Thermal and Thermo-oxidative Degradation Properties of Poly(benzimidazole amide imide) Copolymers

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ABSTRACT: In this study, 3,3′-dinitrobenzidine was first reacted with excess isophthaloyl chloride to form a monomer with dicarboxylic acid end groups. Two types of aromatic dianhydride, [viz., pyromellitic dianhydride (PMDA) and 3,3′,4,4′-sulfonyldiphthalic anhydride (DSDA)] also were reacted with excess 4,4′-diphenyl- methane diisocyanate (MDI) to form polyimide prepolymers terminated with isocyanate groups. The prepolymers were reacted further with the diacid monomer to form a nitro group–containing aromatic poly(amide imide) copolymers. The nitro groups in these copolymers were hydrogenated to form amine groups and cyclized at 180°C to form the poly(benzimidazole amide imide) copolymers in polyphosphoric acid (PPA), which acts as a cyclization agent. From the viscosity measurements, copolymer appeared to be a reasonably high molecular weight. From the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements it was shown that the glass transition temperature of copolymers was in the range of ~270–322°C. The 10% weight loss temperatures were in the range of 460 ~ 541°C in nitrogen and ~441–529°C in air, respectively. The activated energy and the integration parameter of degradation temperature of the copolymers were evaluated with the Doyle-Ozawa method. It indicated that these copolymers have good thermal and thermo-oxidative stability with the increase in imide content. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2072–2081, 2004

Key words: 3,3′-dinitrobenzidine; poly(benzimidazole amide imide); Doyle-Ozawa method

INTRODUCTION

Aromatic polyimides have been known to be one of the good materials for use in the high-temperature application.[1-3] This is because of their aromatic and heterocyclic structure. Generally, polyimides are used in aircraft, osmotic membrane, and microelectronics applications. However, their rigid structure and low concentration of hydrogen bonding in the polyimides chain, which, although could impart properties such as thermo-oxidative stability,[4-6] makes these materials hard to process because of their poor solubility.[7-10]

In our previous works, we successfully used the diacid-terminated poly[m-phenylene isophthalamide] (PmIA) prepolymer (Nomex-type prepolymer) and the naphthalate structure to modify the polyimides to copoly(amide imide) copolymers.[11-14] In this article, we focus on the of 3,3-dinitrobenzidine to modify polyimides to form poly(benzimidazole amide imide) copolymers[15] and to study the thermal and thermo-oxidative degradation properties of these new copolymers.

EXPERIMENTAL

Materials

Commercially available dianhydride, namely, 3,3′,4,4′-sulfonyl diphthalic anhydride (DSDA) was dried in a frozen vacuum at −40°C for 4 h to remove moisture. 4,4′-Diphenylmethane diisocyanate (MDI) was used without further purification. Both 3,3′-dinitrobenzidine and isophthaloyl chloride were of high purity and were used as received. Raney Nickel, polyphosphoric acid (PPA), and hydrazine monohydrate were of high purity and were used as received. N-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation with calcium hydride. Triethylamine, which was used as a catalyst, was used without further purification.
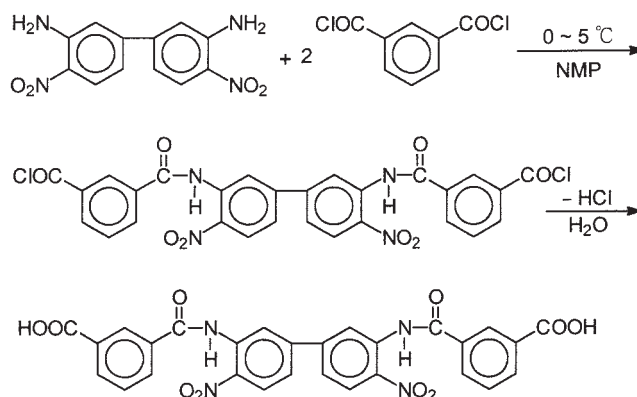
Synthesis of aromatic polyimide

