

Synthesis of Thermally Stable Aromatic Poly(imide amide benzimidazole) Copolymers

Huei-Hsiung Wang, Shu-Ping Wu

Graduate School of Textile Engineering, Feng-Chia University, Taichung 40724, Taiwan, Republic of China

Received 26 July 2002; accepted 6 January 2003

ABSTRACT: 3,3'-Dinitrobenzidine was first reacted with excess *m*-chlorophenyl acid to form a monomer with dicarboxylic acid end groups. Two types of aromatic dianhydrides (Pyromellitic dianhydride (PMDA) and 3,3',4,4'-sulfonyl diphthalic anhydride) were also reacted with excess 4,4'-diphenylmethane diisocyanate to form polyimide prepolymers terminated with isocyanate groups. The prepolymers were further extended with the diacid monomer to form nitro groups containing aromatic poly(imide amide). The nitro groups in these copolymers were hydrogenated to form amine groups and then were cyclized at 180°C to form poly(imide amide benzimidazole) in poly(phosphoric acid), which acted as a cyclization agent. The resultant copolymers

were soluble in sulfuric acid and poly(phosphoric acid), in sulfolane under heating to 100°C, and in the polar solvent *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 temperatures of the copolymers were 270–322°C. The 10% weight-loss temperatures were 460–541°C in nitrogen and 441–529°C in air. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1435–1444, 2003

Key words: 3,3'-dinitrobenzidine; poly(imide amide benzimidazole); thermally stable

INTRODUCTION

Aromatic polyimides are known to be among the best materials for use in high-temperature applications.^{1–3} They can sustain 500°C for a few minutes or 300°C for several months. Polyimides can be used in aircraft, osmotic membranes, and microelectronics. However, the rigid structure and low concentration of hydrogen bonding in the polyimide chains, although they can impart properties such as thermooxidative stability,^{4–6} can also make the materials hard to process because of their poor solubility.^{7–10}

Polybenzimidazole also has good thermal resistance in high-temperature environments. It has a higher limited oxygen index and can be used in aircraft and aerospace applications. It also has chemical proofing due to its chemically aromatic and heterocyclic structure^{11–13} and can be used in medical applications. However, the poor solubility and processability also lead to its applications being limited.

In this study, we introduced amide groups into polyimides to improve the solubility of the polymers, but to maintain the thermal stability, we also introduced benzimidazole groups into polyimides. In this way, a good balance of thermal resistance and solubility was obtained.

EXPERIMENTAL

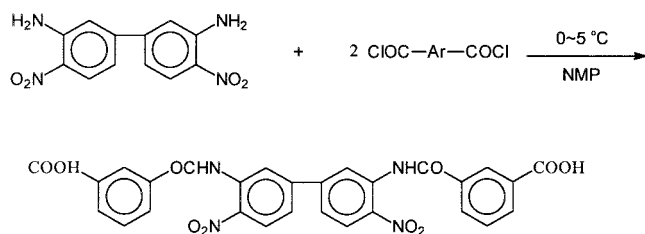
Materials

A commercially available dianhydride, 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA), was dried *in vacuo* at –40°C for 4 h for the removal of possible moisture. 4,4'-Diphenylmethane diisocyanate (MDI) was used without further purification. Both the 3,3'-dinitrobenzidine and *m*-dichlorophenyl acid monomers were of high purity and were used as received from the manufacturer. Raney nickel, poly(phosphoric acid), 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. Triethylamine, employed as a catalyst, was used without further purification.

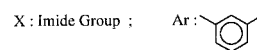
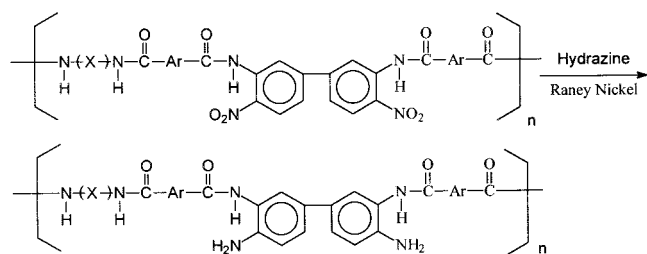
Synthesis of the diacid monomer

A mixture of 0.05 mol of 3,3'-dinitrobenzidine and 0.12 mol of *m*-dichlorophenyl acid was dissolved in NMP with a solid content of 30%, poured into a 500-mL, four-necked reaction flask, and cooled to 0–5°C for 5 h. The mixture was then poured into acetone for precipitation and purification. The precipitate was poured into water to yield yellow crystals (yield = 85%). The reaction is shown in Scheme 1.

