

Catalysts for the Preparation of Polybenzimidazoles

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SYNOPSIS

The single-stage preparation of poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI), from 3,3',4,4'-tetraaminobiphenyl (TAB) with isophthalic acid (IPA) in the presence of a catalyst, was explored and developed. The effects of a variety of catalysts on the polymerization of TAB with IPA and/or diphenyl isophthalate were screened and evaluated. Many organo phosphorus and silicon compounds catalyzed the PBI condensation reactions, increased the molecular weight, and improved the quality of PBI polymers. Fiber and reverse osmosis membrane properties of PBI prepared from TAB and IPA were comparable to those for commercial standard PBI prepared from TAB and diphenyl isophthalate. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Many aromatic polybenzimidazoles, characterized by a high thermal stability, have been reported and reviewed.¹⁻⁴ They are prepared by the general method of polycondensation of 3,3',4,4'-tetraaminobiphenyl (TAB) with aromatic dicarboxylic acid derivatives or acids. The polycondensations were carried out, generally in two stages, i.e., a combination of melt polymerization of TAB with diphenyl isophthalate (DPIP),⁵⁻⁹ isophthalic acid (IPA), dimethyl isophthalate, or isophthalonitrile,¹⁰ followed by a second-stage solid-state polymerization at an elevated temperature. A single-stage melt polymerization of TAB with DPIP was also reported.¹¹

Polybenzimidazoles are also prepared by a two-stage solution polymerization of TAB with aromatic dialdehyde in DMAc,¹² with isophthalonitrile in DMF,¹³ or by a single-stage, polycondensation e.g., of TAB with IPA in solution of polyphosphoric acid,¹⁴ with isophthalaldehyde bis (bisulfite adduct) in refluxing DMAc¹⁵ or with DPIP in a refluxing sulfone solvent, e.g., sulfolane or phenyl sulfone,^{16,17} with bisorthoesters in DMSO.¹⁸

Polybenzimidazole was also prepared by the interfacial polymerization of TAB with isophthaloyl dichloride, followed by a subsequent dehydration.¹⁹ The mechanism for the melt polymerization has been described previously.²⁰

Hoechst Celanese Corp. commercialized one of the aromatic polybenzimidazoles, poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], under the trade name of PBI®, and an extensive study was carried out on this polymer because of its toughness, non-flammability,²¹ thermal and chemical stabilities, and processability.

The polycondensation of TAB with DPIP or IPA is of commercial importance, especially the use of IPA for an economic advantage over DPIP. A limited study was reported on a catalytic polymerization of TAB with DPIP with catalysts²² such as ammonium chloride, hydrochloric acid, *p*-toluenesulfonic acid, phosphoric acid, triphenylphosphate, or boron trifluoride etherate. In the technical report, the data indicated that phosphorus-containing catalysts such as phosphoric acid and triphenyl phosphate are effective for increasing the inherent viscosity of a PBI resin. However, there is formation of a gel and insoluble black specks that tend to affect adversely the plugging value property of the PBI products. There remains a need for an improved method of producing PBI that overcomes the various disadvantages of the prior art procedures and which method yields an improved type of PBI product particularly suitable for the formation of fibers having a high melting point and a high degree of thermal stability. It is highly desirable to obtain an improved two- or single-stage polymerization process for the production of high molecular weight PBI, which is characterized by an improved plugging value and an improved color specification.

In the present work, the effects of a variety of catalysts on the polymerization of TAB with IPA and/or DPIP were evaluated to increase the molecular weight of polymer and to improve the quality and economics of polymer. Fiber and reverse osmosis membrane properties of PBI prepared from TAB and IPA are compared to those for commercial standard PBI prepared from TAB and DPIP.

EXPERIMENTAL

Raw Materials

3,3',4,4'-Tetraaminobiphenyl (TAB) (Lot # p-218-221AIB) had an assay of 96.7% of TAB, 2.9% triaminobiphenyl, and 0.2+% of extraneous impurities (0.2% peak A, 0.066% peak C, 0.083% peak D, 0.035% peak E, 0.010% peak E, and 0.01% peak F) as analyzed by HPLC. DSC showed a melting point peak at 177.0°C. The isophthalic acid supplied by AMOCO under the trade name of IPA 220 was used as received without further purification. This monomer grade isophthalic acid (IPA) showed 99.9+% purity and 0.052% of terephthalic acid by HPLC and a moisture content of 0.007% and exhibited a melting point of 339°C by DSC. The thermal stability of IPA between 80 and 400°C was determined by TGA/MS by analyzing off-gases formed from a thermal treatment. Only a very minute amount of water was detected, but not carbon dioxide that would have been formed if IPA had decomposed by decarboxylation. Diphenyl isophthalate (DPIP) (Lot #AB748) from Burdick and Jackson Co. showed a 99.5% purity and a melting point of 136°C, acidity of 0.002–0.005 meq/g, ash of 210 ppm and chlorine of 220–240 ppm, and 0.013% of volatile matter.