Equimolar amounts of MDI and dianhydride were dissolved in NMP (solid content of 15%) and taken in a 250-mL reaction flask and heated at 60°C for 4 h. Then, catalyst, 0.03 g/L of triethylamine, was added. Viscosity gradually increased, and bubbles of gas (carbon dioxide) evolved. The viscosity was adjusted by adding solvent. After 1 h, the temperature was raised to 80°C and held for 2 h and then 110°C for another 1 h. A golden-colored viscous solution of polyimide was obtained. The reaction is shown in Scheme 1.
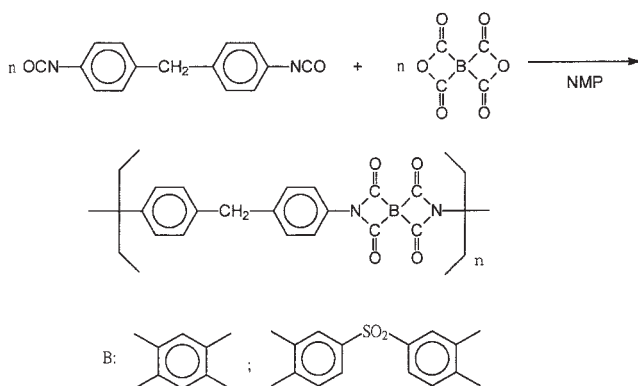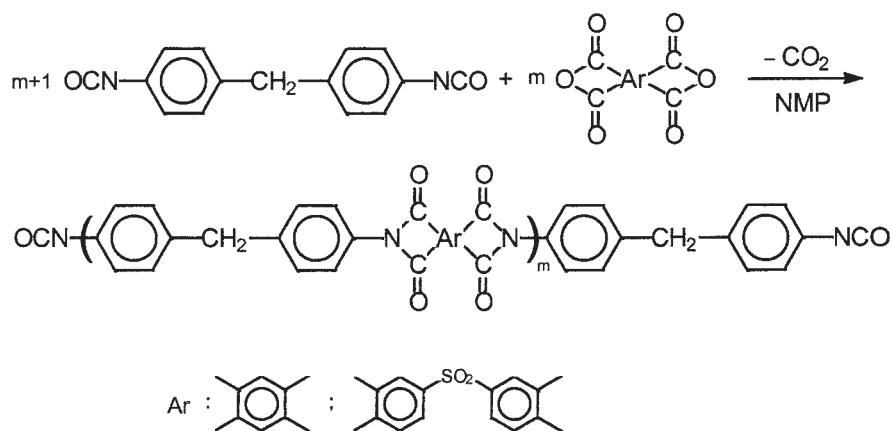
Scheme 1

Scheme 2

Synthesis of diacid monomer and aromatic poly(amide imide)

A mixture of 0.05 mol of 3,3′-dinitrobenzidine and 0.12 mol of isophthaloyl chloride was dissolved in NMP (solid content of 30%), taken in a 500-mL four-neck reaction flask, and cooled to ~0–5°C for 5 h. Then, the mixture was poured into acetone for precipitation. The precipitate then was poured into water to yield yellow crystals in an 85% yield. The reaction is depicted in Scheme 2.

The copoly(amide imide) was synthesized by initial preparation of diisocyanate-terminated polyimide prepolymer with excess of MDI′ as shown in Scheme 3. The dicarboxylic acid monomer then was poured into the reaction flask containing the diisocyanate polyimide prepolymer maintained at 60°C for 0.5 h; next, the catalyst, 0.03 g/L of triethylamine was added. The temperature was raised gradually to 80°C and maintained at that temperature for 1 h. A pale golden viscous solution finally was obtained. The reaction is represented in Scheme 4.

Hydrogenation of aromatic poly(amide imide) and its cyclization into aromatic poly(benzimidazole amide imide) copolymers

The obtained poly(amide imide) copolymers were dissolved in NMP, and the temperature was raised to 80°C. Then, hydrazine monohydrate and Raney nickel were added into the reaction flask, and the reaction continued for 8 h (Scheme 5).

The hydrogenated copolymers were dissolved in PPA. The temperature was raised to 180°C and held for 6 h for thermal cyclization. Next, the reaction mixtures were neutralized with NaOH and washed with water and the resulting polymers were dried in the vacuum oven. Table I shows ratios of monomers and classification of copolymers. The cyclization reaction is shown in Scheme 6.

Measurements

Inherent viscosity measurements were performed on a Connon-type viscometer (Rheotec Co., Radeburg, Germany) in a constant temperature water bath at 25°C in

Scheme 3

Scheme 4
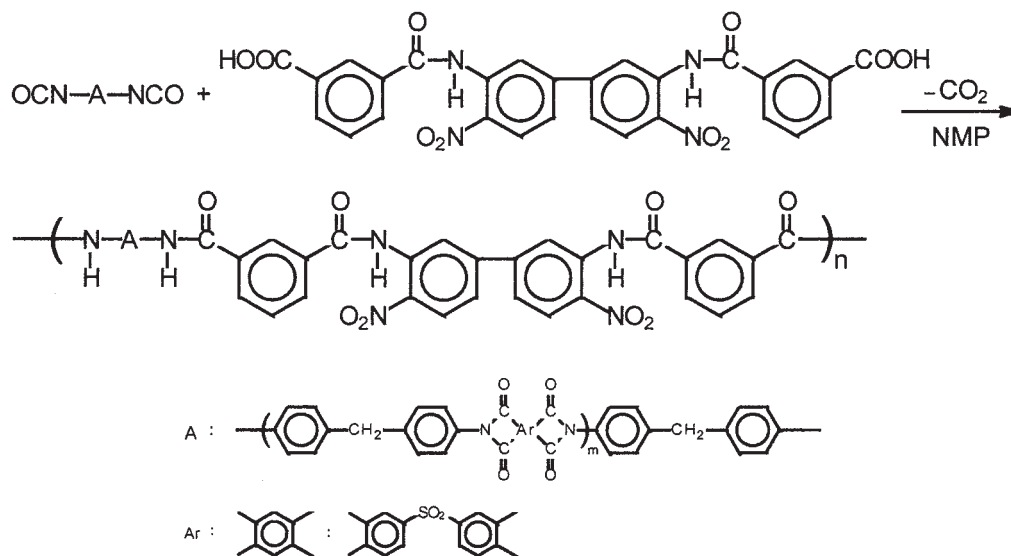
NMP. Inherent viscosity (η_{inh}) was calculated as η_{inh} = $(\ln(t/t_o))/C$, where t_o is the flow time of pure solvent, t is the flow time of polymer solution, and C is the polymer concentration (g/dL).

