric acid and had an inherent viscosity of 1.03. This result is probably due to both the higher reaction temperature (370°C versus 270°C) and the better solubilizing ability of phenyl sulfone versus sulfolane. Although the reaction in phenyl sulfone is somewhat less convenient to run than that in sulfolane because of the high melting point of the former (125°C), the reaction can still be initiated as a solution or suspension by the addition of a low boiling solvent such as toluene which is removed during the heating process. Phenyl sulfone thus appears to be a useful solvent for those PBI preparations where either low reactivity or low product solubility create a problem with sulfolane, or where a faster reaction time is desired.

The enhancement in reaction time was shown dramatically by the preparation of I in phenyl sulfone. A total of two hours of reaction time, including one hour to remove added xylene, afforded I with a viscosity of 0.91 for a 0.3% solution. The product was not soluble in boiling DMAc, but dissolved readily in DMAc containing 1% LiCl to give solutions with up to 20% concentration.

The reaction of 3,3', 4,4'-tetraaminodiphenyl ether (VII) with III in sulfolane afforded a 90% yield of poly[2,2'-(m-phenylene)-5,5'-di(benzimidazole)ether] (VIII) (Reference 6). Similarly, the reaction of 3,3', 4,4'-tetraamino-benzophenone (IX) with III led to a 71% yield of the heretofore unreported poly[2,2'-(m-phenylene)-5,5'-di(benzimidazole)ketone] (X). The relatively low viscosities obtained for VIII and X are probably due to the purity of the corresponding tetraamines as well as to lack of optimization of reaction conditions. The use of sulfolane for PBI-type condensation polymerizations, with the consequent advantages outlined previously, thus appears to be extendable to other tetraamine-diester systems.



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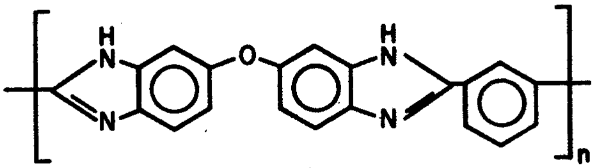

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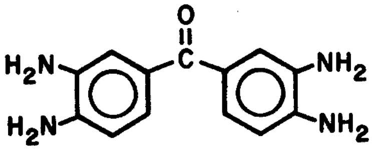

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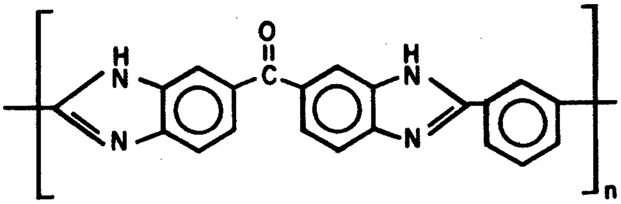

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SECTION III

EXPERIMENTAL

Melt preparation of poly 2,2'-(m-phenylene)-5,5'-bibenzimidazole (I)

3,3',4,4'-Tetraaminodiphenyl (5.357g., 0.0250 mole) and diphenyl isophthalate (7.958g., 0.0250 mole) were weighed into a 200 ml. 3-neck round bottom flask. The solid reactants were washed to the bottom of the flask with 25 ml. of toluene, stirred under a brisk stream of nitrogen for 30 min., and then heated at 2° per min. with a bath of Wood's metal. The toluene distilled off first, and then, above ca. 200°C, water and phenol began to distill. The bath temperature was taken up to 295-305°C and maintained in that range for 3 hours. The yellow solid present was then allowed to cool to room temperature, under nitrogen, and ground in a mortar. The yellow powder was reheated under nitrogen to 345°C for 5.5 hours and then to 390°C for 2 hours. The solid mass was cooled to room temperature under nitrogen, and taken up in concentrated H_2SO_4. The solution was filtered (no appreciable residue was left on the filter), and poured, with stirring, into 2 l of H_2O. The yellow precipitate was filtered, washed with water, and dried *in vacuo* for 24 hours at 160°C. The material was then ground in a mortar, extracted continuously in a Soxhlet apparatus with water for 48 hours followed by ethanol for 24 hours, and redried to constant weight *in vacuo* at 160°C (96 hours) to give 8.59g. (112%) of I. The material was insoluble in boiling DMAc. An inherent viscosity was run on a 0.5% solution in H_2SO_4 at 30°C to give Ninh = 0.28.

