

# Synthesis and Characterization of Thermally Stable Polymers (Polybenzimidazoles)

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**ABSTRACT:** In this study, an alternative synthesis of polybenzimidazoles was performed with aromatic hydroxamoyl chloride. In contrast to the literature, polybenzimidazoles were obtained through the reaction of hydroxamoyl chlorides with 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene. The characterization of the polymers was performed with Fourier transform infrared, <sup>1</sup>H-NMR, elemental analysis, LC mass spectrometry, and differential

thermogravimetry/thermogravimetric analysis. Finally, the adhesion, corrosion resistance, and conducting properties of the synthesized polymers were examined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1861–1870, 2008

**Key words:** coatings; conjugated polymers; heteroatom-containing polymers; high temperature materials; synthesis

## INTRODUCTION

A quite versatile and practical chemical synthesis of polybenzimidazoles (PBIs) is provided by the interaction of an *o*-phenylene diamine with nitrile compounds, dicarboxylic acids, dicarboxylic acid dichlorides, and esters or anhydrides of dicarboxylic acids. There have been many studies performed in the past concerning the synthesis of PBIs<sup>1–11</sup> in which hydroxamoyl chloride was not used as the starting material. However, in this study, PBIs were obtained through the reaction of dihydroxamoyl chlorides and 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene. It is known that hydroxamoyl chlorides are more active than the other starting reactants used in the previous studies.

The molecular structures of these compounds were identified by analyses of the inherent viscosity, Fourier transform infrared (FTIR), LC mass spectrometry, differential thermogravimetry/thermogravimetric analysis (DTG–TGA), and elemental analysis. The inherent viscosities, FTIR, LC mass spectrometry, DTG–TGA, and conductivity characteristics of the synthesized polymers were compared with those of PBIs previously synthesized with different starting materials. Additionally, doping the polymers with 1M HCl during the synthesis led to changes, with the conductivity increasing from less than 10<sup>-11</sup> S/cm for the undoped polymers to

10<sup>-5</sup> S/cm for their acid-loaded derivatives (both at room temperature).

As is known, various functional groups (carboxyl, acyl, epoxy, chlorohydrin, and C=C double bonds) in the aromatic ring of the polymer are appropriate for obtaining polymeric coatings with high adhesion properties and corrosion resistance.<sup>12</sup> In our study, PBIs were used as coating materials: the coating films of the synthesized PBIs presented higher adhesion properties and were more resistant to corrosion.

## EXPERIMENTAL

### Materials and reagents

4-Hydroxybenzaldehyde, 3,3'-diaminobenzidine, and 1,2,4,5-tetraaminobenzene tetrahydrochloride were supplied by Merck Chemical Co. (Germany) and TCI Tokyo Kasai (Japan); terephthalaldehyde, 4-fluorobenzaldehyde, NiCl<sub>2</sub>, chlorobenzene, triphenylphosphine, zinc, potassium polysulfide, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were obtained from Aldrich.

### Instrumentation

Solution NMR spectra were obtained on a Bruker Avance DPX-400, and the elemental analyses for carbon, hydrogen, nitrogen, and sulfide were performed in the laboratories of the Scientific and Technical Research Council (TUBITAK) of Turkey in Ankara. The FTIR spectra were obtained with a PerkinElmer model 1605 apparatus, and the viscometric measurements were taken at a constant temperature of 25 ± 0.5°C with Oswald viscometers and a solvent in

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the laboratories of chemistry department of Selcuk University in Konya (Turkey). A Seteram TG-DSC8 and a Dupont 951 were used for DTG-TGA in the laboratories of TUBITAK of Turkey in Ankara. Conductivity measurements of the polymers were performed with a four-probe method.

## Synthesis

### Synthesis of bis(4-formylphenyl)ether

The synthesis of bis(4-formylphenyl)ether was performed according to previous studies in the literature.<sup>13</sup> 4-Hydroxybenzaldehyde (15 g, 0.12 mol), 13.5 g (0.15 mol) of 4-fluorobenzaldehyde, and 20.5 g (0.15 mol) of potassium carbonate were refluxed in 250 mL of DMF in a nitrogen atmosphere at 100°C for 48 h. The mixture was cooled and then added to 1.5 L of water. After the solution was extracted with ethyl acetate five times (5 × 80 mL), the extracted solutions were washed with water before being dried with MgSO<sub>4</sub>. The solvent in the solution was removed with the help of an evaporator, and the raw product that was formed was crystallized from an ethyl acetate/hexane mixture (2:1). The obtained data related to the melting point, elemental analysis, FTIR, and <sup>1</sup>H-NMR were found to be compatible with the results of the previous studies in the literature.

mp: 69°C. Yield: 90%. <sup>1</sup>H-NMR (DMSO, δ): 9.94 (d, 2H, *J* = 7.1 Hz), 7.97 (hydrogen adjacent to the formyl group; d, 4H, *J* = 4.76 Hz), 7.27 (hydrogen adjacent to the phenoxy group; d, 4H, *J* = 5.01 Hz). ANAL. calcd for C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>: C, 74.34%; H, 4.42%. Found: C, 74.68%; H, 4.40%.

