

# Reduction and Cyclization to Form Poly(benzimidazole amide imide) Copolymers

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**ABSTRACT:** Poly(amide imide) copolymers were synthesized with different molar ratios of 4,4-diphenylmethane diisocyanate, two types of aromatic dianhydrides (pyromellitic dianhydride (PMDA) and 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA)), and a diacid, which was derived from 3,3'-dinitrobenzidine and isophthaloyl chloride in a previous work. In this study, the copolymers were further reacted with a reducing agent, and the nitro groups in the copolymers were hydrogenated into amine groups. Then, the amine-group-containing poly(amide imide) copolymers were cyclized at 180°C to form the poly(benzimidazole imide amide) copolymers in poly(phosphoric acid), which acted as a cyclizing agent. The resultant copolymers were

soluble in sulfuric acid and poly(phosphoric acid) at room temperature and in sulfolane or *N*-methyl-2-pyrrolidone under heating to 100°C with 5% lithium chloride. According to wide-angle X-ray diffraction, all the copolymers were amorphous. According to thermal analysis, the glass-transition temperature ranged from 270 to 322°C, and the 10% weight-loss temperature ranged from 460 to 541°C in nitrogen and from 441 to 529°C in air. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 378–386, 2004

**Key words:** poly(imide amide benzimidazole); poly(amide imide); thermally stable

## INTRODUCTION

Because of the increasing need for materials that can be used in high-temperature environments, high-performance polymers with high temperature resistance have been researched for over 50 years.

Aromatic polyimide is known to be one of the best materials for high-temperature applications.<sup>1–3</sup> This is due to its aromatic and heterocyclic structure. However, the rigid structure and low concentration of hydrogen bonding in the polyimide chain, though imparting properties such as thermooxidative stability,<sup>4–6</sup> make the material hard to process because of its poor solubility.<sup>7–9</sup> Polybenzimidazole also has good thermal resistance to high temperatures, even better than that of polyimide. It has good thermooxidative stability and chemical proofing because of its chemically aromatic and heterocyclic structure.<sup>10–12</sup> However, the poor solubility and processability limit its applications.

Aromatic polyamide has better solubility but less thermal resistance. Therefore, we introduced the amide group into copolymers to obtain a good balance of the solubility and thermal resistance.<sup>13–15</sup>

In this research, we continued a previous study:<sup>16</sup> poly(amide imide) copolymers were hydrogenated

and cyclized to form poly(benzimidazole amide imide) copolymers. The chemical structure, solubility, thermal properties, and crystallinity of these new copolymers are discussed.

## EXPERIMENTAL

### Materials

Raney nickel, poly(phosphoric acid) (PPA), and hydrazine with monohydrate were of high purity and were used as received from the manufacturer. Solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and sulfolane were purified by vacuum distillation with calcium hydride.

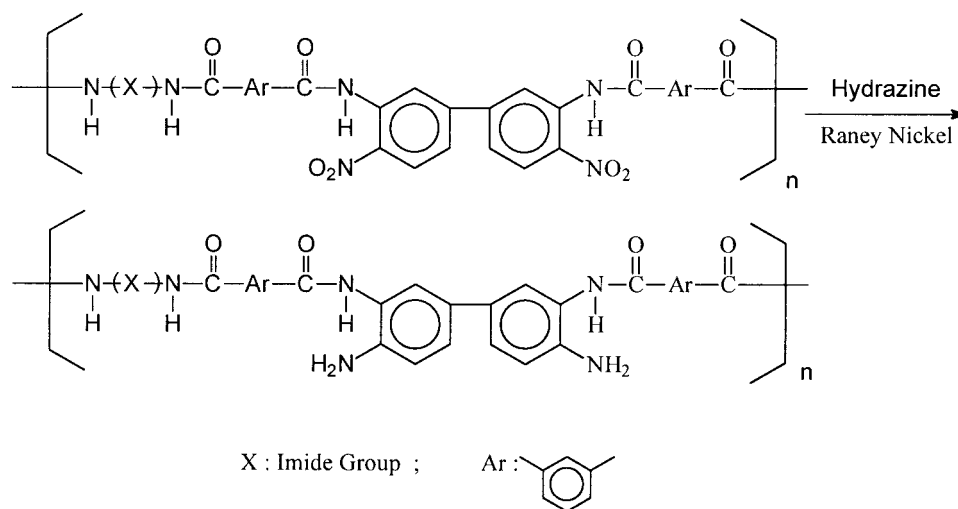
### Hydrogenation of the aromatic poly(amide imide) copolymers

The poly(amide imide) copolymers from our previous research were dissolved in NMP, and the temperature was then raised to 80°C. Hydrazine with monohydrate and Raney nickel were then added into the reaction flask, and the reaction continued for 8 h. The reaction is shown in Scheme 1.