The product was reheated under nitrogen at 380-390°C for 18 hours to give a 16% weight loss (thus lowering the yield to 94%). The resultant material was almost entirely insoluble in H_2SO_4.

Preparation of isophthalaldehyde bis (bisulfite adduct) IV

Isophthalaldehyde (5.00g., 0.037 mole) and sodium bisulfite (8.80g., 0.085 mole) were stirred for 18 hours in a mixture of methanol (500 ml.) and water (75 ml.). The white precipitate was then filtered and washed with methanol to give 5.60g. (44%) of IV.

Solution preparation of I in DMAc

A mixture of 3,3',4,4'-tetraaminodiphenyl (1.893g., 0.00882 mole) and isophthalaldehyde bis (bisulfite adduct) (3.116g., 0.00912 mole) in DMAc (300 ml.) was deaerated by stirring and passing nitrogen through the mixture for 15 minutes, and then was refluxed for 5 hours under nitrogen. While heating to reflux temperature, the original suspension turned first to an orange solution and then to a dark green solution. The reaction mixture was allowed to cool to room temperature while stirring overnight, and was then poured with stirring into 1 l. of distilled water. The yellow precipitate which formed was filtered, and the filter cake was taken up in DMAc (300 ml.) and refiltered to given an orange filtrate and leave behind a small amount of DMAc-insoluble material which was taken up in H_2SO_4. The DMAc solution was poured, with stirring, into 1200 ml. of distilled water, and the resultant precipitate was filtered, washed with water, and dried in *vacuo* at 160°C to give 1.76g. (65%) of I. A 0.5% solution in formic acid at 30°C gave Ninh = 0.14. A 0.5% solution in H_2SO_4 at 30°C gave Ninh = 0.21.

The H_2SO_4 solution of DMAc was precipitated with water and dried in vacuo at 160° to give 0.20g. (7%). A 0.5% solution in formic acid at 30°C gave Ninh = 0.65.

A second run was made under the conditions described above, except that, upon completion of the reflux period, the DMAc solution was concentrated to ca. 33% of its original volume, and reprecipitation was carried out from an H_2SO_4 solution with water to give, after drying, 1.97g. (93%) of I. A 0.5% solution in H_2SO_4 at 30°C gave Ninh = 0.14.

Analysis of IV

Isophthalaldehyde (9.1g.) was extracted with 700 ml. of 4% Na_2CO_3 solution and filtered to give 7.5g. This was recrystallized from 400 ml. of cyclohexane to give 6.4g. of mp 85°-87.5°C ((Reference 5) 89.5°C). The recrystallized isophthalaldehyde still had the same light brown color as the original material from the bottle, and was reacted with 10.0g. of sodium bisulfite in a mixture of 600 ml. of methanol and 90 ml. of water to give 10.7g. (65%) of IV. Acidification of an aqueous solution of IV with dilute HCl, extraction with ether, and concentration to dryness left light brown colored IV, mp 82°-85°C.