### Synthesis of bis(4-formylphenyl)disulfide

Bis(4-formylphenyl)disulfide was synthesized by the adaptation of the synthesis of bis(4-formylphenyl)sulfide in the literature.<sup>13</sup> However, in contrast to the literature, potassium polysulfite was used instead of potassium sulfite. During the synthesis, 6 g (0.075 mol) of 4-fluorobenzaldehyde and 2.64 g (0.037 mol) of potassium polysulfide were placed in a three-necked flask and refluxed in 260 mL of DMSO in a nitrogen atmosphere at 100°C for 24 h. At the end of this period, the reaction mixture was cooled and poured into 1.5 L of water. After the solution was extracted with ethyl acetate, the organic phase was performed with MgSO<sub>4</sub>. The raw product was isolated by column chromatography using chloroform. The data of the melting point, elemental analysis, FTIR, and <sup>1</sup>H-NMR were in accordance with those in the literature.

mp: 100–101°C. Yield: 75%. <sup>1</sup>H-NMR (DMSO, δ): 9.94 (s, 2H), 7.81 (hydrogen adjacent to the formyl group; d, 4H, *J* = 2.5 Hz), 7.65 (hydrogen adjacent to

the sulfide group; d, 4H, *J* = 2.57 Hz). ANAL. calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>S: C, 59.85%; H, 3.65%; S, 23.36%. Found: C, 59.96%; H, 3.72%; S, 23.08%.<sup>13</sup>

### Synthesis of 4,4'-diformylbiphenyl

4,4'-Diformylbiphenyl was synthesized according to the methods reported in the literature.<sup>14</sup> Zinc (131 g, 2.00 mol), 15 g (0.146 mol) of NaBr, 131 g (0.50 mol) of TTP, and 6.56 g (0.050 mol) of NiCl<sub>2</sub> were placed in a four-necked flask (with a dripping funnel, a mechanical mixer, a thermometer, and reverse cooler mechanisms) with a circular still of 2 L. DMF (600 mL) was added to the mixture in a nitrogen gas environment. While the mixture was heated not beyond 60°C, a solution of 145 g (1.0 mol) of *p*-chlorobenzaldehyde in 100 mL of DMF was added to it in two equal parts, the first of which was added slowly in the first 20 min and the second of which was added in the subsequent 40 min. Refluxing the solution at 70°C for 3 h finally produced a red solution, which was filtered. The solution was extracted four times with 500 mL of distilled water and once with 200 mL of a saturated NaCl solution. After the organic phase was completed through drying with Na<sub>2</sub>SO<sub>4</sub> for 1 h, filtration to remove the excess zinc, and evaporation, the residual solid was filtered and then dried. Later, the obtained data related to the melting point, elemental analysis, FTIR, and <sup>1</sup>H-NMR were determined to be compatible with those of the literature.

mp: 145°C. Yield: 60%. <sup>1</sup>H-NMR (DMSO, δ): 10.10 (m, 2H), 8.04 (q, 8H, *J* = 7.01 Hz). ANAL. calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>: C, 80.00%; H, 4.76%. Found: C, 79.72%; H, 4.70%.<sup>14</sup>

### General procedure for the synthesis of oxime compounds from *p*-dialdehydes with hydroxylamino hydrochloride

Dialdoxime compounds were obtained through the reaction of 20 mmol of hydroxylamino hydrochloride in 80 mL of water with 8 mmol of dialdehyde compounds [terephthaldehyde, bis(4-formylphenyl)ether, bis(4-formylphenyl)disulfide, and 4,4'-diformylbiphenyl] in a 120-mL alcohol solution. After the slow addition of 80 mL of 10% NaOH to this solution, the reaction solution was refluxed through stirring at 100°C for 3 h. The oxime compounds were filtered from the reaction solution and then washed with distilled water. The subsequent recrystallization process was also performed in a 2:1 alcohol/water mixture. The synthesis reactions of the oxime compounds are shown in Figure 1.

*Terephthalaldoxime*. Terephthalaldoxime was obtained according to the literature.<sup>15</sup>

mp: 223°C. Yield: 83%. <sup>1</sup>H-NMR (DMSO, δ): 10.8 (m, 2H, *J* = 4.8 Hz), 8.04 (q, 8H, *J* = 7.01 Hz). ANAL.

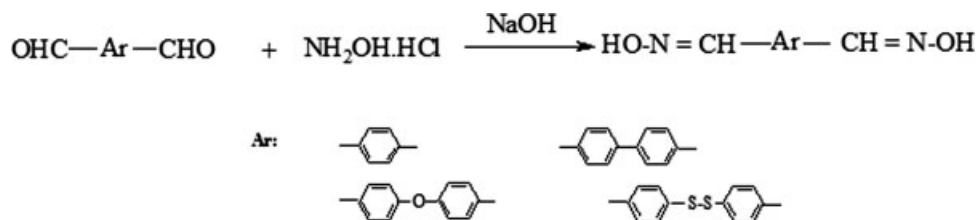


Figure 1 Synthesis reaction of the oxime compounds.

calcd for  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ : C, 58.54%; H, 4.88%. Found: C, 58.79%; H, 4.42%.<sup>15</sup>

*Bis(4-formaldoximphenyl)ether*. The synthesis of bis(4-formaldoximphenyl)ether was performed by the modification of the synthesis of terephthalaldehyde.

mp: 142–143°C. Yield: 82%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 11.19 (s, 2H), 7.64 (d, 4H,  $J = 4.9$  Hz), 7.07 (d, 4H,  $J = 4.92$  Hz), 8.15 (s, 2H). ANAL. calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ : C, 65.60%; H, 4.69%; N, 10.90%. Found: C, 65.91%; H, 4.12%; N, 11.45%.

*Bis(4-formaldoximphenyl)disulfide*. Bis(4-formaldoximphenyl)disulfide synthesis was performed by the modification of the synthesis of terephthalaldehyde.

mp: 207–208°C. Yield: 78%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 11.46 (s, 1H), 11.35 (s, 1H), 7.69–7.54 (q, 8H,  $J = 5.4$  Hz), 8.22 (m, 2H,  $J = 4.8$  Hz). ANAL. calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$ : C, 55.30%; H, 3.95%; N, 9.21%; S, 21.11%. Found: C, 55.79%; H, 4.02%; N, 9.72%; S, 21.60%.