The following examples are given as typical laboratory methods for the single-stage preparation of PBI from IPA and TAB, and for the standard two-stage preparation of PBI from TAB and DPIP. These represent general procedures with the exception of the concentrations of catalysts as indicated for the specific runs in the tables.

Single-stage Preparation of PBI from TAB and IPA: General Procedure

Into a three-necked flask equipped with a nitrogen inlet and outlet, a mechanical stirrer, and a condenser were placed 56.35 g (0.263 mol) of TAB, 43.69 g (0.263 mol) of IPA, and the specified amount of catalyst (i.e., 0.6 g of triphenyl phosphite). The flask

was degassed and then filled with nitrogen. The degassing step was repeated at least three times. The mixture was heated rapidly from 200 to 310°C with stirring for a period of 15 min. The rate of stirring was reduced from 200 rpm at about 250°C to 0 rpm at 310°C. The resulting polymer was heated for a period of 45 min to an elevated temperature (i.e., 415°C) as designated in the specific runs. A 17 mL quantity of water was collected. The temperature of the reaction mixture was maintained at the elevated temperature (i.e., 415°C) for another hour. The resulting product was cooled to room temperature to provide a quantitative yield of the PBI. The PBI exhibited an inherent viscosity of 0.77 dL/g when measured in a concentration of 0.4 g of the PBI in 100 mL of 97% sulfuric acid. The weight-average molecular weight was 140,000 with a molecular weight distribution of 2.69. The polymer was completely soluble in dimethylacetamide containing 2% lithium chloride. A reverse osmosis membrane prepared from this polymer in dimethylacetamide containing 2% lithium chloride at 21% polymer solids had a flux property of 20.1 gal/ft²/day and a salt rejection of 91.65%.

Two-stage Preparation of PBI from TAB and DPIP: General Procedure

Into a three-necked flask equipped with a nitrogen inlet and outlet, a mechanical stirrer, and a condenser were placed 23.3 g (0.1089 mol) of TAB, 34.6 g (0.1089 mol) DPIP, and a specified amount of catalyst (i.e., 0.2 g of dichlorophenylphosphine). The flask was degassed and then filled with nitrogen. The degassing was repeated at least three times. The mixture was heated rapidly with stirring to 225°C. The stirring was stopped. The temperature of the reaction mixture was then raised to 270°C and held at that temperature for the next 1.5 h. The resulting prepolymer was cooled to room temperature and then was ground.

The ground prepolymer was placed in a flask, and after the degassing step was repeated, the prepolymer was heated at 360°C for 1 h. The resulting PBI exhibited a weight-average molecular weight of 230,000 with a molecular weight distribution of 3.00 and an inherent viscosity of 1.20 dL/g, when measured in a concentration of 0.4% of PBI in 100 mL of 97% sulfuric acid. The plugging value was 0.60 g/cm² when measured in 97% sulfuric acid.

Plugging Value (P.V.)

The plugging value (P.V.) is a measure of solution filterability and was determined from the filtration

rate through a fine filter paper as described in the Air Force Materials Laboratory Technical Report.²³ The PBI polymer to be evaluated was dissolved in 97.0 ± 0.1% sulfuric acid at a known concentration of 5–7%. The solution was prepared by weighing the desired quantity of sulfuric acid (e.g., 95 g) into a 250 mL glass-stoppered Erlenmeyer flask and then weighing the desired quantity of polymer (e.g., 5 g) with the flask. The polymer was dissolved by shaking in a wrist-action shaker for a minimum of 2–3 days depending upon the intrinsic viscosity (I.V.) level (i.e., longer for higher I.V.s). The filtration apparatus consists of a 2 in. stainless-steel pressure filter (Gelman Instrument Co.), Model 4240, and Gelman Type A, 2 in. glass filter papers. The solution after shaking was poured into the filter chamber and 1 atmosphere of pressure from a nitrogen cylinder was applied. Zero time was taken as the first drop reached the receiver located on a balance below the filtration unit. The weight of the solution that passed through the filter was recorded with respect to time. Data were continuously generated until either the filter was emptied or the filtration rate was very slow as a result of plugging.