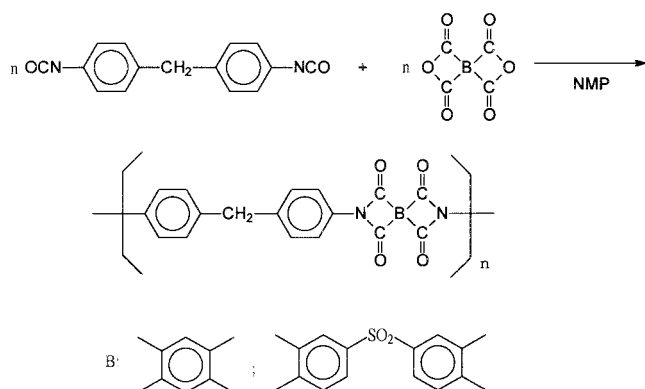
Correspondence to: H.-H. Wang.



Scheme 1

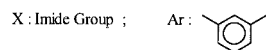
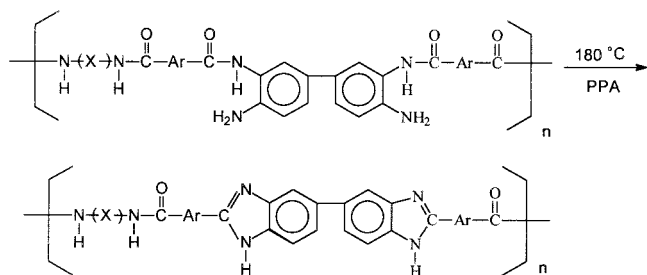


Scheme 5

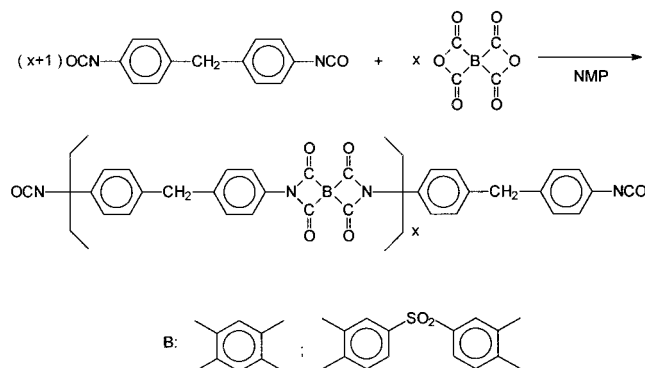


Polymer: PI-P:PMDA-MDI=1-1 PI-D:DSDA-MDI=1-1

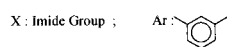
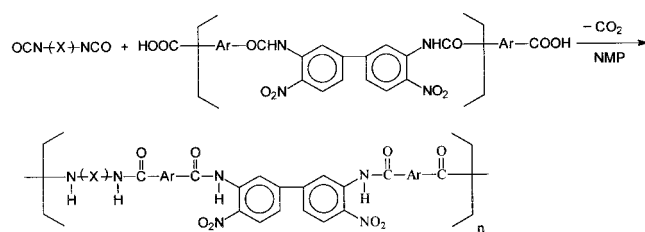
Scheme 2



Scheme 6



Scheme 3



Scheme 4

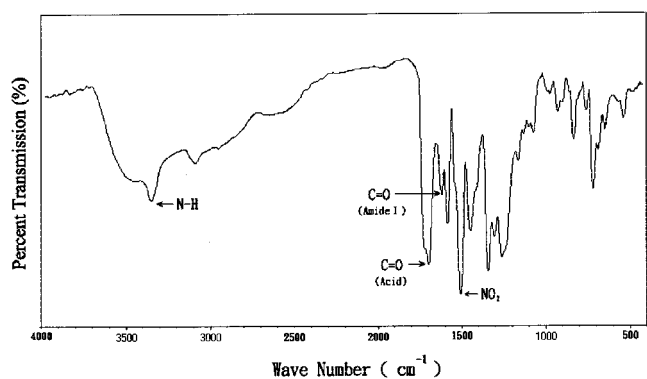


Figure 1 IR spectrum of the diacid monomer.

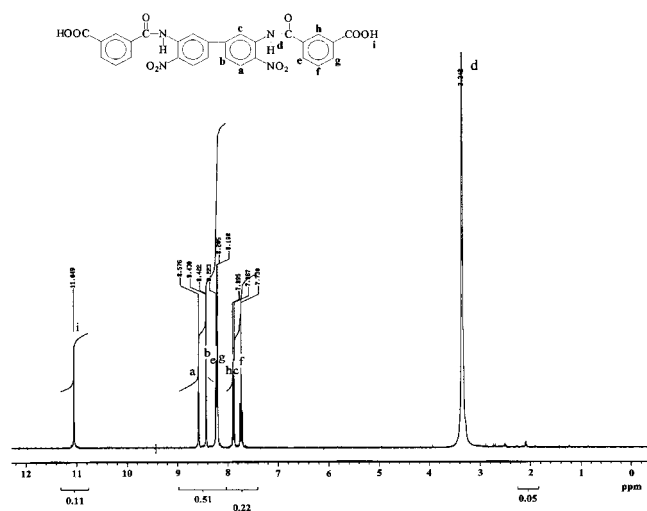
Figure 2 ¹H-NMR spectrum of the diacid monomer.