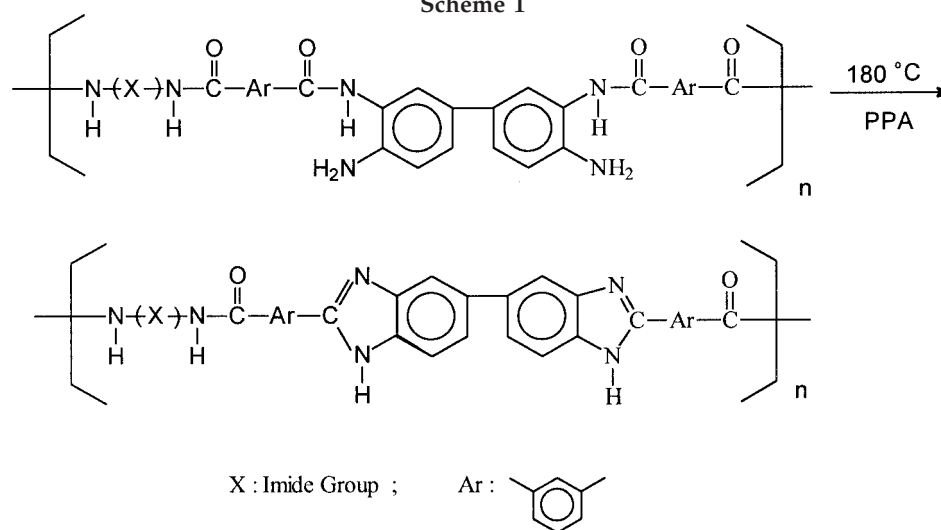
### Cyclization of the aromatic poly(benzimidazole imide amide) copolymers

The hydrogenated copolymers were then dissolved in PPA. The temperature was raised to 180°C for 6 h. The

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Scheme 1



Scheme 2

TABLE I  
Polymer Codes

Code	Polymer	4,4-Diphenylmethane diisocyanate	Dianhydride	Dicarboxylic acid
PIP	Polyimide (PMDA)	1	1	0
PAI-P1	Poly(amide imide) (PMDA)	2	1	1
PAI-P2		3	2	1
PAI-P3		4	3	1
PAI-P4		5	4	1
PBI-P1	Poly(benzimidazole imide amide) (PMDA)	2	1	1
PBI-P2		3	2	1
PBI-P3		4	3	1
PBI-P4		5	4	1
PID	Polyimide (DSDA)	1	1	0
PAI-D1	Poly(amide imide) (DSDA)	2	1	1
PAI-D2		3	2	1
PAI-D3		4	3	1
PAI-D4		5	4	1
PBI-D1	Poly(benzimidazole imide amide) (DSDA)	2	1	1
PBI-D2		3	2	1
PBI-D3		4	3	1
PBI-D4		5	4	1

**TABLE II**  
Inherent Viscosity of Polymers

Code	Inherent viscosity	Imide content (%)	Amide content (%)	Imidazole content (%)
PIP	0.71	100	0	0
PBI-P1	0.73	37.4	32.3	30.3
PBI-P2	0.79	54.4	23.5	22.1
PBI-P3	0.89	64.2	18.5	17.3
PBI-P4	0.89	70.5	15.2	14.3
PID	0.85	100	0	0
PBI-D1	0.70	45.0	28.4	26.6
PBI-D2	0.77	62.0	19.6	18.4
PBI-D3	0.80	71.0	14.9	14.0
PBI-D4	0.91	76.6	12.1	11.3

**TABLE III**  
Elemental Analysis of Polymers

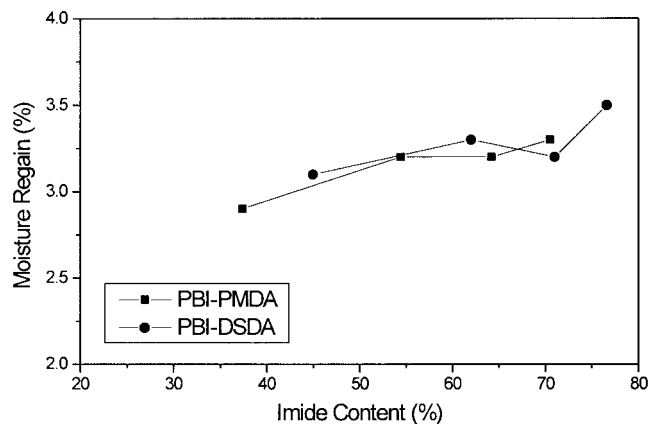
Code	Elemental content	C(%)	H(%)	N(%)	Moisture regain (%)
PBI-P1	Calcd	75.58	3.96	11.02	2.9
	Found	74.01	4.24	10.34	
	Corrected	76.16	4.12	10.64	
PBI-P2	Calcd	74.77	3.75	10.03	3.2
	Found	72.99	4.11	8.84	
	Corrected	75.33	3.98	9.12	
PBI-P3	Calcd	74.31	3.63	9.09	3.2
	Found	72.95	3.97	8.77	
	Corrected	75.28	3.84	9.06	
PBI-P4	Calcd	74.02	3.55	9.09	3.3
	Found	72.24	3.91	8.77	
	Corrected	74.62	3.78	9.06	
PBI-D1	Calcd	72.65	3.83	9.69	3.1
	Found	70.11	3.99	9.24	
	Corrected	72.28	3.87	9.53	
PBI-D2	Calcd	70.87	3.60	8.35	3.3
	Found	67.98	3.87	7.99	
	Corrected	70.22	3.74	8.25	
PBI-D3	Calcd	69.93	3.49	7.65	3.2
	Found	66.83	3.88	7.21	
	Corrected	68.97	3.76	7.44	
PBI-D4	Calcd	69.36	3.41	7.21	3.5
	Found	66.01	3.83	6.84	
	Corrected	68.32	3.70	7.08	