*4,4'-Biphenyldialdoxime*. 4,4'-Biphenyldialdoxime synthesis was performed by the modification of the synthesis of terephthalaldehyde.

mp: 212°C. Yield: 80%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 11.33 (s, 2H), 7.72 (s, 2H), 8.24 (s, 2H). ANAL. calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 70.00%; H, 5.00%; N, 11.67%. Found: C, 70.10%; H, 5.47%; N, 12.24%.

#### General synthesis of dihydroximoyl chloride compounds

Terephthalohydroxamoyl chloride, 4,4'-bis(phenylhydroxamoyl chloride)ether, 4,4'-bis(phenyl hydroxamoyl chloride)disulfide, and 4,4'-bis(phenylhydroxa-

moyl chloride) were synthesized by the passage of chloride gas (dried and then passed under safe conditions) through a dioxime solution of terephthalaldehyde and  $\text{CCl}_4$  solutions of bis(4-formaldoximephenyl)ether, bis(4-formaldoximephenyl)disulfide, and 4,4'-biphenyldialdoxime through stirring for 2 h.<sup>15,16</sup> The synthesis reactions of the dihydroxamoyl chloride compounds are shown in Figure 2.

*Terephthalohydroxamoyl chloride*. Terephthalohydroxamoyl chloride was synthesized according to the literature.<sup>15,16</sup>

mp: 195°C. Yield: 81%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 12.11 (s, 1H), 11.82 (s, 2H), 6.5–7.4 (m, 4H,  $J = 7$  Hz). ANAL. calcd for  $\text{C}_8\text{H}_6\text{N}_2\text{O}_2\text{Cl}_2$ : C, 41.20%; H, 2.58%; N, 11.67%; Cl, 30.47%. Found: C, 41.93%; H, 2.60%; N, 12.62%; Cl, 31.95%.

*4,4'-Bis(phenylhydroxamoyl chloride)ether*. The synthesis of 4,4'-bis(phenylhydroxamoyl chloride)ether was performed by the modification of the synthesis of terephthalohydroxamoyl chloride.

mp: 133–134°C. Yield: 70%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 12.61 (s, 1H), 11.97 (s, 1H), 6.9–7.8 (m, 8H,  $J = 8.7$  Hz). ANAL. calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_3\text{Cl}_2$ : C, 51.69%; H, 3.09%; N, 8.64%; Cl, 21.60%. Found: C, 50.52%; H, 3.16%; N, 9.03%; Cl, 20.80%.

*4,4'-Bis(phenylhydroxamoyl chloride)disulfide*. The synthesis of 4,4'-bis(phenylhydroxamoyl chloride)disulfide was performed by the modification of the synthesis of terephthalohydroxamoyl chloride.

mp: 177–178°C. Yield: 68%. <sup>1</sup>H-NMR (DMSO,  $\delta$ ): 11.37 (s, 2H), 7.87–7.53 (m, 8H,  $J = 1.92$  Hz). ANAL. calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2\text{Cl}_2$ : C, 45.04%; H, 2.69%; N, 7.51%; Cl, 19.03%; S, 17.16%. Found: C, 45.02%; H, 2.65%; N, 7.53%; Cl, 19.22%; S, 17.14%.

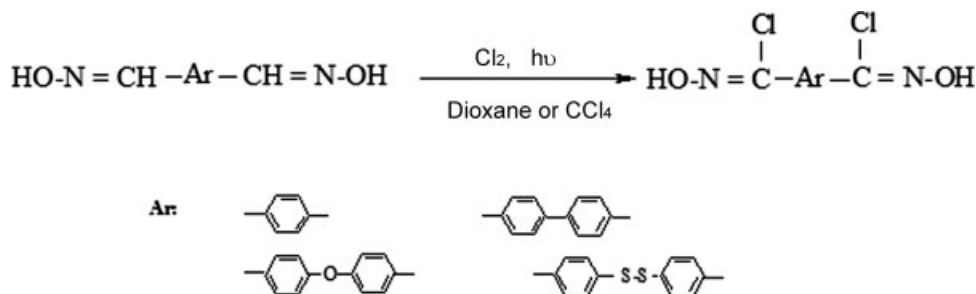


Figure 2 Synthesis reaction of the dihydroxamoyl chloride compounds.

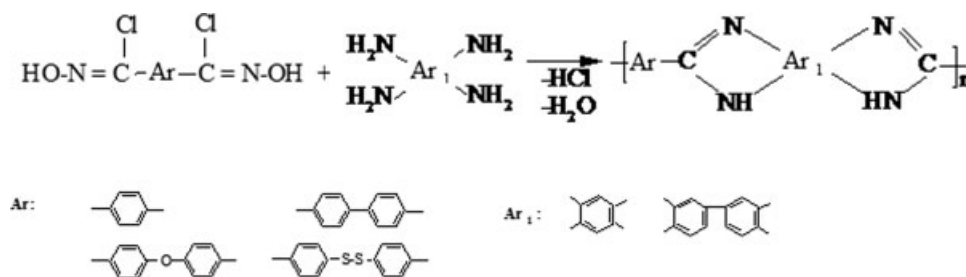


Figure 3 Synthesis reaction of the PBIs.

4,4'-Bis(phenylhydroxamoyl chloride). The synthesis of 4,4'-bis(phenylhydroxamoyl chloride)disulfide was performed by the modification of the synthesis of terephthalohydroxamoyl chloride.

mp: 170–172°C. Yield: 60%. <sup>1</sup>H-NMR (DMSO, δ): 11.35 (s, 1H), 7.88 (q, 8H, *J* = 17.43 Hz). ANAL. calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 54.50%; H, 3.25%; N, 9.10%; Cl, 22.73%. Found: C, 54.00%; H, 3.95%; N, 9.01%; Cl, 21.98%.