TABLE I
Polymer Symbols

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

The table demonstrates the molar ratios of various copolymers.

TABLE II
Elemental Analysis of the Diacid Monomer

	C%	H%	N%	Moisture regain (%)
Calcd	58.93	3.18	9.82	
Found	57.87	3.23	9.65	1.8
Corrected	58.91	3.17	9.82	

TABLE III
Inherent Viscosities of the Polymers

Code	Inherent viscosity	Imide content (%)	Amide content (%)	Imidazole content (%)
PIP	0.71	100	0	0
PAI-P1	0.67	34.2	65.8	0
PAI-P2	0.63	50.9	49.1	0
PAI-P3	0.70	60.9	39.1	0
PAI-P4	0.69	67.5	32.5	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
PAI-D1	0.59	41.5	58.5	0
PAI-D2	0.65	58.7	41.3	0
PAI-D3	0.68	68.1	31.9	0
PAI-D4	0.68	74.0	26.0	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 IV
Elemental Analysis of the Polymers (PMDA Series)

Code	Element content	C%	H%	N%	Moisture regain (%)
PAI-P1	Calcd	69.06	3.62	10.07	
	Found	67.09	3.98	9.32	
	Corrected	69.77	3.82	9.69	4.0
PAI-P2	Calcd	69.97	3.51	9.38	
	Found	67.88	3.85	9.01	
	Corrected	70.53	3.70	9.36	3.9
PAI-P3	Calcd	70.51	3.44	8.97	
	Found	68.02	3.82	8.51	
	Corrected	70.33	3.69	8.80	3.4
PAI-P4	Calcd	70.86	3.40	8.70	
	Found	68.41	3.80	8.60	
	Corrected	70.80	3.67	8.90	3.5
PBI-P1	Calcd	75.58	3.96	11.02	
	Found	74.01	4.24	10.34	
	Corrected	76.16	4.12	10.64	2.9
PBI-P2	Calcd	74.77	3.75	10.03	
	Found	72.99	4.11	8.84	
	Corrected	75.33	3.98	9.12	3.2
PBI-P3	Calcd	74.31	3.63	9.09	
	Found	72.95	3.97	8.77	
	Corrected	75.28	3.84	9.06	3.2
PBI-P4	Calcd	74.02	3.55	9.09	
	Found	72.24	3.91	8.77	
	Corrected	74.62	3.78	9.06	3.3

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 at ambient temperature. For C and N, Corrected value = Found value \times (100% + Moisture content %).

TABLE V
Elemental Analysis of the Polymers (DSDA Series)

Code	Element content	C%	H%	N%	Moisture content %
PAI-D1	Calcd	67.08	3.54	8.94	4.2
	Found	65.32	3.68	7.81	
	Corrected	68.06	3.53	8.14	
PAI-D2	Calcd	67.03	3.41	7.90	4.1
	Found	65.20	3.54	7.24	
	Corrected	67.87	3.39	7.54	
PAI-D3	Calcd	67.01	3.34	7.33	3.7
	Found	65.31	3.55	7.15	
	Corrected	67.73	3.42	7.41	
PAI-D4	Calcd	67.00	3.29	6.97	3.4
	Found	64.97	3.51	6.68	
	Corrected	67.18	3.39	6.91	
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 at ambient temperature. For C and N, Corrected value = Found value \times (100% + Moisture content %).

Synthesis of the aromatic polyimide

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

Synthesis of the aromatic poly(imide amide)

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

Hydrogenation of the aromatic poly(imide amide) copolymers

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

Cyclization of the aromatic poly(imide amide benzimidazole) copolymers

The obtained hydrogenated copolymers were dissolved in poly(phosphoric acid). The temperature was raised to 180°C for 6 h. The products were then neutralized with NaOH, washed, and dried. Table I shows the ratios of each component and the codes of the copolymers. The reaction is shown in Scheme 6.