Infrared (IR) spectra of poly(benzimidazole amide imide) copolymers were obtained using a Shimazu 8300 Fourier transform (FT)–IR spectrometer (Hitachi, Tokyo, Japan) over a range of 400-4000 cm^{-1}. The samples were in the form of a film about 10 μm thick.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Du Pont 9900 differential scanning calorimeter (Du-Pont, Wilmington, DE) and a Seiko SSC-5000 type thermogravimetric analyzer (Seiko, Chiba, Japan). The DSC measurement was performed at a heating rate of

20°C/min in nitrogen atmosphere. The TGA measurement was performed at different heating rates of 20, 10, 5, and 1°C/min under both nitrogen atmosphere and air to obtain the weight loss at different heating rates.

RESULTS AND DISCUSSION

Synthesis of diacid monomer and poly(benzimidazole amide imide) copolymers

Diacid-terminated monomer was synthesized from 3,3'-dinitrobenzidine and isophthaloyl chloride. The molecular weight of the diacid monomer was 570 (melting point (mp) = 219°C).[15]
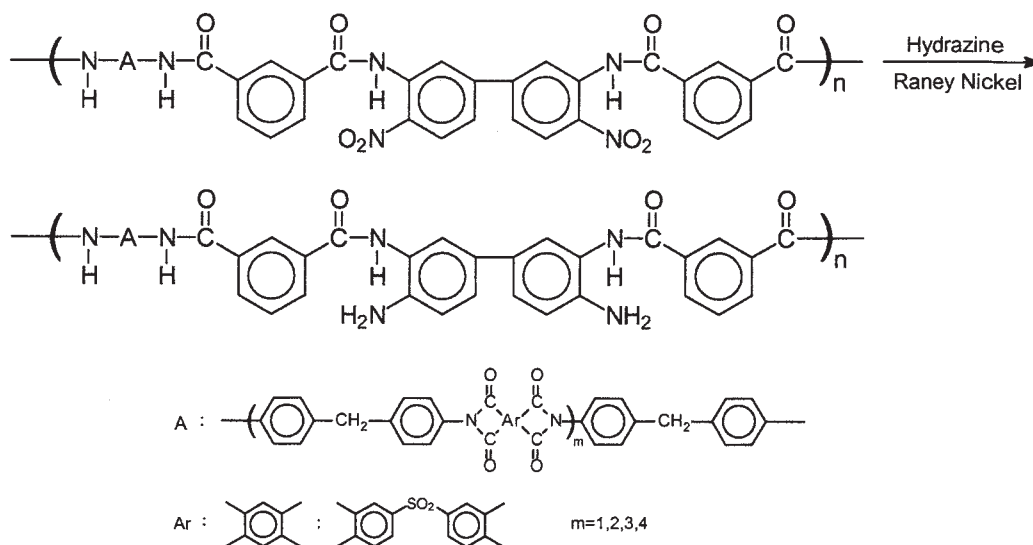

Scheme 5

TABLE I
Preparation of Copolymers

Code	Polymer	MDI	Dianhydride	Dicarboxylic acid
PIP	Polyimide (PMDA)	1	1	0
PBI-P1	Cyclized Poly(imide amide benzimidazole) (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
PBI-D1	Cyclized Poly(imide amide benzimidazole) (DSDA)	2	1	1
PBI-D2		3	2	1
PBI-D3		4	3	1
PBI-D4		5	4	1

The table demonstrates the molar ratio of various copolymers.

Poly(benzimidazole amide imide) copolymers were prepared as shown in Table I. The inherent viscosities of the resulting polymers are listed in Table II. Inherent viscosities of the polymers were in the range of 0.70–0.91 dL/g. The theoretical contents of benzimidazole, amide, and imide groups of the copolymers also were calculated with the weight content of these groups in each repeat unit and are indicated in Table II.

Polymers can be cast into transparent films. Figures 1 and 2 show the IR spectra of poly(benzimidazole amide imide) in pyromellitic dianhydride (PMDA) and DSDA series, respectively. The characteristic absorption at 1720, 1780, 1360, and 720 cm^{-1} indicates the existence of the imide group in the PMDA series. Moreover, the absorption peaks of 1660 and 3300–3400 cm^{-1} show the —NH stretching vibration of the amide group. And the absorption peaks of 1120–1160 cm^{-1} show the absorption of

SO$_2$ group in the spectra of DSDA series. Also, in Figures 1 and 2, the absence of the NO$_2$ group in 1521 and 1340 cm^{-1} and the presence of the NH$_2^+$ in 2800–2000 cm^{-1} in poly(benzimidazole amide imide) show the successful cyclization of the amide into benzimidazole group. Besides, the existence of C=N group of benzimidazole in 1656 cm^{-1} and Ar—NH—R in 1257 cm^{-1} also prove the presence of the benzimidazole group in the copolymer.