Moisture content (%) =  $W - W_0 / W_0 \times 100\%$ , where  $W_0$  is the weight of the polymer dried *in vacuo* at 100°C for 10 h and  $W$  is the weight of the polymer remaining at room temperature. For C and N, Corrected value = Found value  $\times (100\% + \text{Moisture content } \%)$ . For H, Corrected value = Found value  $\times (100\% - \text{Moisture content } \%)$ .

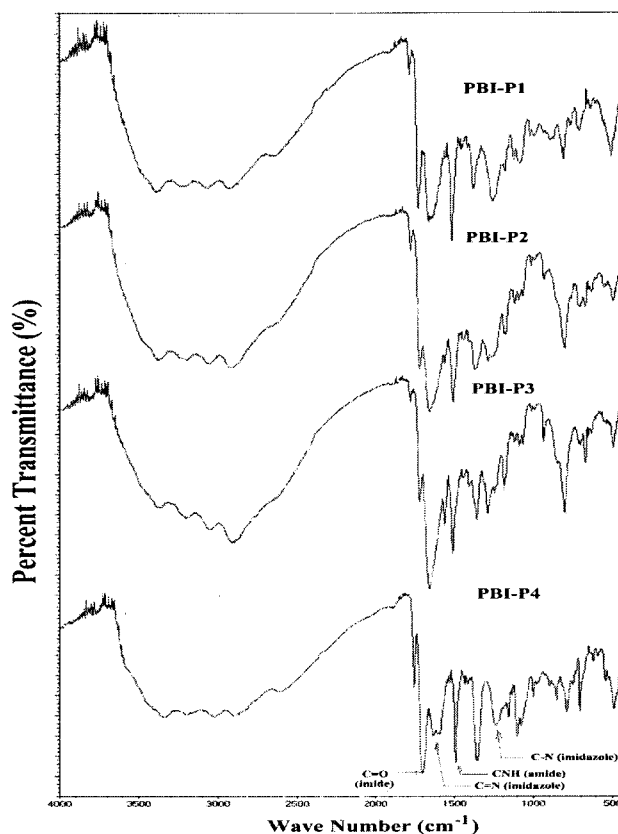
products were neutralized with NaOH, washed, and dried. The reaction is shown in Scheme 2.

### Measurements

Infrared (IR) spectra of polyimides and copoly(amide imide)s were obtained with a Shimadzu 8300 Fourier



**Figure 1** Relationship between the moisture regain and imide content.



**Figure 2** IR spectra of the PMDA series copolymers.

transform infrared spectrometer (Hitachi, Tokyo, Japan) from 400 to 4000  $\text{cm}^{-1}$ . The samples were films about 10  $\mu\text{m}$  thick.

Elemental analysis (C, H, and N) was performed with a PerkinElmer 2400 analyzer (PerkinElmer, Shelton, CT).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a DuPont 9900 differential scanning calorimeter (Du-

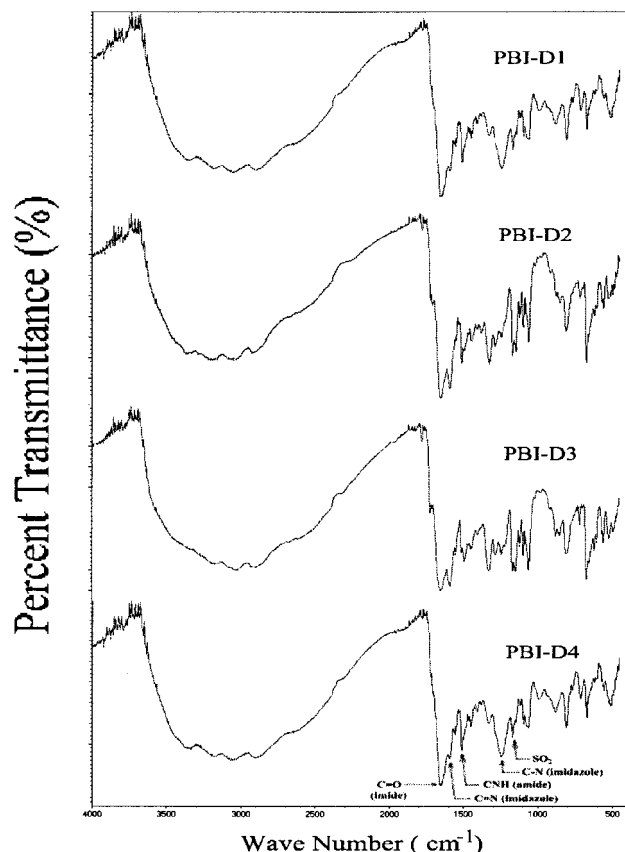


Figure 3 IR spectra of the DSDA series copolymers.