General synthesis of PBIs from 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene with dihydroxamoyl chloride compounds

PBIs were synthesized by the gentle heating of a stoichiometric mixture of 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene and dihydroxamoyl chloride compounds [terephthalohydroxamoyl chloride, 4,4'-bis(phenylhydroxamoyl chloride) ether, 4,4'-bis(phenylhydroxamoyl chloride) disulfide, and 4,4'-bis(phenylhydroxamoyl chloride)] in dry DMF under a nitrogen atmosphere, and then the mixtures were slowly heated up to a maximum temperature of 150°C for 1 h before the viscous polymerization mixtures were poured into water for thorough washing. At the end of this experiment, poly[2,2'-(*p*-phenylene)-5-benzobis(imidazole)] (PBI-1), poly[2,2'-(*p*-phenylene)-5,5'-bis(benzimidazole)] (PBI-2), poly[2,2'-(*p,p'*-diphenylether)-5-benzobis(imidazole)] (PBI-3), poly[2,2'-(*p,p'*-diphenylether)-5,5'-bis(benzimidazole)] (PBI-4), poly[2,2'-(*p,p'*-diphenylsulfide)-5-benzobis(imidazole)] (PBI-5), poly[2,2'-(*p,p'*-diphenylsulfide)-

5,5'-bis(benzimidazole)] (PBI-6), poly[2,2'-(*p,p'*-diphenylene)-5-benzobis(imidazole)] (PBI-7), and poly[2,2'-(*p,p'*-diphenylene)-5,5'-bis(benzimidazole)] (PBI-8) were obtained. The solid polymers were filtered and washed several times with water and ether before being dried *in vacuo* at 80°C for 24 h. The reactions of the PBI synthesis are given in Figure 3, whereas the physical properties of the synthesized polymers are tabulated in Table I.

Investigation of the coating properties of PBI

A 10% polymer solution in DMSO was prepared for the investigation of the coating properties (adhesion and anticorrosion) of PBI. A 100–120-μm-thick film was applied to the surface of steel (metal with a moderate carbon content) with dimensions of 50 mm × 100 mm × 1 mm. The film was dried first at room temperature and then in an oven at 100°C for 4 h. The adhesion properties of the polymer film on the metal surface and its conditions inside 3% NaCl, 10% NaOH, and 10% HCl solutions were studied.

Determination of the adhesion properties of the coatings

The adhesion property of the PBI coatings was determined with the lattice method. The polymer coatings on the metal surfaces were divided into equal small squares (1 mm × 1 mm) with a razor blade, and an insutape was suddenly pulled. As a result of this

TABLE I  
Physical Properties, Inherent Viscosities in Concentrated H<sub>2</sub>SO<sub>4</sub> at 30°C, and Elemental Analysis Data of the PBIs

Compound	Color	Melting point (°C)	Yield (%)	Found (calcd)				Inherent viscosity (dL/g)
				C (%)	H (%)	N (%)	S (%)	
PBI-1	Black	>350	67	77.87 (72.41)	4.49 (3.45)	26.4 (24.14)	—	—
PBI-2	Dark brown	>350	72	76.41 (77.92)	5.72 (3.89)	20.38 (18.18)	—	3.73
PBI-3	Dark brown	>350	74	75.02 (74.10)	3.58 (3.70)	20.63 (17.28)	—	—
PBI-4	Black	>350	60	80.12 (78.00)	3.68 (3.00)	15.40 (14.00)	—	3.6
PBI-5	Black	>350	75	65.3 (64.52)	3.70 (3.23)	15.43 (17.20)	17.32 (17.20)	—
PBI-6	Black	>350	57	73.42 (69.64)	3.98 (3.57)	11.87 (12.5)	15.10 (14.29)	4.09
PBI-7	Black	>350	78	78.13 (77.92)	2.96 (3.89)	18.58 (18.18)	—	—
PBI-8	Black	>350	69	84.40 (81.25)	4.09 (4.16)	14.52 (14.58)	—	—

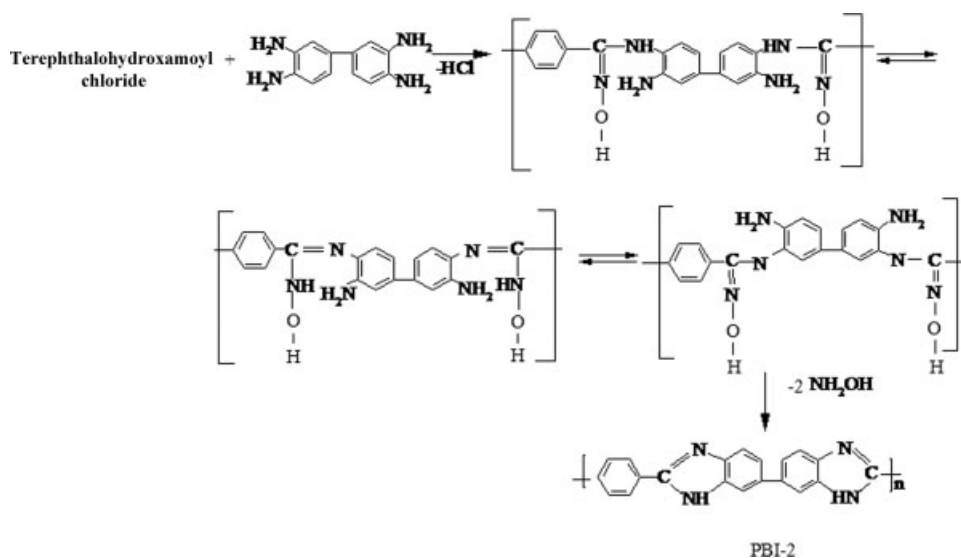


Figure 4 Mechanism of the synthesized PBIs.

operation, the adhesion percentage was calculated with the following expression:

$$\text{Adhesion (\%)} = [(a - b)/a] \times 100$$

where  $a$  is the total number of squares and  $b$  is the number of squares removed from the coating.