Thermal properties of polymers

The thermal property and the heat-weight loss of copolymers were evaluated by DSC and TGA, and the results are shown in Table III. Figure 3 shows the typical second heating curve of DSC measurements of copolymer in the PBI-P series (cyclized poly(imide amide benzimidazole) from PMAD series). From the experimental results, it is seen that all of the copoly-
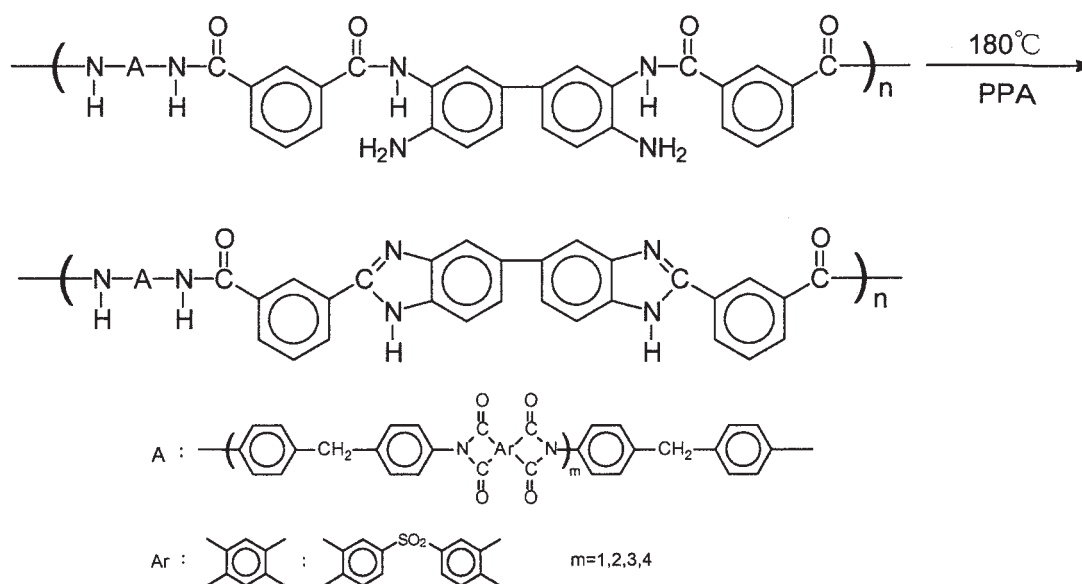
Scheme 6

TABLE II
Inherent Viscosities 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

mers were amorphous and without a melting point. The glass transition temperatures of copolymers were in the range ~270–322°C and decreased as the amide content increased. This showed that incorporation of amide linkage into the polyimide backbone could increase the flexibility of the copolymer chain and, hence, lowered the glass transition temperature in the copolymers. The glass transition temperatures of the PMDA series copolymer were higher than that of the DSDA series. The reason for this is because the struc-

Figure 1 IR Spectra of the poly(benzimidazole amide imide) copolymers of the PMDA series.

ture of PMDA is more rigid than that of DSDA, which contains the flexible sulfonyl group. The relationship between glass transition temperatures and imide content of copolymers is shown in Figure 4. The formation of the benzimidazole group (where the amide group cyclizes into the benzimidazole group) decreases hydrogen bonding while promoting rigidity. Thus, the glass transition temperatures are increased. Also, from Figure 4, the glass transition temperature of most copolymers increased smoothly upward with the increase of the imide group. As the imide content increases beyond 65%, the curve turns up sharply; this is caused by the formation of the benzimidazole groups with higher rigidity. At these imide contents, the glass transition temperatures are comparable with homopolyimides.