Pont, Wilmington, DE) and a Seiko SSC-5000 thermogravimetric analyzer (Seiko, Chiba, Japan) at a heating rate of 20°C/min under a nitrogen atmosphere to obtain the glass-transition temperature and the weight loss, respectively.

Wide-angle X-ray photographs were taken with Ni-filtered Cu K $\alpha$  radiation with a Rigaku D/max-II X-ray diffractometer (Rigaku, Tokyo, Japan).

## RESULTS AND DISCUSSION

### Synthesis of the poly(benzimidazole amide imide) copolymers

Table I shows the codes for all polymers with their various ratios. The inherent viscosities of the polymers are listed in Table II. All of the polymers have inherent viscosities in the range of 0.70–0.91 dL/g. In the table, the theoretical contents of benzimidazole, amide, and imide groups of the copolymers are also listed. The results for the elemental analyses of all polymers are listed in Table III. The empirical values agree well with the calculated ones. The moisture regain values of the polymers are also listed in Table III for correc-

TABLE IV  
Solubility of Polymers

Code	NMP	DMF	DMSO	DMAc	Pyridine	Sulfuric acid	Sulfolane
PIP	++	–	–	–	–	++	+
PBI-P1	+-	+-	+-	+-	+-	++	+
PBI-P2	+-	+-	+-	+-	–	++	+
PBI-P3	+-	+-	+-	–	–	++	+
PBI-P4	+-	–	+-	–	–	++	+
PID	++	–	+	–	–	++	++
PBI-D1	+-	+-	+-	+-	+-	++	+
PBI-D2	+-	+-	+-	+-	–	++	+
PBI-D3	+-	+-	+-	+-	–	++	+
PBI-D4	+-	–	+-	–	–	++	+

++ = soluble at room temperature; + = soluble when heated to 100°C; +- = soluble with 5% LiCl and when heated to 100°C; – = dissoluble.

TABLE V  
Glass-Transition Temperature ( $T_g$ ) of the Polymers

Code	$T_g$ (°C)	Imide content (%)	Amide content (%)	Imidazole content (%)
PIP	351	100	0	0
PBI-P1	277	37.4	32.3	30.3
PBI-P2	283	54.4	23.5	22.1
PBI-P3	289	64.2	18.5	17.3
PBI-P4	322	70.5	15.2	14.3
PID	319	100	0	0
PBI-D1	270	45.0	28.4	26.6
PBI-D2	279	62.0	19.6	18.4
PBI-D3	281	71.0	14.9	14.0
PBI-D4	314	76.6	12.1	11.3

TABLE VI  
TGA of the Polymers

Code	$T_{d10}$ (°C; air)	$T_{d10}$ (°C; N <sub>2</sub> )	Imide content (%)	Amide content (%)	Imidazole content (%)
PIP	575	583	100	0	0
PBI-P1	475	510	37.4	32.3	30.3
PBI-P2	496	518	54.4	23.5	22.1
PBI-P3	509	522	64.2	18.5	17.3
PBI-P4	529	541	70.5	15.2	14.3
PID	552	560	100	0	0
PBI-D1	441	460	45.0	28.4	26.6
PBI-D2	452	474	62.0	19.6	18.4
PBI-D3	474	482	71.0	14.9	14.0
PBI-D4	525	539	76.6	12.1	11.3

$T_{d10}$  = 10% weight loss temperature.

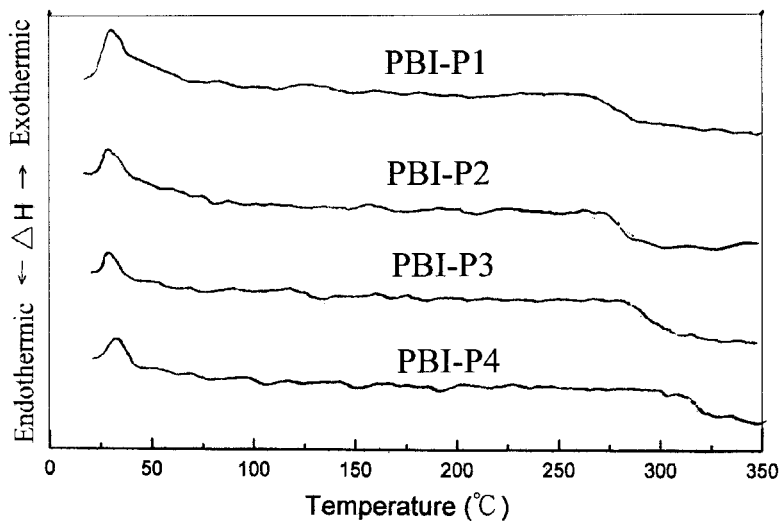


Figure 4 DSC curves of the PMDA series copolymers.