#### Determination of the corrosion resistance

Polymer coatings (100–120  $\mu\text{m}$  thick) were formed over the metal surfaces with a prepared polymer solution and were exposed to solutions of 3% NaCl, 10% NaOH, 10% HCl, and pure water and open air for 10 days. Then, the coated plates were removed from their existing media, and the amount of decomposition observed with the naked eye was taken as a measure of the corrosion resistance of the coating.

## RESULTS AND DISCUSSION

In general, some PBI syntheses have been performed through the reaction of 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene with dicarboxylic acid, anhydride, or nitrile by the use of poly(phosphoric acid) at high temperatures.<sup>1–10</sup> In this study, an aromatic hydroxamoyl chloride [terephthalohydroxamoyl chloride, 4,4'-bis(phenylhydroxamoyl chloride)ether, 4,4'-bis(phenylhydroxamoyl chloride)disulfide, or 4,4'-bis(phenylhydroxamoyl chloride)] produced a heteroaromatic closing reaction with 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene. These polymers, whose molecular structures were identified by inherent viscosity measurements, FTIR, LC mass spectrometry, DTG–TGA, and elemental analysis, were prepared readily by direct polycondensa-

tion. The structures of the synthesized PBIs were in accordance with the PBIs produced with conventional syntheses in the past.

Although in general the previous PBI syntheses were extremely long (4–20 h), the times spent for the syntheses in this study were shorter. The polycondensation process occurred fast and was completed within 1 h at 150°C. PBI might be produced by the heteroaromatization of the intermediate dihydroxamoyl chloride compounds after the elimination of hydroxylamine. The mechanism of the synthesized PBIs is shown in Figure 4.

The PBIs synthesized with conventional methods do not dissolve in organic solvents.<sup>6</sup> Therefore, general information about their molecular weights has usually been obtained from comparisons of their inherent viscosity values. Although the reaction period was long in past studies, the inherent viscosity values of the synthesized PBIs ranged from 0.5 to 8 dL/g (in concentrated sulfuric acid or methane sulfonic acid).<sup>1–8</sup> In this study, because some of the synthesized PBIs (PBI-1, PBI-3, PBI-5, PBI-7, and PBI-8) did not dissolve in a concentrated H<sub>2</sub>SO<sub>4</sub> solution, their inherent viscosity values could not be determined; despite this, the lowest value was determined to be 3.6 dL/g (Table I). Therefore, it can be stated that the molecular weights of these polymers were larger than those of PBIs synthesized with conventional methods. In 1961, Vogel and Marvel<sup>3</sup> found that the molecular weights of PBIs with an inherent viscosity of 0.8 dL/g were about 54,000; this means that the molecular weights of our polymers were much higher.

In the former syntheses, various acid catalysts were used to increase the activities of the reactants. Because the starting material used in this study, the

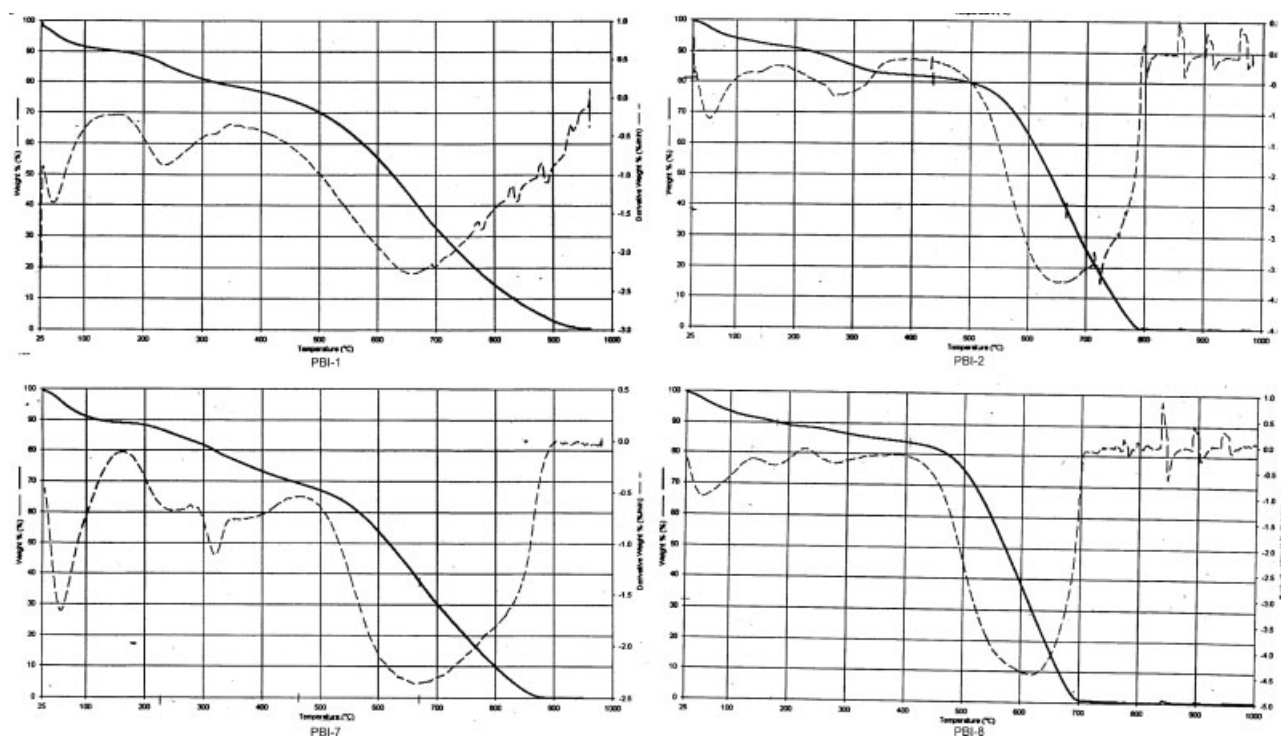


Figure 5 TGA of PBI-1, PBI-2, PBI-7, and PBI-8.

hydroxamoyl chloride compound, had a more active structure than the other reactants (dicarboxylic acid, esters of dicarboxylic acid, or nitrile) used before, an additional catalyst was not used in the synthesis, and the reaction occurred more easily in a short period of time.