Measurements

Infrared (IR) spectra of polyimides and poly(imide amide benzimidazole) copolymers were obtained with a Shimadzu 8300 FTIR spectrometer (Hitachi, Tokyo,

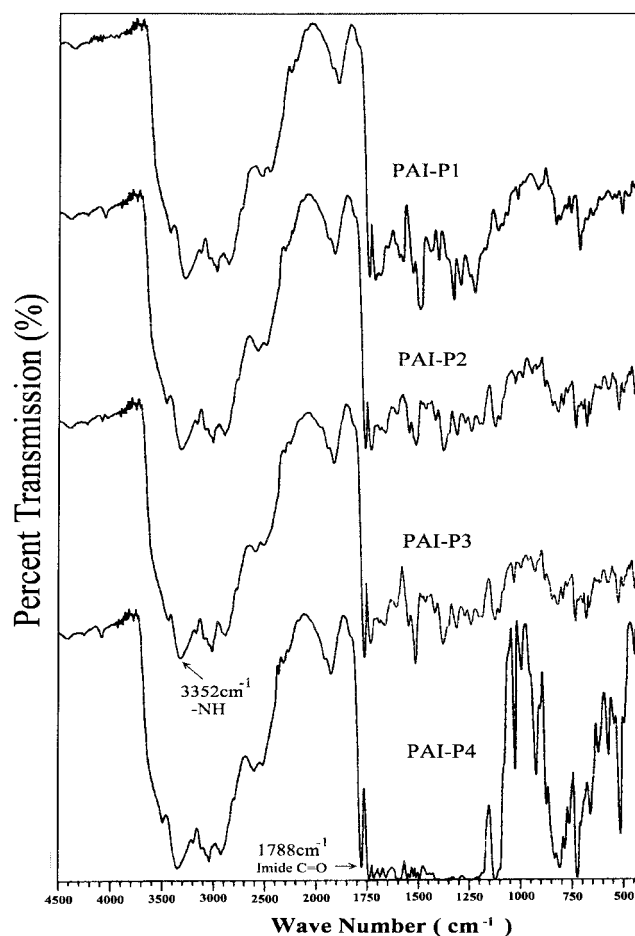


Figure 3 IR spectra of the poly(imide amide) copolymers of the PMDA series.

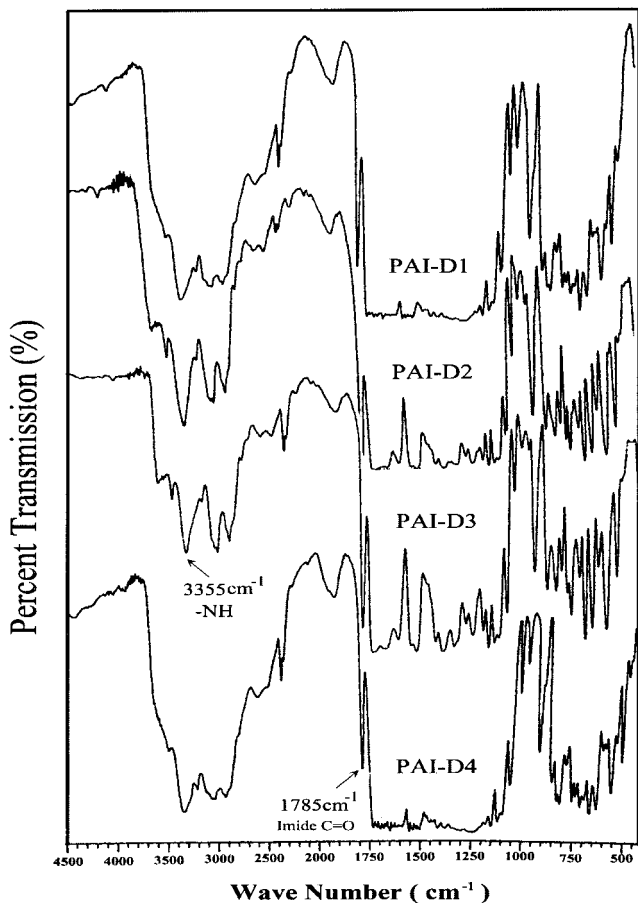


Figure 4 IR spectra of the poly(imide amide) copolymers of the DSDA series.

Japan) over a range of 400–4000 cm^{-1} . The samples were in the form of a film about 10 μm thick.

Elemental analysis (for carbon, hydrogen, and nitrogen) was performed with a PerkinElmer 2400 analyzer (Shelton, CT).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a DuPont 9900 differential scanning calorimeter (Du 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 (T_g) and weight loss, respectively.

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

RESULTS AND DISCUSSION

Synthesis of the diacid monomer

The diacid-terminated monomer was synthesized from 3,3'-dinitrobenzidine and isophthaloyl chloride. The molecular weight of the diacid monomer was 570 ($\text{mp} = 219^\circ\text{C}$). The elemental analysis shows that the found values are in good agreement with the calcu-

Figure 6 IR spectra of the poly(imide amide benzimidazole) copolymers of the DSDA series.