Solution preparation of I in sulfolane

A stirred solution of 3,3',4,4'-tetraaminodiphenyl (8.035g., 0.0375 mole) and diphenyl isophthalate (11.937g., 0.0375 mole) in freshly distilled sulfolane (200 ml.) was degassed with nitrogen for 30 min. and then refluxed under nitrogen for 72 hours. During the first 16 hours, a suspension formed. The reaction temperature was 275°C. The outlet tube from the reaction was wrapped with aluminum foil and served as a condenser for the refluxing sulfolane. The water and phenol from the reaction passed through the outlet tube and were collected in a Dean-Stark trap. The reaction mixture was allowed to cool to room temperature, and was poured, with stirring, into a mixture of methanol (1 l.) and acetone (500 ml.). The precipitate was stirred overnight, filtered, washed with acetone, and dried for 20 hours, in vacuo at 160°C. The yellow solid was then ground in a mortar and redried in vacuo at 160°C for 7 days. The product gained weight slowly upon exposure to air, and had to be weighed immediately after removal from the cooled vacuum oven. The yield of I was 11.43 g. (99%). A 0.5% solution in DMAc at 30°C gave Ninh = 0.69.

Two other runs were made under the conditions described above for shorter periods of time, and with somewhat more dilute solutions, as shown in the table below. In both cases, no polymer precipitated from the reaction mixture until it was cooled.

II	III	sulfolane	time	yield	Ninh
2.678g.	3.979g.	125ml.	3.5 hrs.	9%	0.024 (in H_2SO_4)
2.678g.	3.979g.	125ml.	17 hours	85%	0.43 (in H_2SO_4)

Reaction of Diphenyl Terephthalate (V) with 3,3',4,4'-Tetraaminodiphenyl (II) in Phenyl Sulfolane

A mixture of sulfolane (200 ml.), V (11.987g., 0.0375 mole), and II (8.035g., 0.0375 mole) was de-aerated with nitrogen for 20 min. and then stirred and refluxed under nitrogen for 40 hours. Evolution of water and phenol from the reaction mixture commenced immediately after reflux was attained, and continued through the reaction period. The nature of the reaction mixture changed from a suspension (the diester was only partially soluble at 30°C) to an orange solution, from which an orange gel came out of the walls of the flask. At the end of the reaction period, the gel had turned to a brownish-yellow solid which was completely insoluble in concentrated H_2SO_4.

The above reaction was repeated with a 2% solution of LiCl in sulfolane for a reflux period of 20 hrs. The same gelation and subsequent production of insoluble polymer occurred as described above.

Reaction of Diphenyl Terephthalate (V) with 3,3',4,4'-Tetraaminodiphenyl (II) in Phenyl Sulfone

A mixture of phenyl sulfone (200g), V(5.357g., 0.0250 mole), II (7.958g., 0.0250 mole) and toluene (50 ml.) was deaerated with nitrogen and stirred with heating. The damp suspension changed to an orange solution as the toluene was driven off. After 1 hr. of heating, the pot temperature reached 270°C at which point a small amount of precipitation could be seen. After an additional 30 min. of heating, the pot temperature reached 370°C with gentle reflux occurring, and a large amount of precipitate was present. Refluxing was continued for 5.5 hrs., at which time the yellow suspension was cooled to 150°C and poured, with stirring, into 2.5 l. of acetone. The reaction flask was washed with additional acetone (500 ml. total), and the yellow precipitate was collected and blended with acetone (3x500 ml). The product was then extracted continuously for 24 hrs. with ethanol and for 24 hrs. with benzene. Drying in vacuo at 120°C to constant weight gave 7.7 g. (100%) of VI. A 0.5% solution in H_2SO_4 at 30°C gave Ninh = 1.03.

Preparation of I in Phenyl Sulfone

A mixture of diphenyl isophthalate (15.92g., 0.0500 mole), 3,3',4,4'-tetraaminodiphenyl (10.71g., 0.0500 mole), and phenyl sulfone (100g.) was weighed into a 500 ml. 3-necked round bottom flask equipped with a mechanical stirrer (glass blade) in the center neck and a short distilling head above a gas-inlet equipped distilling adapter in a second neck. p-Xylene (100 ml.) was added, and the resultant mixture was stirred and de-aerated with nitrogen for 20 minutes. The reaction mixture was then heated and the xylene was distilled off over a 1 hour period. The pot temperature was raised to 370°C and maintained there for a 1 hour period. During this time, phenol and water distilled off and a tan suspension formed. The reaction mixture was then cooled to ca. 150°C and poured into 1 l. of acetone. The precipitate was filtered, washed three times in a blender with acetone, and dried for 16 hours in a vacuum oven at 120°C. The resultant polymer was soluble and had an intrinsic viscosity at 30°C in conc. H_2SO_4 of 0.93. It would not dissolve in refluxing DMAc, but dissolved readily in refluxing DMAc containing 1 per cent LiCl. Concentrations of 5, 10, 15 and 20 per cent were obtained with no undissolved residue. The Ninh of a 0.3% solution was 0.91.