Figure 5 shows the typical heat-weight loss of the copolymers of PBI-P in air atmosphere. Table III summarizes the thermogravimetric data for all of these copolymers. As indicated in the table, all of the polymers possess good thermal and thermo-oxidative stability. The 10% weight loss temperatures (T_{10}) are in the range of ~460–541°C in nitrogen and ~441–529°C in air, respectively. With the increase of imide content, the T_{10} temperature was increased. Figure 6 shows the typical relationship between T_{10} temperatures and imide content in air. The amide linkage contributes less thermo-oxidative stability than the imide and benzimidazole linkages. Also, from Figure 6, it is seen that the T_{10} temperature of both the PMDA and the DSDA series is linear at lower imide contents, with the exception of PBI-P4 (one of PBI-P series with imide content of 70.5%) and PBI-D4 (one of PBI-D series with imide content of 76.6%), both in air and in nitrogen. The T_{10} temperatures of PBI-P4 and PBI-D4 were much higher than other ratios. This shows the formation of the benzimidazole group at the expense of the amide group (cyclization of amide into benzimidazole). This increases thermal stability and the thermal degradation properties of copolymers. These would behave like homopolyimide at high imide contents.
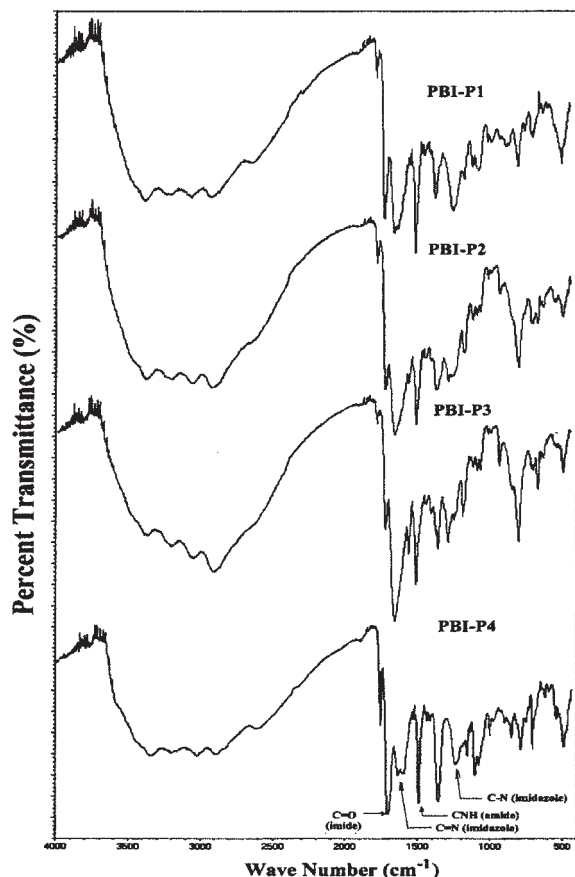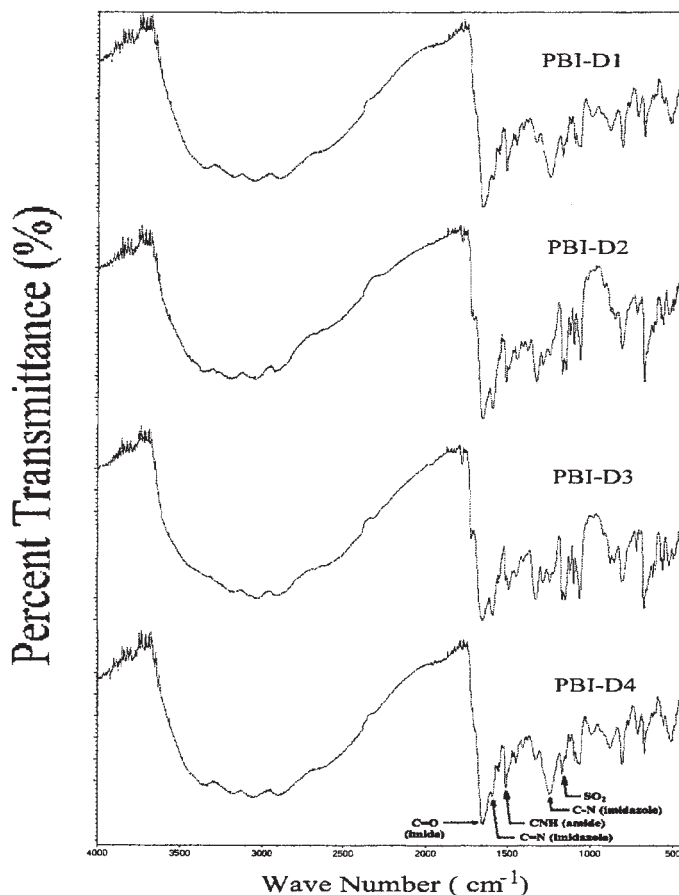
Figure 2 IR Spectra of the poly(benzimidazole amide imide) copolymers of the DSDA series.

Thermo-oxidative degradation properties of polymers

In general, we can define the weight loss ratio α as

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty}$$

where α is the weight loss ratio, W_0 is initial weight, W is weight at temperature T, and W_∞ is final weight (at complete decomposition $W_\infty = 0$).

TABLE III
Glass Transition Temperature and TGA of Polymers

Code	T_g (°C)	T_{d10} (°C) (air)	T_{d10} (°C) (N$_2$)
PIP	351	575	583
PBI-P1	277	475	510
PBI-P2	283	496	518
PBI-P3	289	509	522
PBI-P4	322	529	541
PID	319	552	560
PBI-D1	270	441	460
PBI-D2	279	452	474
PBI-D3	281	474	482
PBI-D4	314	525	539

Heating rate at 20°C/min.

The heating rate ϕ can be defined as follows:

$$\phi = \frac{dT}{dt}$$

where T is temperature and t is time.

Doyle deduced the relation between the heating rate ϕ and the weight loss α from the rate law and the
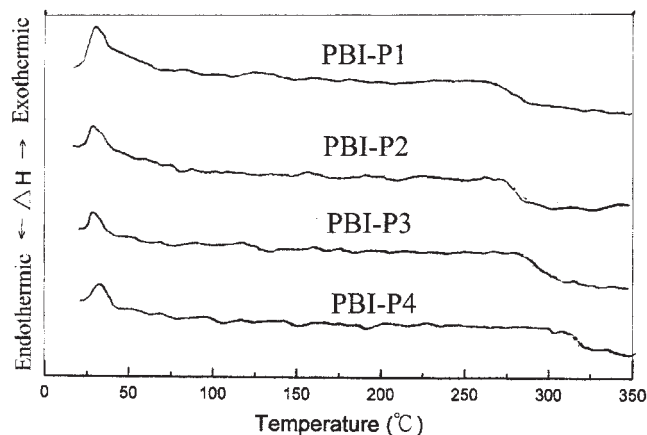