Calculation of the Plugging Value was as follows:

1. Each time in minutes was divided by the corresponding weight in grams of solution (total) through the filter at that time.
2. The obtained values were plotted against time. The resulting graph approximates a straight line. The initial curvature is disregarded as well as the last few points if curvature would again exist.
3. The reciprocal slope of the graph represents the theoretical weight in grams of solution that would pass through the filter in infinite time in order to plug it. This is designated as W_{∞} :

$$P.V. = \frac{W_{\infty} \times \text{Concentration}}{\text{Filter area}}$$

Molecular Weight and Inherent Viscosity (I.V.)

PBI molecular weight constants referred to herein were determined by employing a Waters 201 instrument with two porous silica columns (Waters μ -Bondagel E-linears) at the concentration of 0.2 g wt/vol in DMAc containing 2% LiCl. The calculations were based on a calibration curve obtained with 11 polystyrene molecular weight standards with the range between 2100 and 1,800,000, and the PBI molecular weight corresponds to the polystyrene

equivalent molecular weight. I.V. was measured at the concentration of 0.4% PBI in 97% sulfuric acid at 25°C.

RESULTS AND DISCUSSION

PBI fiber was commercialized by the Hoechst Celanese Corp. for end-uses requiring good textile properties and inherent nonflammability in 1983. A reduction in PBI cost would improve the position for its entry into a commercial market. In an attempt to reduce the cost of PBI, an alternate low-cost synthetic method for the preparation of PBI from TAB and IPA in the presence of a catalyst was explored, developed, and described here. Their fiber and reverse osmosis membrane properties were evaluated and found to be equivalent to the controls made from the DPIP-based PBI and are reported here.

The three criteria for a good fiber-grade PBI are as follows: (1) PBI with an I.V. range between 0.70 and 0.75 dL/g; (2) PBI with a plugging value of > 0.5 g/cm²; and (3) the insoluble matter in DMAc-containing 2% lithium chloride of < 1%. These are the target properties that we hope to achieve for a fiber-grade PBI.

Polymerization Conditions

Our standard two-stage reaction conditions that produced standard PBI polymers with target properties were used initially in an attempt to produce PBI from IPA and TAB. The reaction conditions were the first-stage heating of the monomer mixture for 1.5 h at 270°C, followed by a second-stage heating of the pulverized first-stage prepolymer for 1 h at 360°C.

Table I contains the properties of PBI samples prepared by the two-stage heating cycle using IPA and/or DPIP with and without a catalyst. These

Table I Comparison of IPA vs. DPIP in the Two-stage PBI Process

Monomers	I.V. (dL/g)	P.V. (g/cm ²)
TAB + DPIP	0.72	0.78
TAB + DPIP + cat. ^a	1–1.2	> 5
TAB + IPA	0.26	0.21
TAB + IPA + cat. ^a	0.31	0.20

Standard heating cycle: 1.5 h at 270°C for the first stage, 1.0 h at 360°C for the second stage.

^a Catalyst = triphenyl phosphite 1% based on the weight of DPIP or IPA.

results show that the standard two-stage process gives satisfactory PBI when DPIP is used (both with and without catalyst), but the use of IPA under comparable conditions does not provide sufficient molecular weights for fiber formation. These results indicated that alternate reaction conditions are needed for the polymerization of IPA with TAB. To best determine what these were, a saturated fractional factorial experiment was carried out to evaluate the effects of reaction temperature, reaction (hold) time, rate of heating, catalyst concentration, vacuum vs. nitrogen sweep, and first- vs. second-stage polymerization. Initial results on the saturated factorial experiment are summarized in Table II. Data on the individual effects of various factors are beyond the scope of this article. From the individual results shown in Table II, it was concluded that the best polymerization condition is a single-stage heating of the monomer mixture of TAB and IPA in the presence of a catalyst at about 1% level based on the IPA weight to a maximum temperature of $\sim 400^\circ\text{C}$ within 1 h, and then holding it at that temperature for 1 h under a nitrogen sweep.

Single-stage Preparation of PBI from TAB and IPA

Potentially lower-cost synthetic routes to PBI were examined. The routes involved the replacement of moderately expensive DPIP with inexpensive IPA, dimethyl isophthalate, isophthalonitrile, or isophthaloyl dichloride. PBI polymers using TAB and these monomers instead of DPIP were prepared and characterized. Results indicated that use of the least expensive IPA might be a viable option and that the polymerization of TAB with dimethyl isophthalate, isophthalonitrile, or isophthaloyl dichloride provided only low molecular weight PBI polymers having an I.V. of less than 0.2 dL/g.