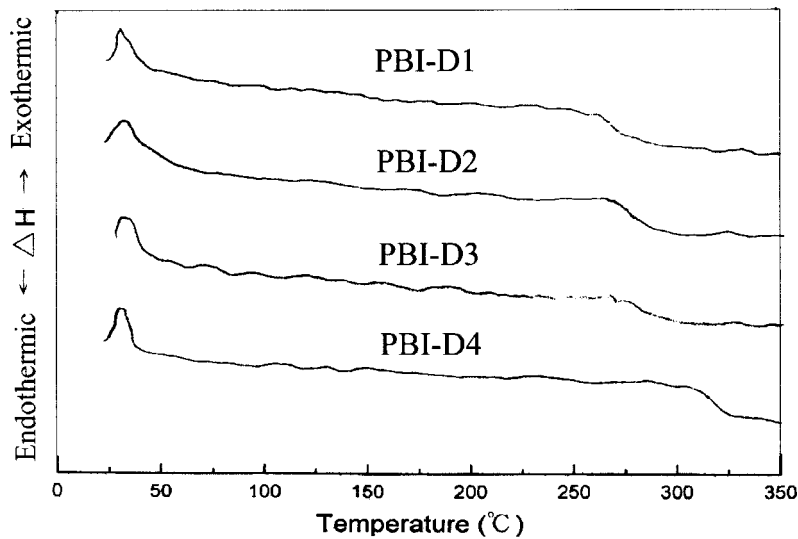


Figure 5 DSC curves of the DSDA series copolymers.

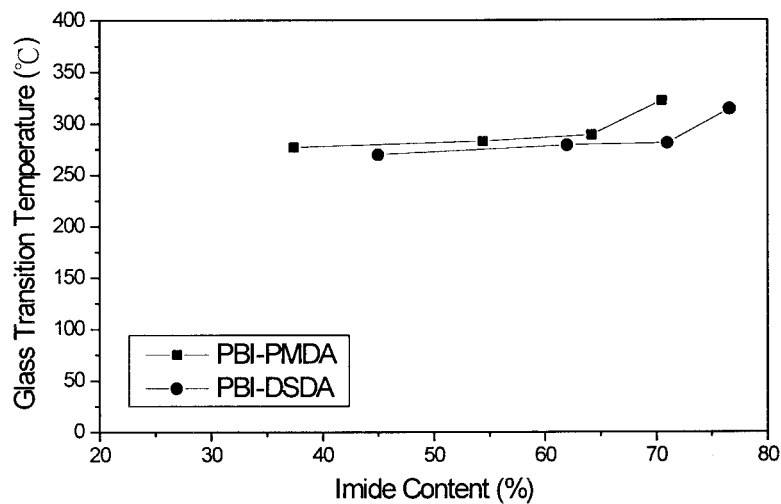


Figure 6 Relationship between the glass-transition temperature and the imide content.

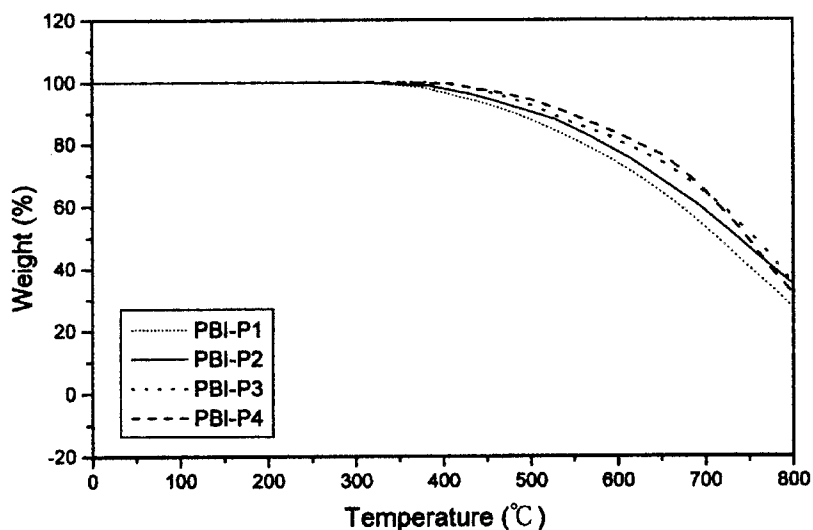


Figure 7 Heat weight loss of the PMDA series in air.