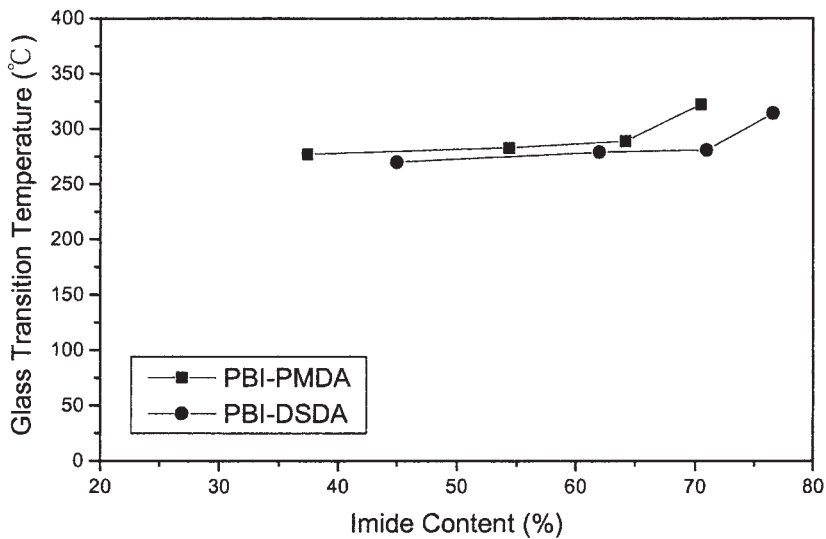**Figure 3** The DSC curves of the PBI-PMDA series.

Figure 4   The relationship between glass transition temperatures and the imide content of copolymers.
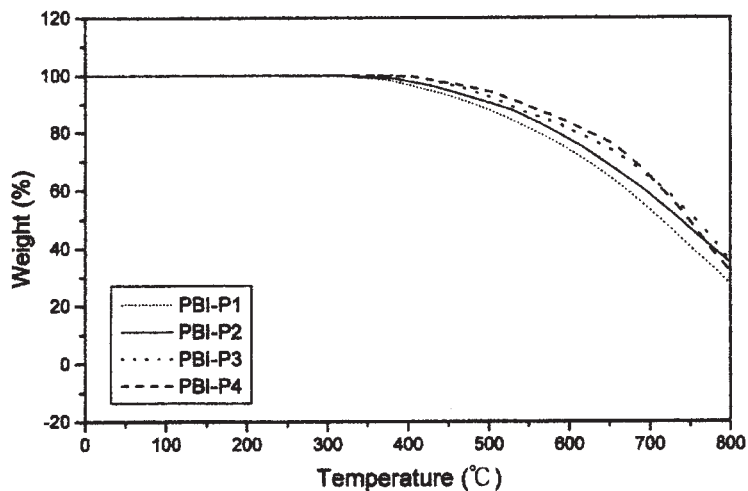

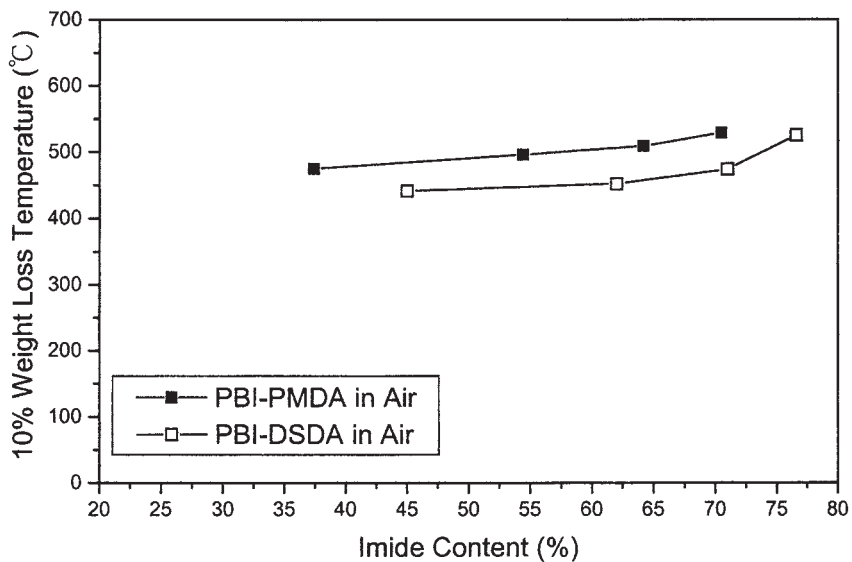**Figure 5**   The heat-weight loss of the PBI-PMDA series in air.