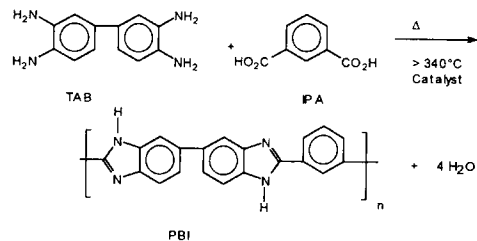
Table II Results of Saturated Fractional Factorial Experiments

Effects Evaluated	Best Results
Reaction temperature: 340–400°C	400°C
Heating rate: 30 vs. 60 min	Uncertain
Hold-time at maximum temperature: 0–3 h	1 h
Catalyst concentration: 0–1%	1%
Vacuum vs. nitrogen sweep	Nitrogen sweep
Single vs. two stages	Single stage

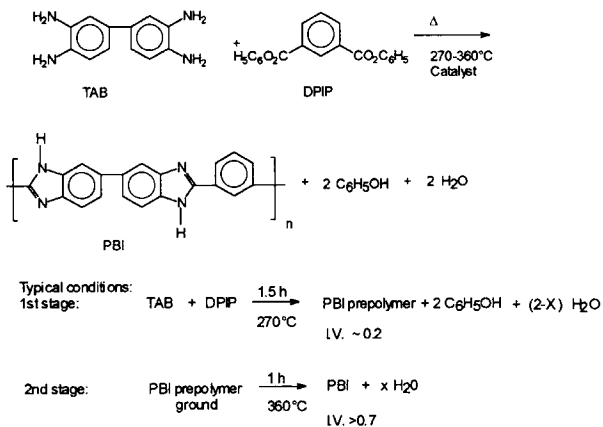
This method involves a new process for producing high molecular weight PBI from TAB and IPA by a melt polymerization of the two monomers in the presence of a catalyst, at temperatures higher than the melting point of IPA ($> 340^\circ\text{C}$). This method differs from the prior art in that this melt polymerization can be conducted in the absence of a solvent such as polyphosphoric acid or dimethyl acetamide. Another feature of this process is that the only by-product formed in the new process is water, which can be removed readily. Furthermore, this process does not need an antifoaming additive²⁴ because the process generates only a very small amount of foam. This will enable us to charge a larger amount of monomers into a given reactor to produce a greater output. Another advantage is that PBI can be prepared in a single step. The major advantage would be an estimated cost reduction.

The chemical equations for the new single-stage and our current standard two-stage processes for PBI preparation are shown below for a comparison. PBIs prepared from the monomer with an assay of 96.7% of TAB containing 2.9% triaminobiphenyl as an impurity have about 1.5% of polyamide linkage that were formed by reaction of the impurity with IPA or DPIP.

Single-stage PBI preparation:



Current standard two-stage process:



Catalysts

By using the best polymerization conditions described above for the single-stage preparation of PBI from TAB and IPA, the effect of various types of catalysts on the polymerization of IPA and TAB were screened and evaluated at the catalyst concentration of ~ 1.5 wt % based on IPA.²⁵⁻³¹ The catalysts listed in Table III catalyzed the PBI polymerization and provided PBI polymers meeting our target properties of I.V. greater than 0.7 dL/g, plugging values greater than 0.5 g/cm², and the insoluble matter in DMAc less than 1%.

These catalysts are dichlorophenylphosphine, chlorodiphenylphosphine, triphenyl phosphite, diphenylphosphine oxide, diphenyl chlorophosphate, triphenyl phosphate, dimethoxyphenylphosphine, dibutoxyphenylphosphine, *o*-phenyl phosphorochloridite, phenyl *N*-phenylphosphoramidochloridate, and dichlorodimethylsilane.

Results were obtained on other catalysts, which, on evaluation, under the same conditions were found to be somewhat less effective in that they gave PBI polymers with a lesser or moderate I.V. range between 0.7 and 0.6 dL/g. These catalysts include di-

phenylphosphine, *o*-phenylene phosphorochloridate, tris(*p*-methoxyphenyl)phosphine, and tributyl phosphite.

The preliminary results also indicated that, although all of the following catalysts showed a weak but positive catalytic effect, they did not provide PBI polymers with a sufficiently high enough I.V. to meet the target specification. The I.V.s were between 0.5 and 0.60 dL/g. The catalysts include sulfamide, diphenylether, tetramethylammonium chloride, bipyridyl, diphenylacetamide, *p*-xylylenebis(triphenyl phosphonium bromide), tris(*m*-chlorophenyl)phosphine, tetraphenylphosphonium chloride, triphenylarsene, triphenylantimony oxide, chlorotrimethylsilane, dichlorodiphenylsilane, stannous chloride, stannic chloride, dibutyltin oxide, and bismuth germanium oxide.