Reaction of Diphenyl Isophthalate (III) with 3,3',4,4'-Tetraaminodiphenyl Ether (VII) in Sulfolane

A solution of III (9.549g., 0.0300 mole) and VII(6.909g., 0.0300 mole) in sulfolane (250 ml) was de-aerated with nitrogen for 20 min, and then stirred and refluxed under nitrogen for 42 hours, during which time water and phenol were evolved. The resultant brown solution, containing a small amount of brown solid, was cooled under nitrogen to 60°C and then poured, with stirring, into 1800 ml of methanol. The purple-gray precipitate was collected, washed with methanol, and dried in vacuo at 125°C for 24 hrs to give 8.75g (90%) of VIII. A 0.5% solution in H_2SO_4 at 30°C gave Ninh = 0.29.

Reaction of Diphenyl Isophthalate (III) with 3,3',4,4'-Tetraaminobenzophenone (IX) in Sulfolane.

A mixture of III (6.36g., 0.0200 mole), IX (5.966 g., 0.0200 mole), and sulfolane (300 ml.) was de-aerated with nitrogen for 20 min., and then was stirred and refluxed under nitrogen for 40 hrs., during which time water and phenol were evolved. The dark brown solution was cooled to 25°C, affording a brownish-yellow precipitate, and poured, with stirring into 1500 ml. of methanol. The precipitate was collected, washed with methanol and dried in vacuo at 125°C for 24 hrs. to give 4.80g. (71%) of X. A 0.5% solution in H_2SO_4 at 30°C gave Ninh = 0.22. The polymer was very hygroscopic as with other polybenzimidazoles, and even after further drying <u>in vacuo</u> at 190°C for 72 hrs. analyzed for 0.8% water. Anal. Calcd, for $C_{21}H_{12}N_4O\cdot$ (0.8 H_2O): C, 71.90; H, 3.90; N, 15.97; O, 8.21; Found: C, 71.93, 71.81; H, 4.20, 4.07; N, 15.74, 15.64; O, 7.75, 7.78.

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12. SPONSORING MILITARY ACTIVITY
Air Force Materials Laboratory
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13. ABSTRACT

To investigate the suitability of a sample of 3,3',4,4'-tetraaminodiphenyl, from a new commercial source, for the synthesis of polybenzimidazoles (PBI), two standard procedures were used. The first procedure, melt phase reaction with diphenyl isophthalate, afforded a hydrated product of low viscosity. The second procedure, reaction with isophthaldehyde bis (bisulfite adduct), in refluxing N,N-dimethylacetamide, did not give meaningful results because of difficulties in purifying the bis (bisulfite adduct). A new method of PBI synthesis was then developed in which the tetraamine was reacted with diphenyl isophthalate in refluxing sulfolane. The product obtained by this method had a satisfactory inherent viscosity and showed no evidence of any appreciable cross-linking or hydration. The sample of tetraamine was therefore concluded to be of suitable quality for PBI synthesis. A critical comparison is given of the three synthetic methods used. The scope of the sulfolane solvent system for PBI-type syntheses was also explored by examining other tetraamine-diphenyl ester combinations. For cases where low reactivity of monomers or low solubility of products precluded the use of sulfolane, phenyl sulfone proved to be a satisfactory alternative solvent.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Benzimidazole Polymers						
High-Temperature Polymers						
Solution Polymerization						

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