Figure 6   The relationship between 10% weight loss temperatures and imide content of copolymers in air.
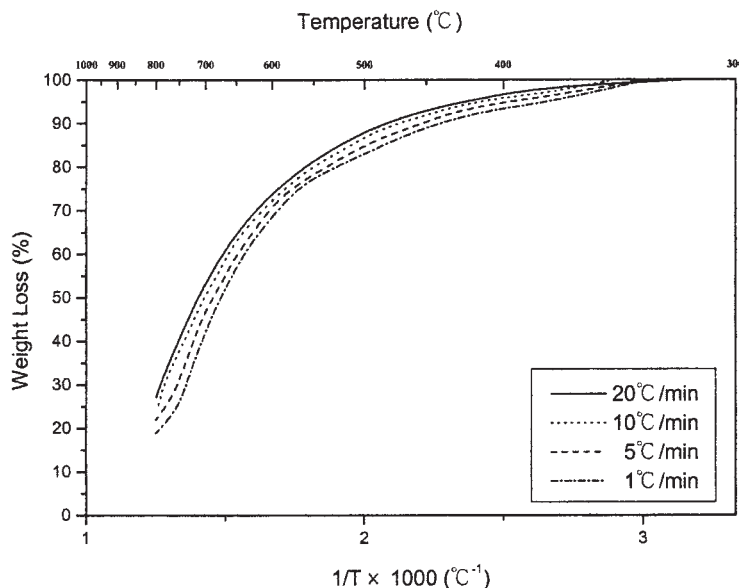
Figure 7 The relationship between the inverse of decomposition temperature and weight loss of the PBI-P1 copolymer (in air).

Arrhenius equation. The following equation[16] of heating rate ϕ was arrived at:

$$\log\phi = \log\frac{AE}{RF(\alpha)} - 2.315 - 0.4567\frac{E}{RT}$$

Ozawa further deduced that if the weight loss α is constant, $F(\alpha)$ would be constant with any order of degradation. The Doyle equation can be rewritten as[16,17]

$$\log\phi_1 + 0.4567\frac{E}{RT_1} = \log\phi_2 + 0.4567\frac{E}{RT_2} = \cdots$$

Thus, the activated energy could be calculated from the relations between the heating rate and the degradation temperature.

Figure 7 shows the typical relationship between the inverse of decomposition temperature and heatweight loss curves in the air with various heating rates of PBI-P1. From these curves, it was seen that the curve would shift to higher temperatures as the heating rate was increased. Polymer molecules do not have enough time to absorb and exhaust the heat as the heating rate increases, which makes the degradation rate slower.

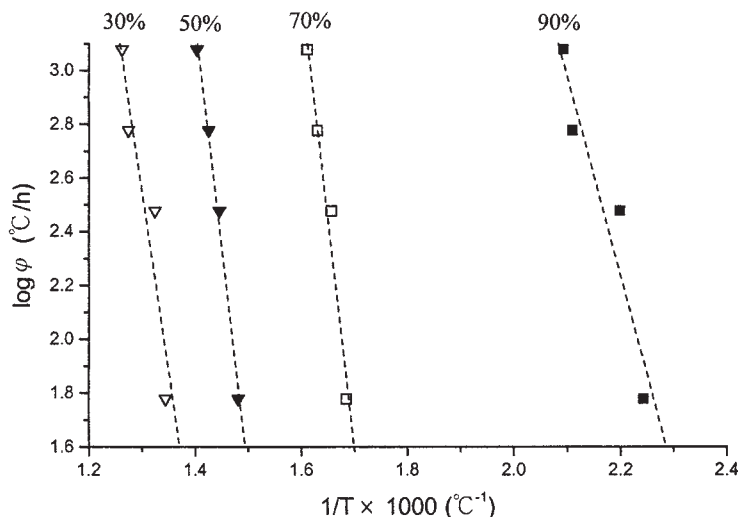Figure 8 shows the typical relationship between the

Figure 8 The relationship between the inverse of the decomposition temperature and the logarithm of the heating rate of the PBI-P1 copolymer with various residual weight.

Code	Residual weight (%)			
	90%	70%	50%	30%
PBI-P1				
Slope	−7.38394	−17.0034	−16.75578	−13.32408
E (kcal/mol)	32.1291	73.9855	72.908	57.9759
PBI-P4				
Slope	−6.4475	−20.40827	−20.81214	−18.6044
E (kcal/mol)	28.0545	88.8008	90.5581	80.9517
PBI-D1				
Slope	−8.23562	−7.74941	−9.33257	−8.67308
E (kcal/mol)	35.835	33.7194	40.608	37.7384
PBI-D4				
Slope	−6.22808	−12.55652	−12.53105	−12.50189
E (kcal/mol)	27.0997	54.6361	54.5253	54.3984

inverse of the decomposition temperature and the logarithm of the heating rate in the air with a different residual weight of PBI-P1. From these figures, it is seen that the slopes of various residual weights are similar with the exception of the 90% residual weight. The polymer molecules react with oxygen in the initial stages of degradation, which decelerated the rate of weight loss. It also can be seen that the PMDA series is more thermally resistant than the DSDA series.