Several compounds showed no catalytic effect, including methyltriphenylphosphonium bromide, bisbenzylphenylphosphine, and germanium diethoxide. The few catalysts that showed a negative catalytic effect are triphenylphosphine oxide, tris(*p*-chlorophenyl)phosphine, triphenylantimony dichloride, triphenylantimony, lead dioxide, and manganese diacetate. There was some speculation

Table III Results of Single-stage Polymerization of IPA and TAB with Various Catalysts:

$$\text{TAB} + \text{IPA} \xrightarrow[\text{Cat.}]{400^\circ\text{C}, 1\text{ h}} \text{PBI} + 4\text{H}_2\text{O}$$

Catalyst (%) ^a	I.V. (dL/g)	P.V. (g/cm ²)
None	0.45	0.40
Dichlorophenylphosphine	0.79	> 5
Chlorodiphenylphosphine	0.84	1.29
triphenyl phosphite ^b	0.70	2.37
Diphenylphosphine oxide	0.81	> 5
Dichlorodimethylsilane	0.80	5.57
Diphenyl chlorophosphate	0.78	> 5
Di(methoxy)phenylphosphine	0.75	> 5
Triphenyl phosphate	0.74	> 5
Phenyl <i>N</i> -phenylphosphoramidochloridate	0.72	8.14
<i>o</i> -Phenyl phosphorochloridite	0.71	> 5
Dibutoxyphenylphosphine	0.70	> 5
Diphenylphosphine	0.69	> 5
<i>o</i> -Phenylene phosphorochloridate	0.69	0.33
Tris(<i>p</i> -methoxyphenyl)phosphine	0.62	> 5
Tributyl phosphite	0.61	> 5

^a 1.5 wt % based on IPA.

^b 1.0 wt % based on IPA.

that the negativity of the catalysts' effect on these materials may make them suitable stabilizers. This is strictly a hypothetical conclusion and no follow-up effort was made.

Effect of Catalyst Concentration

The effect of catalyst concentration on polymer inherent viscosity was examined in detail to optimize the catalyst concentration for the IPA process (Table IV). Two catalysts, dichlorophenylphosphine and triphenyl phosphite, from Table III were selected. Their effects of concentration on I.V. were evaluated at 400°C by polymerizing the IPA and TAB mixture with several levels of catalyst concentration in a range from 0 to 3% based on the weight of IPA. The I.V.s of PBI polymers were plotted against the catalyst concentration for the two catalysts and are depicted in Figure 1. Preliminary results showed that the I.V. increases as the catalyst concentration increases and appears to approach a plateau at about a 1% level, which also appears to be a minimum concentration to attain an acceptable fiber-grade PBI meeting the target properties. The concentration of 1.5 wt % catalyst based on IPA was chosen for a scale-up experiment to ensure the presence of a sufficient quantity of catalyst in the polymerization mixture.

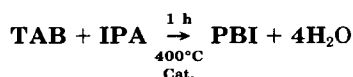
Effect of Polymerization Temperature

One factor affecting the cost of polymerization is the energy requirement of polymerization that involves temperature. Assuming that a lower reaction temperature requires a lower energy cost, it would be desirable to polymerize the monomers at the lowest possible polymerization temperatures. To determine the lowest possible polymerization temperature for the IPA process, the effect of temperature on PBI I.V. was determined with the two selected catalysts dichlorophenylphosphine and triphenyl phosphite at 1 and 2.0%. The results in Table V indicated that a minimum temperature of 400°C for triphenyl phosphite and 390°C for dichlorophenylphosphine are required to produce satisfactory polymers meeting the target properties.

In another attempt to reduce the polymerization temperature, a combination of catalysts of dichlorophenylphosphine (1.5%) with triphenyl phosphite (0.5%) was examined at the temperature range from 360 to 400°C. Preliminary results indicated that a satisfactory PBI polymer meeting the target properties was prepared at a temperature as low as 380°C.

The use of other combinations of catalysts, such as diphenylphosphine oxide, dimethoxyphenylphosphine, or triphenyl phosphate with triphenyl phosphite, did not provide a synergistic catalytic effect. Also, the addition of lithium chloride or lithium phosphate to the triphenyl phosphite catalyst did not show a significant increase in molecular weight.