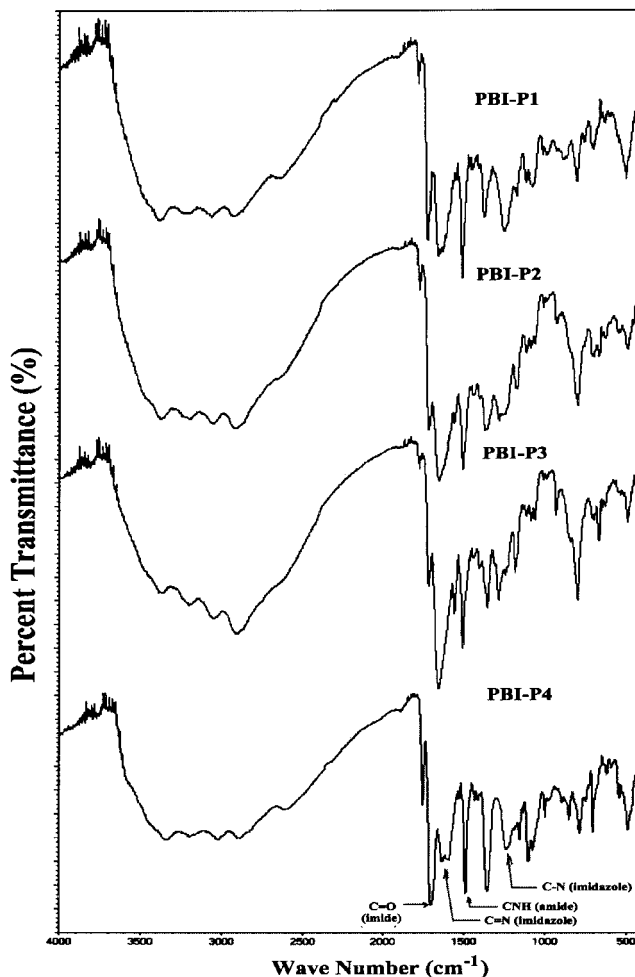


Figure 5 IR spectra of the poly(imide amide benzimidazole) copolymers of the PMDA series.