The thermal properties of the polymers were evaluated with DTG-TGA. A typical thermogravimetric analysis (TGA) for the polymers is shown in Figure 5. In the TGAs of the polymers, mass losses were observed for CO, NHOH, and N<sub>2</sub> groups due to hydroxamic acid and amine groups, which probably

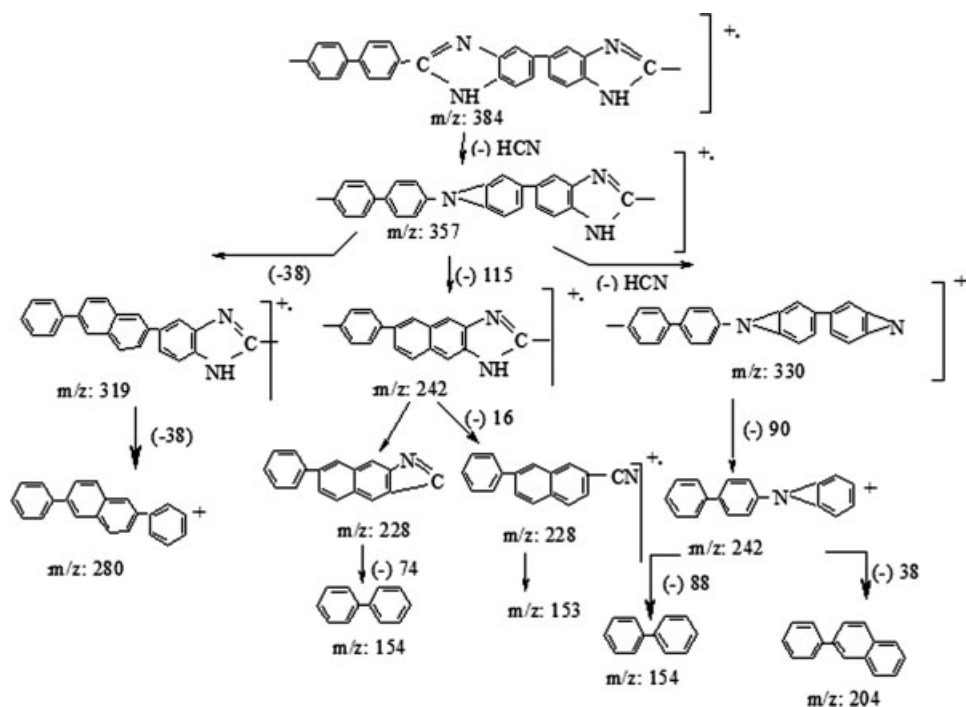


Figure 6 Fragmentation pattern of PBI-8.

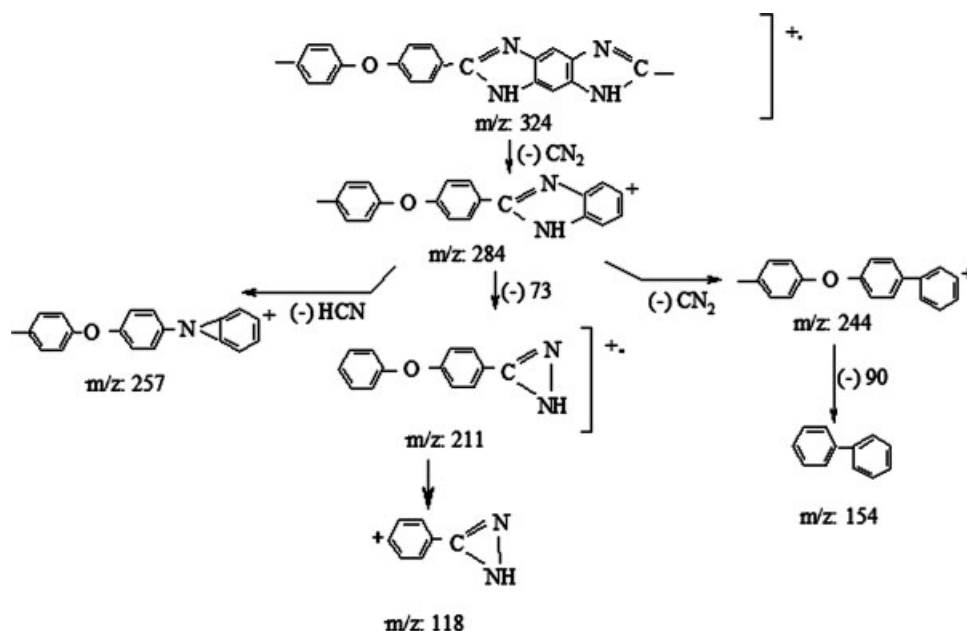


Figure 7 Fragmentation pattern of PBI-3.

remained at the end sections of the polymers, at temperatures up to 389°C. Moreover, mass losses due to humidity also took place. The polymers presented minimal weight loss at temperatures between 389 and 457°C and exhibited thermooxidative stability at temperatures higher than 457°C. For PBI, the thermal decomposition of one of the heterocyclic rings begins at 400°C, becomes maximum at 600–670°C with losses of  $CN_2$  and HCN, and continues up to temperatures between 700 and 920°C. The decomposition of PBIs synthesized with the conventional method begins at 400°C and continues up to 800°C. It can also be concluded that the PBIs synthesized in this study had thermal stability similar to that of PBIs synthesized by the conventional methods in the past.<sup>1,3,4,7,17–19</sup>