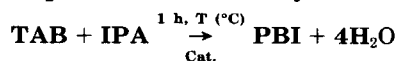
Table IV Effect of Dichlorophenylphosphine and Triphenyl Phosphite Catalyst Concentration on PBI Polymer Molecular Weight:



Catalyst	Concn (%) ^a	Polymerization ^b Temp (°C)	I.V. (dL/g)	P.V. (g/cm ²)	Weight-average Mol. Wt.	MWD
None	0	400	0.45	0.40	71,300	2.23
C ₆ H ₅ PCl ₂	1	400	0.77	> 5	146,000	2.77
C ₆ H ₅ PCl ₂	1.5	400	0.82	5.0	147,000	2.78
C ₆ H ₅ PCl ₂	2	400	0.79	> 5	122,000	2.73
C ₆ H ₅ PCl ₂	3	400	0.86	—	—	—
(C ₆ H ₅ O) ₃ P	0.5	400	0.58	> 5	—	—
(C ₆ H ₅ O) ₃ P	1.0	400	0.70	2.4	109,000	2.44
(C ₆ H ₅ O) ₃ P	2.0	400	0.71	> 5	132,000	2.65
(C ₆ H ₅ O) ₃ P	3.0	400	0.74	1.35	147,000	2.78

^a Based on the weight of IPA.

^b One hour at the indicated temperature.

Table V Effect of Polymerization Temperature on PBI Polymer Molecular Weight:


Catalyst	Concn (%) ^a	Polymerization ^b Temp (°C)	I.V. (dL/g)	P.V. (g/cm ²)	Weight-average Mol. Wt.	MWD
None	0	400	0.45	0.40	71,300	2.23
C ₆ H ₅ PCL ₂	1	390	0.76	4	—	—
C ₆ H ₅ PCL ₂	1	400	0.77	> 5	146,000	2.77
C ₆ H ₅ PCL ₂	1	430	1.10	0.05	217,000	3.22
C ₆ H ₅ PCL ₂	2	380	0.52	—	—	—
C ₆ H ₅ PCL ₂	2	390	0.67	—	—	—
C ₆ H ₅ PCL ₂	2	400	0.79	> 5	122,000	2.73
(C ₆ H ₅ O) ₃ P	1.0	380	0.53	—	—	—
(C ₆ H ₅ O) ₃ P	1.0	400	0.70	2.4	109,000	2.44
(C ₆ H ₅ O) ₃ P	1.0	415	0.72	> 5	127,000	2.47
(C ₆ H ₅ O) ₃ P	1.0	430	0.88	0.22	162,000	2.76
(C ₆ H ₅ O) ₃ P	2.0	380	0.46	—	—	—
(C ₆ H ₅ O) ₃ P	2.0	390	0.57	—	—	—
(C ₆ H ₅ O) ₃ P	2.0	400	0.75	6.15	132,000	2.65
(C ₆ H ₅ O) ₃ P	2.0	430	0.82	0.34	165,000	3.04

^a Based on weight of IPA.

^b One hour at the indicated temperature.

PBI Molecular Weight and Viscosity Relationship

The number (\bar{M}_n)- and weight (\bar{M}_w)-average molecular weights, the molecular weight distribution ($\text{MWD} = \bar{M}_w/\bar{M}_n$), and both intrinsic and inherent viscosities, for the IPA-based PBI polymers that were prepared in the presence of dichlorophenylphosphine, are given in Table VI.

The double logarithm of I.V. (97% H₂SO₄) vs. weight-average molecular weight (DMAc, 2% LiCl) was plotted, and the Mark-Houwink equation for PBI molecular weight was derived from the plot and expressed as

$$[\eta]_{\text{H}_2\text{SO}_4} = 1.35326 \times 10^{-4} \bar{M}_w^{0.73287}$$

The relationship of intrinsic viscosity to inherent viscosity of PBI in 97% sulfuric acid can be expressed as

$$[\eta] = 1.0585\eta_{\text{thr}}$$

By using these expressions, the molecular weight of PBI polymers can be estimated from intrinsic or

inherent viscosities in reasonable agreement with the experimental values.

Two-stage Preparation of PBI from TAB and DPIP

By using our standard two-stage polymerization conditions described earlier, the effect of various types of catalysts on the polymerization of TAB and DPIP were also evaluated.³¹⁻³⁶ The results summarized in Table VII exhibit a desirable combination of high molecular weight and plugging value properties. The catalysts containing phosphorus listed in Table VII, e.g., dichlorophenylphosphine, catalyzed very effectively the PBI polymerization of TAB with DPIP, as was found for the IPA-based PBI.