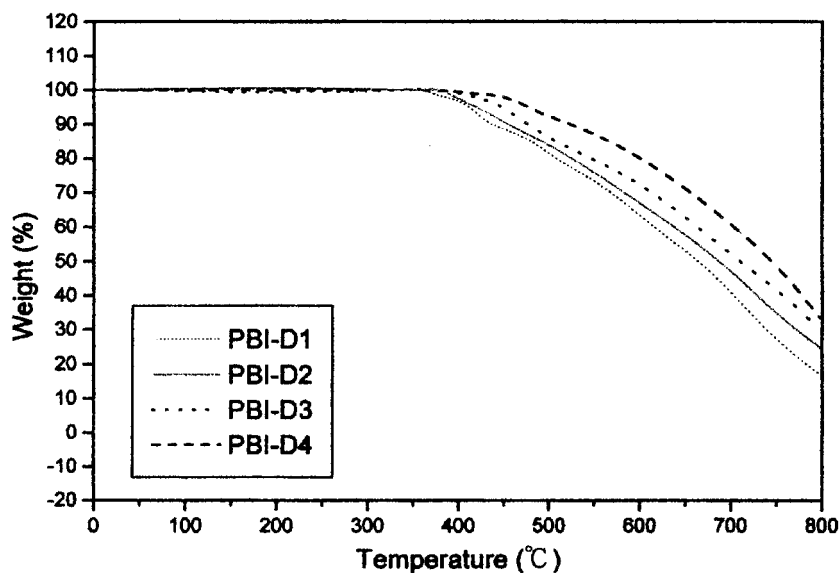


Figure 8 Heat weight loss of the DSDA series in air.

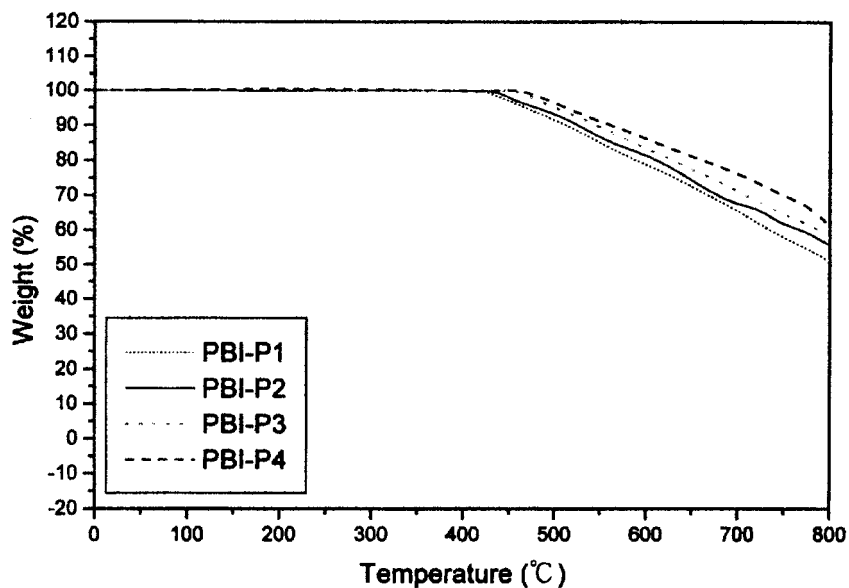


Figure 9 Heat weight loss of the PMDA series in nitrogen.

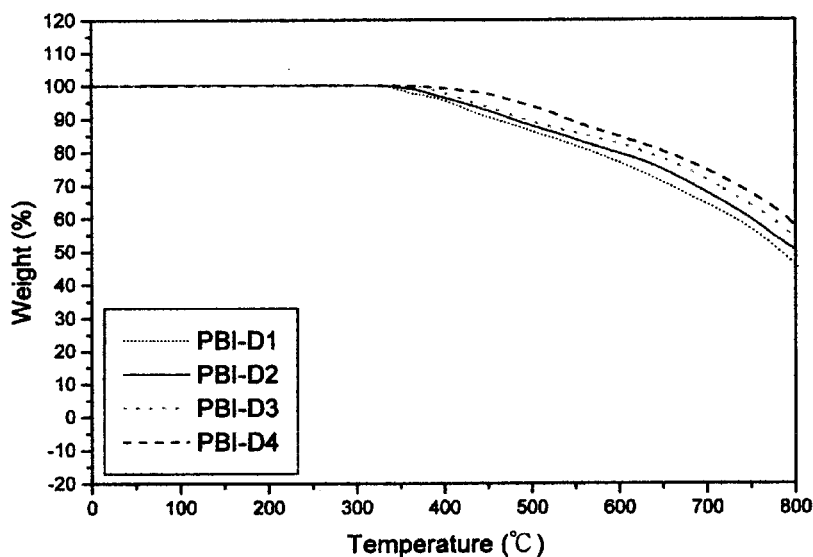


Figure 10 Heat weight loss of the DSDA series in nitrogen.

tion. In Figure 1, the moisture regain of the polymers increases with increasing imide content; this is probably caused by the formation of benzimidazole groups from amide groups and reduces the degree of hydrogen bonding of amide groups, i.e., the number of absorbancy sites; therefore, the moisture regain is obviously reduced.