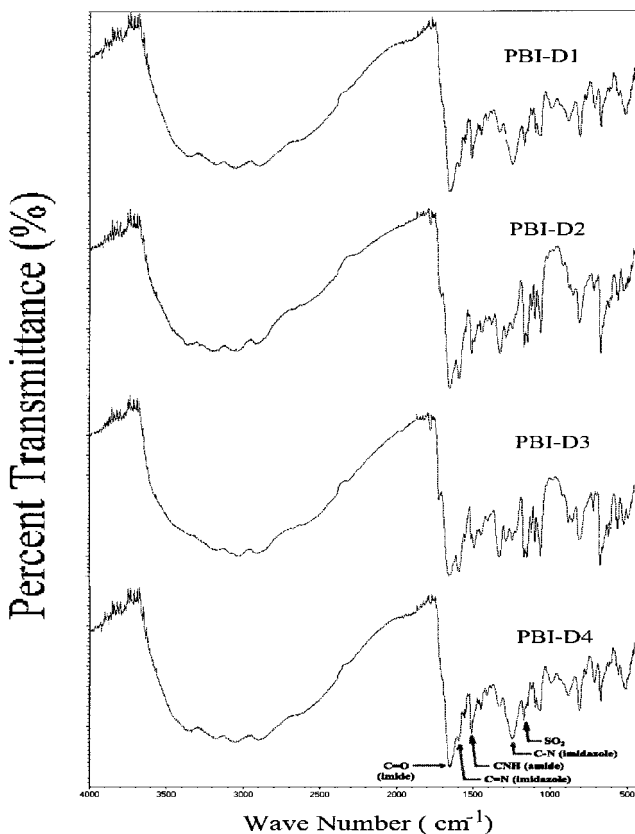


TABLE VI
Solubility of the Polymers

Code	NMP	DMF	DMSO	DMAC	<i>m</i> -Cresol	Pyridine	Sulfuric acid	Sulfolane
PIP	++	-	-	-	+	-	++	+
PAI-P1	++	+	+	+	+	+	++	++
PAI-P2	++	+	+	+	+	+	++	+
PAI-P3	++	+	+ -	+ -	+ -	+ -	++	+
PAI-P4	++	+ -	+ -	+ -	+ -	+ -	++	+
PBI-P1	+ -	+ -	+ -	+ -	+ -	+ -	++	+
PBI-P2	+ -	+ -	+ -	+ -	+ -	-	++	+
PBI-P3	+ -	+ -	+ -	-	-	-	++	+
PBI-P4	+ -	-	+ -	-	-	-	++	+
PID	++	-	+	-	-	-	++	++
PAI-D1	++	++	++	+	+	+	++	++
PAI-D2	++	+	++	+	+	+	++	++
PAI-D3	++	+	+	+	+	+	++	++
PAI-D4	++	+	+	+	+	+ -	++	++
PBI-D1	+ -	+ -	+ -	+ -	+ -	+ -	++	+
PBI-D2	+ -	+ -	+ -	+ -	-	-	++	+
PBI-D3	+ -	+ -	+ -	+ -	-	-	++	+
PBI-D4	+ -	-	+ -	-	-	-	++	+

++ = soluble at room temperature; + = soluble under heating to 100°C; + - = soluble with 5% LiCl added and under heating to 100°C; - = dissoluble.

lated values. The results of the elemental analysis are shown in Table II.

The IR spectrum of the diacid monomer, shown in Figure 1, exhibits —NH stretching vibrations at 3386–3316 cm^{-1} , C=O(amide) stretching at 1628 cm^{-1} , and nitro group absorption at 1521 (asymmetric stretching) and 1340 cm^{-1} (symmetric stretching). Figure 2 show the $^1\text{H-NMR}$ (DMSO- d_6) spectrum of the diacid monomer; all the expected absorptions can be observed. These confirm the formation of the diacid-terminated monomer.

Synthesis of the poly(imide amide benzimidazole) copolymers

The inherent viscosities of the polymers are listed in Table III and range from 0.70 to 0.91 dL/g. In the table,

the theoretical contents of the benzimidazole, amide, and imide groups of the copolymers are also listed. The results of the elemental analyses for all the polymers are listed in Tables IV and V. The empirical values agree well with the calculated ones. The moisture regain of the polymers is listed in Tables IV and V for correction.

These polymers were cast into transparent films. Figures 3 and 4 and Figures 5 and 6 show the IR spectra of poly(imide amide) and poly(imide amide benzimidazole), respectively. The characteristic absorptions at 1720, 1780, 1360, and 720 cm^{-1} indicate the existence of the imide group in the PMDA series. Moreover, the absorption peaks at 1660 and 3300–3400 cm^{-1} demonstrate the —NH stretching vibration of the amide group. The absorption peaks of 1120–1160

TABLE VII
Thermal Properties of the Polymers (10% Weight Loss)

Code	T_g (°C)	T_{d10} (°C) (Air)	T_{d10} (°C) (N)	Imide content (%)	Amide content (%)	Imidazole content (%)
PIP	351	575	583	100	0	0
PAI-P1	258	467	501	34.2	65.8	0
PAI-P2	265	486	507	50.9	49.1	0
PAI-P3	281	490	506	60.9	39.1	0
PAI-P4	298	498	520	67.5	32.5	0
PBI-P1	277	475	510	37.4	32.3	30.3
PBI-P2	283	496	518	54.4	23.5	22.1
PBI-P3	289	509	522	64.2	18.5	17.3
PBI-P4	322	529	541	70.5	15.2	14.3
PID	319	552	560	100	0	0
PAI-D1	247	438	443	41.5	58.5	0
PAI-D2	252	447	454	58.7	41.3	0
PAI-D3	270	464	474	68.1	31.9	0
PAI-D4	287	471	473	74.0	26.0	0
PBI-D1	270	441	460	45.0	28.4	26.6
PBI-D2	279	452	474	62.0	19.6	18.4
PBI-D3	281	474	482	71.0	14.9	14.0
PBI-D4	314	525	539	76.6	12.1	11.3

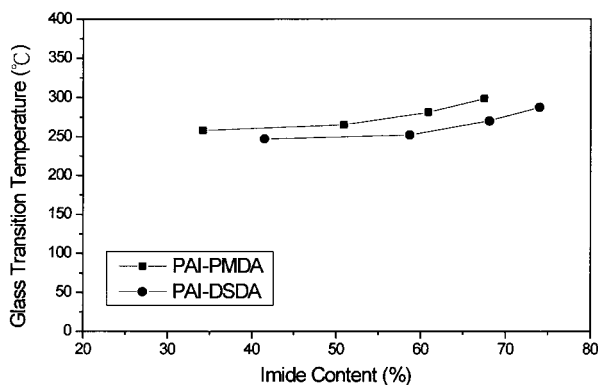


Figure 7 Relationship between T_g and the imide content of the PAI series.

cm^{-1} show the absorption of the SO_2 group in the spectra of the DSDA series. From Figures 3 and 4, the absence of the NO_2 groups at 1521 and 1340 cm^{-1} and the presence of the NH_2^+ groups at 2800 – 2000 cm^{-1} in poly(imide amide benzimidazole) demonstrate the successful cyclization of the amide into benzimidazole groups. Besides, the existence of the $\text{C}=\text{N}$ group of benzimidazole at 1656 cm^{-1} and $\text{Ar}-\text{NH}-\text{R}$ at 1257 cm^{-1} also prove the presence of benzimidazole groups in the copolymers.