Fiber Properties of IPA-based PBI

To ensure that the performance of IPA-based PBI polymers is equivalent to those of the DPIP-based PBI, the IPA-based PBI polymers were scaled-up, converted into yarns and reverse osmosis (RO) membranes, and evaluated in terms of their fiber and RO membrane properties.

The IPA-based PBI polymers were prepared at 400°C in a sufficient quantity for a spinning trial

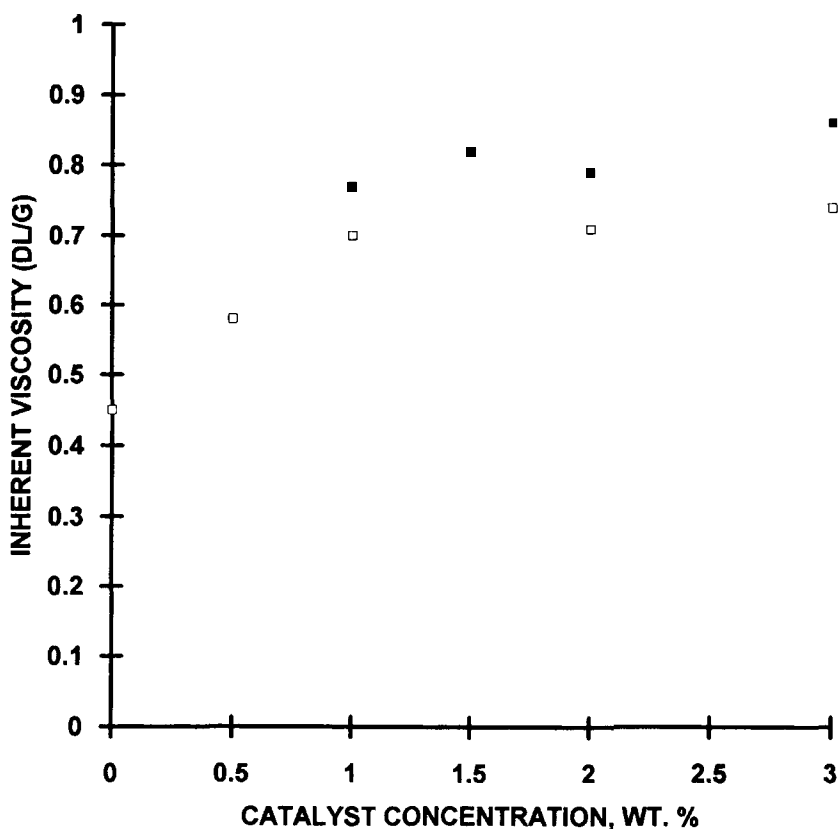


Figure 1 Effect of catalyst concentration on PBI I.V. for the PBI from TAB and IPA at 400°C for 1 h. Open square for triphenyl phosphite series; filled square for dichlorophenylphosphine series.

with two selected catalysts: 1.5% triphenyl phosphite and/or dichlorophenylphosphine. The IPA-based polymers with an inherent viscosity of 0.80 dL/g and P.V. 2.13 g/cm² were solutioned at 24% in DMAc containing 2% lithium chloride in a closed pressure vessel at 240°C and filtered and dry spun through a 20 × 76 μ spinneret to obtain very light golden-colored fibers. The as-spun fiber properties are shown in Table VIII along with those of standard PBI with an I.V. of 0.80 dL/g that was used as a control. As the data show in the Table VIII, the as-spun fiber mechanical properties of IPA-based PBI yarns are equivalent to those of the control.

The yarns spun from PBI made with dichlorophenylphosphine were drawn at the draw ratio of 2.0, 2.1, and 2.2, were treated with sulfuric acid, and then heat-treated. The yarn properties are given in Table VIII along with those for the standard PBI control fiber properties in the parentheses. The properties of IPA-based PBI yarns are equivalent to the control.

Reverse Osmosis (RO) Membrane Properties of IPA-based PBI

The IPA-based PBI polymers with an I.V. range from 0.45 to 1.10 dL/g were evaluated as RO membranes. The IPA-based PBI polymers were solutioned at 21% solids in DMAc containing 2% lithium chloride at 240°C for 2 h. After the dope solutions were filtered through a multifilter composed of a B-stage press, LT-152, and Viscose, they were cast on

Table VI Molecular Weight of PBI

I.V. (dL/g)	[η] (dL/g)	\bar{M}_n	\bar{M}_w , Found	\bar{M}_w , Calcd	MWD
0.45	0.484	32,000	71,300	69,060	2.23
0.68	0.710	46,300	122,000	119,961	2.64
0.82	0.869	52,700	147,000	156,862	2.78
1.10	1.078	67,500	217,000	210,491	3.22