The mass fragmentation pattern of PBI-8 is given in Figure 6. The molecular ion gave a base peak at  $m/z = 384$  corresponding to its monomer weight. Fragments were formed because of the loss of the HCN radical. The mass fragmentation pattern of PBI-3 is given in Figure 7. Molecular ion peaks were visible in the spectra. When the molecular ion lost a  $CN_2$  radical and an HCN radical according to the procedure, a peak was seen at  $m/z = 284$  and at  $m/z = 258$ , respectively. The loss of the second  $CN_2$  molecule from  $m/z = 285$  gave a fragment at  $m/z = 245$ . The mass spectra of the PBIs exhibited signals at 232 ( $m/z$ ) and 233 ( $m/z$ ) for PBI-1, at 308 ( $m/z$ ) and 309 ( $m/z$ ) for PBI-2, at 400 ( $m/z$ ) and 401 ( $m/z$ ) for PBI-4, at 372 ( $m/z$ ) and 373 ( $m/z$ ) for PBI-5, at

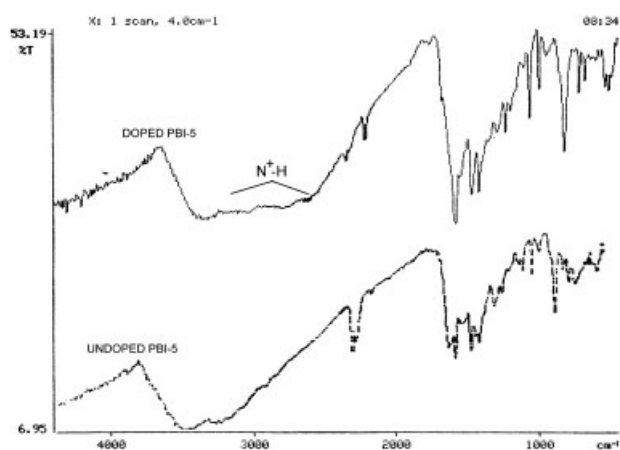


Figure 8 FTIR spectra of doped and undoped PBI-5 (solid powders).



Figure 9 FTIR spectra of doped and undoped PBI-6 (solid powders).

TABLE II  
FTIR Spectroscopy Data of Doped PBIs

Polymer	Wave number (cm <sup>-1</sup> )					
	Free N—H and OH stretching	N <sup>+</sup> —H stretching	C=N stretching	Benzene and imidazole ring	In-plane deformation of the benzimidazole ring	Breathing mode of the imidazole ring
PBI-1	3410–3220	2800–3000	1614	1514	1443	1257
PBI-2	3440–3250	3140	1618	1547	1427, 1464	1257
PBI-3	3395–3200	2500–3250	1620	1522	1427	1270
PBI-4	3430–3260	2500–3000	1608	1518	1476	1277
PBI-5	3450–3250	2750	1670	1570	1443	1258
PBI-6	3400–3250	3116	1607	1514	1427, 1478	1272
PBI-7	3420–3200	3100	1620	1583	1427	1260
PBI-8	3418–3210	3119	1610	1583	1426	1253

448 (*m/z*) and 449 (*m/z*) for PBI-6, and at 308 (*m/z*) and 309 (*m/z*) for PBI-7, which corresponded to their molecular and (M+1)<sup>+</sup> ion peaks, respectively. In the case of polymers PBI-5 and PBI-6, the (M+2)<sup>+</sup> peak was observed at 374 (*m/z*) and 450 (*m/z*) due to the <sup>34</sup>S isotope, and this indicated that PBI-5 and PBI-6 both contained a sulfide atom. The obtained results were in accordance with the results in the literature.<sup>20</sup> The proposed fragmentation patterns of PBI-8 and PBI-3 are shown in Figures 6 and 7.

The FTIR spectra of pristine doped and undoped PBIs are illustrated in Figures 8 and 9. The band assignments for PBI backbones are given in Table II. The sharp bands from 3450 to 3400 cm<sup>-1</sup> were attributed to the isolated N—H stretching of the imidazole. The C=C and C=N stretching appeared in the range of 1607–1620 cm<sup>-1</sup>.<sup>21,22</sup> However, although the vibration related to the C—Cl bond of the hydroxamoyl chlorides was observed in the 619–699-cm<sup>-1</sup> interval, no vibration related to the C—Cl bond was observed for the IR spectra of the polymers. This condition reveals the possibility of hydroxamic acid formation from the hydroxamoyl chloride existing at the end section of the polymer after it was washed with pure water. Moreover, the stress vibrations of the N—O group of the hydroxamic acid group, which probably remained at the end section of the polymers, were observed as 935 cm<sup>-1</sup>.

The broad bands closer to the 3200–2500-cm<sup>-1</sup> interval were assigned to the self-associated NH bonds (when the FTIR spectrum of the doped PBIs was examined). This band was broader in the presence of moisture. In this range, the N<sup>+</sup>—H vibrations appeared because of protonation of the imine in the doped samples. The FTIR spectra of PBIs doped with HCl in the N—H stretching zone revealed the evolution of nitrogen protonation by the acid. In the medium of highly doped samples, the broad band of the N<sup>+</sup>—H stretching became stronger. For instance, a sharp peak was observed for the N<sup>+</sup>—H stretching of some polymers in comparison with the others (PBI-1, PBI-3, PBI-7, and PBI-

8), whereas the unassociated N—H decreased but never disappeared.<sup>4,5,21,23,24</sup> A strong band in the 1426–1478-cm<sup>-1</sup> interval should be related to the in-plane deformation of the benzimidazole rings. In-plane C—H deformations appeared in the 1253–1272-cm<sup>-1</sup> interval, whereas Musto et al.<sup>31</sup> determined the band at 1277 cm<sup>-1</sup> to be the breathing mode of the PBI imidazole ring.