Solubility properties of the polymers

Table VI summarizes the solubilities of all the polymers. The poly(imide amide benzimidazole) copolymers could be dissolved in sulfuric acid at room temperature, in sulfolane at 100°C , and in DMAc and NMP with 5% LiCl at 100°C , and they could slightly be dissolved in *m*-cresol and pyridine. Because of the existence of sulfonyl groups in the DSDA series, they exhibited a slightly better solubility than the PMDA series. In general, the copolymers had better solubility than the homopolyimide and homopolybenzimidazole in the solvents, with the exception of NMP. Moreover, the presence of benzimidazole groups, that is, a

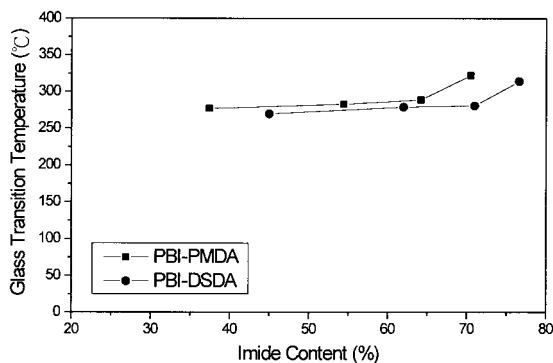


Figure 8 Relationship between T_g and the imide content of the PBI series.

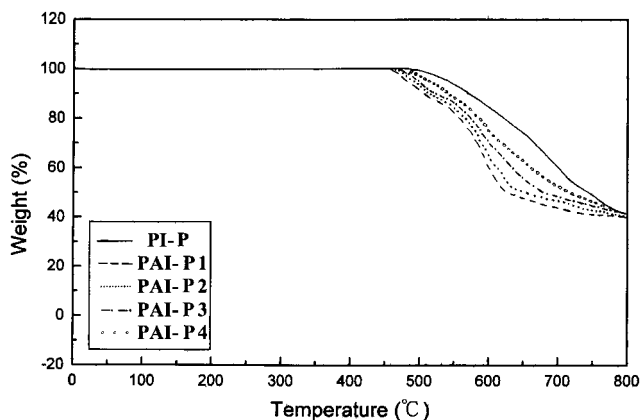


Figure 9 Heat weight loss of the PAI-PMDA series in nitrogen.

lower content of amide groups, led to less hydrogen bonding and, therefore, reduced the solubility of the copolymers.

Thermal properties of the polymers

The thermal properties of all the polymers were evaluated with DSC and TGA and are shown in Table VII. All of the copolymers were amorphous and had no melting point, not forming liquid crystals. T_g 's of the copolymers were in the range of 270 – 322°C and decreased with an increase in the amide contents. This demonstrated that the incorporation of an amide linkage into the polyimide backbone could increase the flexibility of the copolymer chain and, therefore, reduce T_g of the copolymers. T_g in the PMDA series was higher than that in the DSDA series because the structure of PMDA was much rigid than that of DSDA, which contained the sulfonyl group. The relationship between T_g and the imide content of the copolymers is shown in Figures 7 and 8. Most of the copolymers showed smooth upward curves with increasing imide

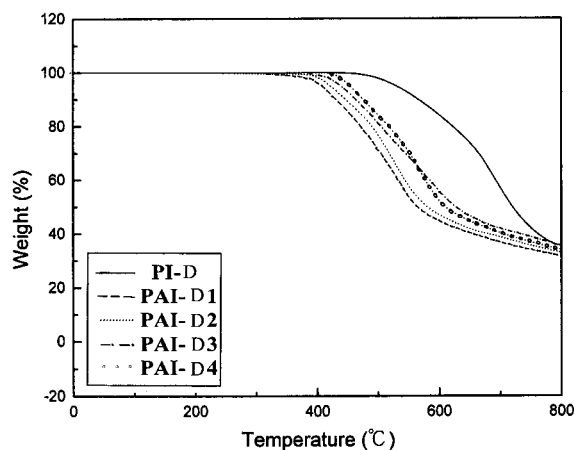


Figure 10 Heat weight loss of the PAI-DSDA series in nitrogen.