Table VII Effect of Catalyst on Standard PBI Polymer Molecular Weight

Catalyst	Concn (%) ^a	I.V. (dL/g)	P.V. (g/cm ²)	Weight-average Mol. Wt.	MWD
None	0	0.68	1.54	113,000	2.56
C ₆ H ₅ PCl ₂	0.57	1.20	0.70	230,000	3.00
C ₆ H ₅ PCl ₂	0.86	1.50	0.13	292,000	3.30
(C ₆ H ₅) ₂ PCl	1.15	1.06	3.30	183,307	5.40
(C ₆ H ₅ O) ₂ PCl	0.85	1.50	1.84	187,229	3.40
HCl	0.57	1.26	0.16	250,000	3.22
NH ₄ Cl	0.57	1.29	0.62	273,000	3.26
Diphenylphosphine	0.86	1.00	7.33	158,909	2.75
Tri(<i>p</i> -methoxyphenyl)phosphine	0.86	0.92	1.60	155,415	2.81
Dimethoxyphenylphosphine	0.86	1.13	3.89	206,507	3.27
Di- <i>n</i> -butoxyphenylphosphine	0.86	1.01	5.49	194,606	2.89
Diphenylphosphinic acid	1.15	1.00	> 5	201,700	2.91
Diphenylphosphine oxide	1.15	0.89	0.4	152,628	3.16

TAB + DPIP: 1.5 h at 270°C (1st stage) + 1 h at 360°C (2nd stage).

^a Based on the weight of DPIP.

a Hollytex® nonwoven fabric support using a modified reverse-roll coater. The membranes were annealed in ethylene glycol and evaluated under standard RO test condition of 400 psi and 0.5% NaCl at room temperature.

The RO membrane properties of selected PBI polymers with I.V.s of interest are summarized in Table IX. The data clearly indicate that IPA-based PBI RO membranes prepared from an I.V. > 0.75 dL/g showed equivalent or better RO membrane properties (higher salt rejection) than those from our standard PBI (based on DPIP) control with an inherent viscosity of 0.77 dL/g.

CONCLUSIONS

The single-stage preparation of PBI, poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], from 3,3',4,4'-tetraaminobiphenyl (TAB) with isophthalic acid (IPA) in the presence of a catalyst, was explored and developed. The effects of a variety of catalysts on the polymerization of TAB with IPA and/or diphenyl isophthalate (DPIP) were screened and evaluated. It was found that many compounds containing phosphorus or silicon catalyzed the single-stage and two-stage PBI condensation reactions, increased the molecular weight, and improved the

Table VIII Fiber Properties of IA-based PBI

Fiber Sample	DPF	Tenacity (gpd)	Elongation (%)	Modulus (gpd)
As-spun ^a	2.1	1.8 (1.8) ^b	71 (81) ^b	49 (47) ^b
Drawn-draw ratio				
2.0	1.0	4.3 (4.2) ^b	26 (29) ^b	86 (83) ^b
2.1	1.2	4.4 (4.0) ^b	28 (30) ^b	78 (82) ^b
2.2	1.1	4.1 (4.1) ^b	28 (28) ^b	78 (82) ^b
Acid treated-heat set ^c				
Draw ratio 2.1	1.5	2.95 (2.6) ^b	20 (19) ^b	79 (70) ^b
Draw ratio 2.2	1.4	3.03 (3.2) ^b	21 (20) ^b	71 (78) ^b

Spinning of IA-based PBI: I.V. = 0.8 dL/g; P.V. = 2.13 g/cm²; M_w = 135,000; MWD = 2.66.

^a Spun through spinneret 20 × 76 μ jet.

^b Standard PBI control fiber properties in parentheses.

^c Drawn and heat set at 470°C in nitrogen, 9% shrinkage after washing.

Table IX Reverse Osmosis (RO) Membrane Properties of IA-based PBI vs. Standard PBI

Polymer	I.V. (dL/g)	Flux (g/ft ² /d)	Salt Rejection (%)
Standard PBI, (DPIP-based PBI) control	0.77	12.7–17.6	86.6
IA-based PBI	0.77	15.9	94.1
IA-based PBI	0.90	13.1	94.0
IA-based PBI	1.10	10.7	92.4

quality of PBI polymers. Fiber and reverse osmosis membrane properties of PBI prepared from TAB and IPA were comparable to those for commercial standard PBI prepared from TAB and DPIP.

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