Table IV shows the activated energies of the thermo-oxidative degradation of PBI-P1, PBI-P4, PBI-D1, and PBI-D4. It is seen that all of these copolymers have lower activated energy in the initial stages of decomposition. The reason is not only the combination of oxygen with copolymer, but also the evaporation or early decomposition of small-size molecules in the initial stage of decomposition. Moreover, it is found that the copolymers with high imide content possessed low activation, especially the 90% residual weight. This indicates that the imide group has a better heat resistant property than that of the amide group, which makes copolymers with low imide content decompose early, i.e., the high molecular weight polymer would decompose later. Moreover, the DSDA series has a lower activated energy than that of PMDA series because of the presence of the sulfonyl group.

Doyle developed an integration parameter of degradation temperature to evaluate the thermal stability of polymers. It is the integration of the thermal gravity curve, which defines T_A as[18].

$$T_A = 800A$$

where T_A is the integration parameter of degradation temperature and A is the proportional area under curve

Table V shows the integration parameter of the degradation temperature of copolymers with a heating rate of 20°C/min in both nitrogen atmosphere and air, respectively. Figures 9 and 10 show the relationship between the integration parameter of degradation temperature and imide content. From the figures, it can be inferred that the integration parameter of degradation temperature increases with the increase of the imide groups.

CONCLUSION

In this experiment, we used a one-step method to form the polyimide prepolymer and employed a low-temperature method to cyclize the amide into the benzimidazole structure. The products of poly(benzimidazole amide imide) copolymers had a reasonable high

TABLE V
Integration Parameter of Degradation Temperature of Copolymers

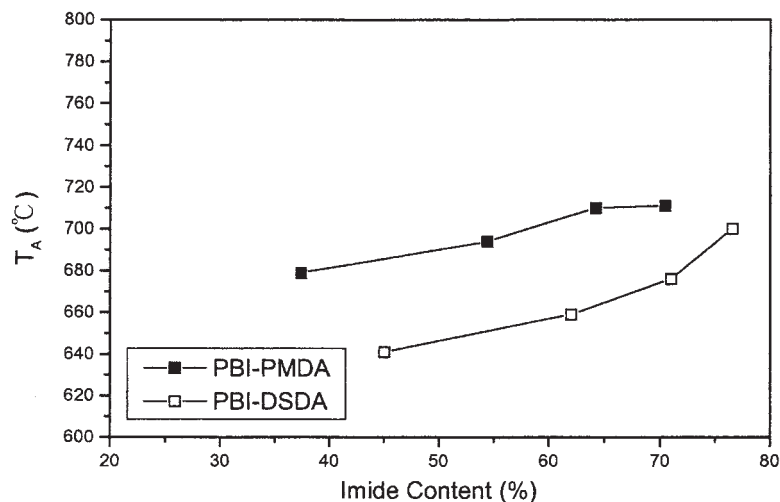| Code	T_A (air) (°C)	T_A (N$_2$) (°C)	Imide content (%)	Amide content (%)	Imidazole content (%)
PBI-P1	679	712	37.4	32.3	30.5
PBI-P2	694	724	54.4	23.5	22.1
PBI-P3	710	729	64.2	18.5	17.3
PBI-P4	711	739	70.5	15.2	14.3
PBI-D1	641	699	45.0	28.4	26.6
PBI-D2	659	711	62.0	19.6	18.4
PBI-D3	676	719	71.0	14.9	14.0
PBI-D4	700	734	76.6	12.1	11.3

Figure 9 The relationship between the integration parameter of degradation temperature and imide content (in air).
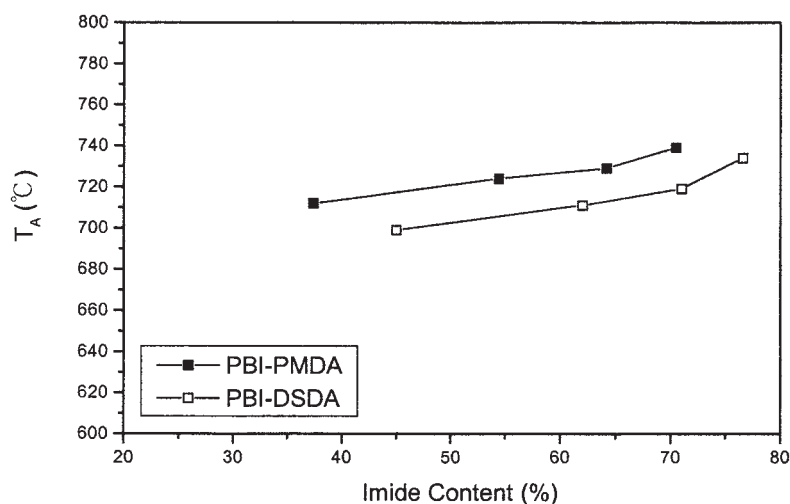

Figure 10 The relationship between integration parameter of degradation temperature and imide content (in nitrogen).

molecular weight. For the thermal and the degradation properties, the formation of the benzimidazole group would be at the expense of the amide group (the amide group cyclized to benzimidazole group). This increased the rigidity and thermal resistance of copolymers. In addition, it was found that as the imide content increased beyond 65%, the thermal properties of the copolymers were comparative with those of homopolyimide. The activation energy and integration parameter of the degradation temperature of copolymers were evaluated by the Doyle-Ozawa method. All of the copolymers exhibited good thermal and high thermo-oxidative stability, which increased with increased imide content.

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