These polymers can be cast into transparent films. Figures 2 and 3 show the IR spectra of poly(benzimidazole amide imide) copolymers. The characteristic absorptions at 1720, 1780, 1360, and 720  $\text{cm}^{-1}$  indicate the existence of the imide group in the pyromellitic dianhydride (PMDA) series. Moreover, the absorption peaks at 1660 and 3300–3400  $\text{cm}^{-1}$  demonstrate the —NH stretching vibration of the amide group. The absorption peaks at 1120–1160  $\text{cm}^{-1}$  show the absorption of the  $\text{SO}_2$  group in the spectrum of the 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA) series. Furthermore, the absence of the  $\text{NO}_2$  group at 1521 and 1340  $\text{cm}^{-1}$  and the  $\text{NH}_2^+$  group at 2800–2000  $\text{cm}^{-1}$  after their cyclization and the existence of the  $\text{C}=\text{N}$  group of benzimidazole at 1656  $\text{cm}^{-1}$  and  $\text{Ar}-\text{NH}-\text{R}$  at 1257  $\text{cm}^{-1}$  provide the formation of benzimidazole groups in the copolymers.

#### Solubility properties of the polymers

Table IV summarizes the solubilities of all the polymers. The poly(benzimidazole amide imide) copolymers can be dissolved in sulfuric acid at room temperature, in sulfolane at 100°C, and in DMAc and NMP with 5% LiCl at 100°C. Because of the existence of sulfonyl group in the DSDA series, that series exhibits a slightly higher solubility than the PMDA series. In general, the copolymers have better solubility

than the homopolyimide and homopolybenzimidazole, with the exception of the solvent NMP. Moreover, the formation of benzimidazole groups from amide groups leads to less hydrogen bonding and thus reduces the solubility of the copolymers.

#### Thermal properties of the polymers

The thermal properties of all the polymers were evaluated with DSC and TGA, and the derived data are shown in Tables V and VI. According to the results, all the copolymers are amorphous and lack melting points. Also, the copolymers do not form liquid crystals. Figures 4 and 5 show the DSC curves of the copolymers. The glass-transition temperatures of the copolymers are 270–322°C, and they decrease as the amide content increases. This demonstrates that the incorporation of an amide linkage into the polyimide backbone can increase the flexibility of the copolymer chain and hence reduce the glass-transition temperatures of the copolymers. The glass-transition temperature of the PMDA series copolymers is higher than that of the DSDA series because the structure of PMDA is more rigid than that of DSDA, which contains a sulfonyl group. The relationship between the glass-transition temperatures and the imide content is shown in Figure 6. The formation of benzimidazole groups reduces the amide group content; this increases the rigidity and glass-transition temperature of the copolymers.

Figures 7–10 show the heat weight losses of the copolymers, and Table VI summarizes the thermogravimetric data for all the copolymers. All the polymers possess good thermal and thermooxidative stability. The 10% weight-loss temperatures ranges from

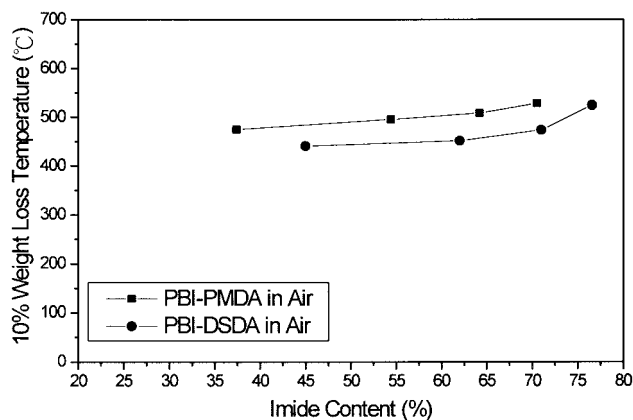


Figure 11 Relationship between the 10% weight-loss temperature and imide content (in air).

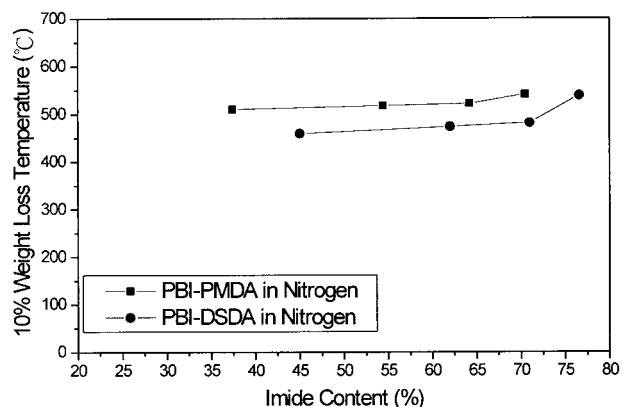


Figure 12 Relationship between the 10% weight-loss temperature and imide content (in nitrogen).