The conductivities of the doped polymers were determined with the polymer powder with the four-probe method. The conductivity and magnetic susceptibility data of the doped polymers at room temperature are shown in Table III. The magnetic susceptibility values of the polymers were negative, revealing diamagnetism. In other words, this analysis indicates that PBIs have diamagnetic properties and that their conducting mechanisms have a bipolaron nature.<sup>25</sup>

Although the doped PBIs of the previous studies had a conductivity of 10<sup>-11</sup> S/cm, the doped PBIs formed with doping acids had a conductivity value of 10<sup>-2</sup> S/cm.<sup>6,23,26-29</sup> Moreover, the effects of the various doping acids used in the former studies were examined in terms of conductivity.<sup>30</sup> In this study, a 1M HCl doping solution was used to dope the polymers, and after the doping process, which took 24 h, the conductivity of the polymers increased from 10<sup>-11</sup> to 10<sup>-5</sup> S/cm. As can be seen in Table III, although the conductivity of some of the poly-

TABLE III  
Conductivity and Gouy Balance Measurements of PBIs

Polymers	Conductivity (S/cm)	Magnetic susceptibility measurement
PBI-1	1.90 × 10 <sup>-5</sup>	-45
PBI-2	7.77 × 10 <sup>-6</sup>	-55
PBI-3	1.03 × 10 <sup>-5</sup>	-42
PBI-4	3.50 × 10 <sup>-6</sup>	-53
PBI-5	4.53 × 10 <sup>-6</sup>	-45
PBI-6	4.69 × 10 <sup>-6</sup>	-52
PBI-7	2.85 × 10 <sup>-5</sup>	-30
PBI-8	1.13 × 10 <sup>-5</sup>	-47





**Figure 10** Microscope images of PBIs coated on metal surfaces after the adhesion test: PBI-4 (left) and PBI-1 (right). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

mers (PBI-1, PBI-3, PBI-7, and PBI-8) was  $10^{-5}$  S/cm, the others (PBI-2, PBI-4, PBI-5, and PBI-6) had a conductivity value of  $10^{-6}$  S/cm. Concerning the inherent viscosities of these polymers, the ones with a conductivity of  $10^{-5}$  S/cm could be said to have longer and more conjugated structures than the others. Despite its higher inherent viscosity, the conductivity of the PBI-5 polymer was measured to be  $10^{-6}$  S/cm because of its structural relation with the  $-S-S-$  group, which reduced the conjugation at the polymer chain. Nevertheless, according to the FTIR spectra, after the polymers were doped, the vibration band in the  $2500-3200\text{-cm}^{-1}$  interval was observed to be sharper for the polymers with a conductivity of  $10^{-5}$  S/cm.<sup>6,23</sup>

PBIs of different molecular weights were homogenized with a DMSO mixture, which could not dissolve the polymers of high molecular weights for 10 days. Therefore, the dissolved polymers of low molecular weights were used for the coating processes. The increase in the adhesion properties was determined for the PBIs having groups of  $-S-S-$ ,  $-O-$ ,  $-C=N-$ , and  $-C-NH-$  on the main chain and  $-NH_2$  and  $-CO-NHOH$  at the terminal group in their structures.<sup>12</sup> For example, the adhesion properties of PBI-4 were higher with respect to

PBI-2. (After the polymers were melted with  $Na_2CO_3$ , the concentration of the chlorine ion was determined with a chlorine-ion electrode, and thus the polymers containing hydroxamic acid were found.)

Consequently, it was determined that the polymers coated on the metal surfaces and having terminal groups of  $-NH_2$  in their structures exhibited high adhesion and anticorrosion properties. Some polymers had lower coating properties. However, hydroxamoyl chloride groups possibly existing at the end groups of some polymers (PBI-2 and PBI-1) turned into hydroxamic acid groups during the polymer purification process, and consequently these polymers presented low adhesion property. Therefore, in this study, PBI-2 and PBI-1 were determined to have extremely low adhesion properties. Images of some polymers after adhesion are presented in Figure 10, and the results are shown in Table IV.

The corrosion resistance of PBIs coated on metal surfaces was investigated for 9–10 days in 3% NaCl, 10% NaOH, and 10% HCl solutions and in the atmosphere. It was determined that the corrosion resistance of the coating against the 10% NaOH solution decreased, depending on the presence of the  $-CO-NHOH$  terminal group in the structure of

**TABLE IV**  
Adhesion and Corrosion Resistance Properties of PBI Polymers

Polymer	Proposed terminal groups ( $-CO-NHOH$ )	Adhesion (%)	Corrosion resistance			
			3% NaCl	10% NaOH	Water	10% HCl
PBI-2 (dissolved part of the polymer)	$\text{HOHN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{---}-(\text{PBI})_n-\text{---}-\text{Ar}(\text{NH}_2)_2$	80	--+	+	+	--+
PBI-1 (dissolved part of the polymer)	$\text{HOHN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{---}-(\text{PBI})_n-\text{---}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHOH}$	40	--+	--	++	++
PBI-4 (dissolved part of the polymer)	$(\text{NH}_2)_2\text{Ar}-\text{---}-(\text{PBI})_n-\text{---}-\text{Ar}(\text{NH}_2)_2$	90	++	++	++	--
Other polymers (undissolved in DMSO)	--	--	--	--	--	--

-- = no resistance; --+ = little resistance; + = medium resistance; ++ = high resistance.

the polymer. The main reason for this was considered to be the interaction of the bond between the hydroxamic acid group and NaOH.

Briefly, in this study, PBIs with high molecular weights, good thermal stability, and semiconductivity were prepared by the application of a direct polycondensation reaction between hydroxamoyl chloride and 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene tetrahydrochloride in DMF without the use of any catalysts. This alternative polycondensation reaction was also very simple and successful in affording PBIs along with the formation of hydroxyl ammonium hydrochloride. Although the method used in this study for the synthesis of PBIs was long and chloride gas was used, the molecular weights of the PBIs synthesized by this method were higher than those of the PBIs in the literature.

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