460 to 541°C in nitrogen and from 441 to 529°C in air. With an increase in the imide content, the 10% weight-loss temperature increases. Figures 11 and 12 show the relationship between the 10% weight-loss temperature and the imide content. The amide linkage contributes less thermooxidative stability than imide and benzimidazole. From Figures 11 and 12, we find that the 10% weight-loss temperatures of both the PMDA and DSDA series are nearly linear with the imide content, with the exception of PBI-P4 and PBI-D4, either in air or in nitrogen. The 10% weight-loss temperatures of PBI-P4 and PBI-D4 are much higher than those of the copolymers with other molar ratios. This may be explained by the fact that the content of amide is much lower than that of imide in both copolymers, and the thermal degradation properties are much closer to those of the homopolyimide.

#### Wide-angle X-ray diffraction (WAXD) of the polymers

The X-ray diffraction curves of the copolymers are shown in Figures 13 and 14. The WAXD patterns of

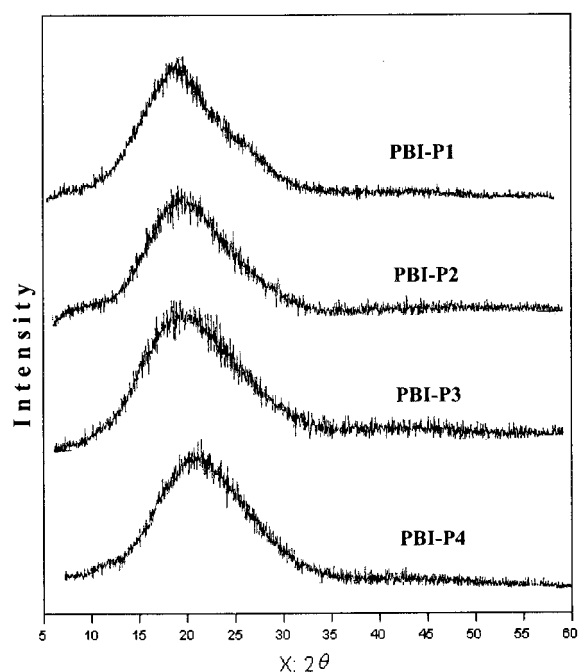


Figure 13 X-ray diffraction curves of the PMDA series.

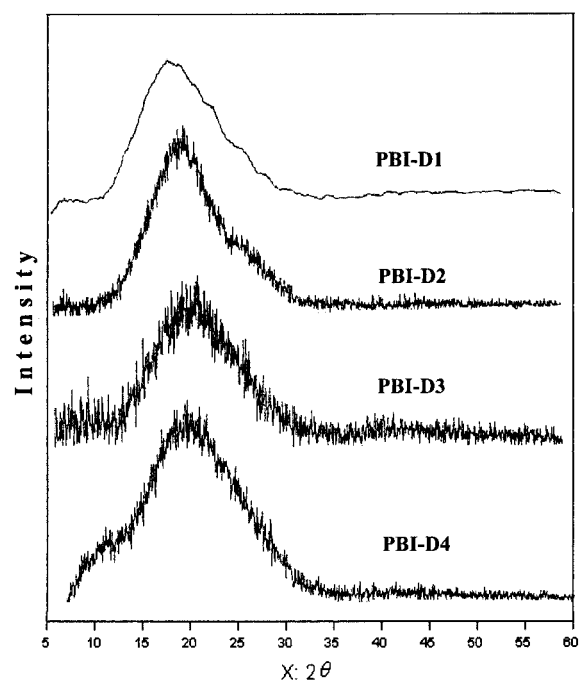


Figure 14 X-ray diffraction curves of the DSDA series.

the polymers were measured with a Rigaku diffractometer. All the polymers are amorphous; this may be due to the presence of heterocyclics such as imide and benzimidazole groups and aromatic structures in the main chain, which limit the molecular mobility of all the polymers and constrict the formation of crystals. Meanwhile, the formation of benzimidazole groups



hinders and reduces the formation of hydrogen bonding. These results agree with the DSC measurements.

### CONCLUSIONS

In this study, we used a low-temperature method to form benzimidazole structures in poly(benzimidazole amide imide) copolymers. The cyclized reaction proceeded in PPA (used as a solvent). The copolymers are soluble in sulfuric acid and PPA at room temperature and in sulfolane or in NMP under heating to 100°C with 5% lithium chloride. According to WAXD, all of these copolymers are amorphous. The formation of benzimidazole groups from amide groups after their cyclization increases the rigidity and glass-transition temperature of the copolymers. All the polymers have good thermal and thermooxidative stability. On the basis of the results, we can confirm that when the content of amide is much less than that of imide, the copolymers behave much more like the homopolyimide.

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