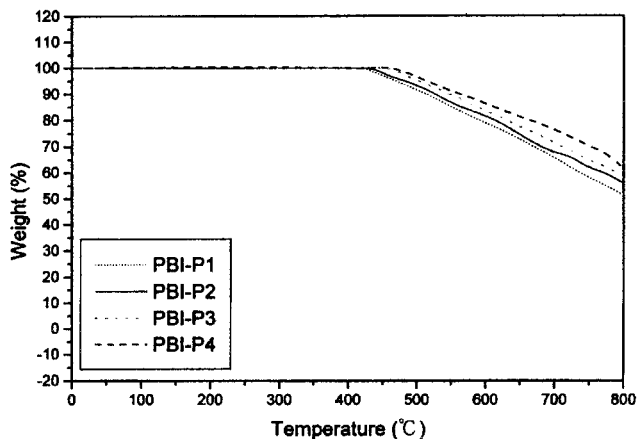


Figure 11 Heat weight loss of the PBI-PMDA series in nitrogen.

contents. Nevertheless, in the PBI series, the curve was very sharply upward. This indicated that the conversion of amide into benzimidazole promoted the rigidity and T_g ; therefore, T_g might even be close to that of the homopolyimide, as most of the amide was converted into benzimidazole.

Figures 9–12 show the heat weight loss of the copolymers in air and in nitrogen, and Table VII summarizes the thermogravimetric data for all the copolymers. All the polymers possessed good thermal and thermooxidative stability. The 10% weight-loss temperatures (T_{d10} 's) were 460–541°C in nitrogen and 441–529°C in air. With an increase in the imide content, T_{d10} increased. Figures 13 and 14 shows the relationship between T_{d10} and the imide content in nitrogen. The amide linkage contributed less thermooxidative stability than that of imide and benzimidazole. Also, T_{d10} 's of both the PMDA and DSDA series were nearly linear with increasing imide contents, with the exception of PBI-P4 and PBI-D4, in either air or nitrogen. This was because the conversion of amide groups into benzimidazole made the copolymers more rigid

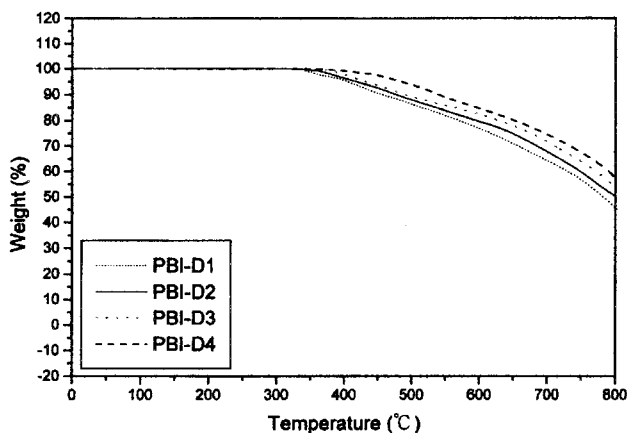


Figure 12 Heat weight loss of the PBI-DSDA series in nitrogen.

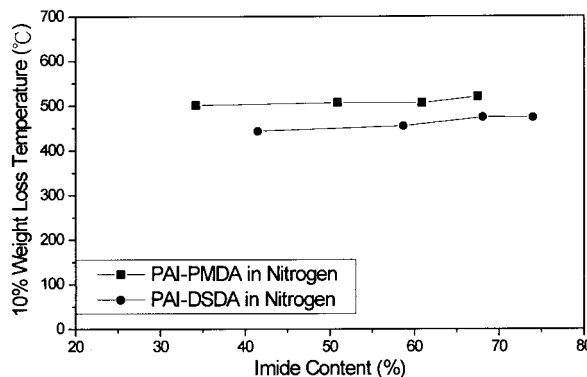


Figure 13 Relationship between the 10% weight-loss temperatures and the imide content of the PAI series (in nitrogen).

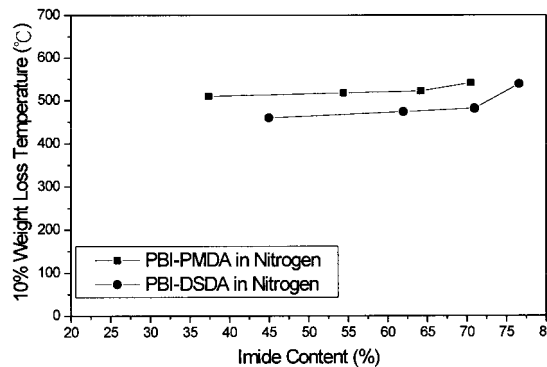


Figure 14 Relationship between the 10% weight-loss temperatures and the imide content of the PBI series (in nitrogen).

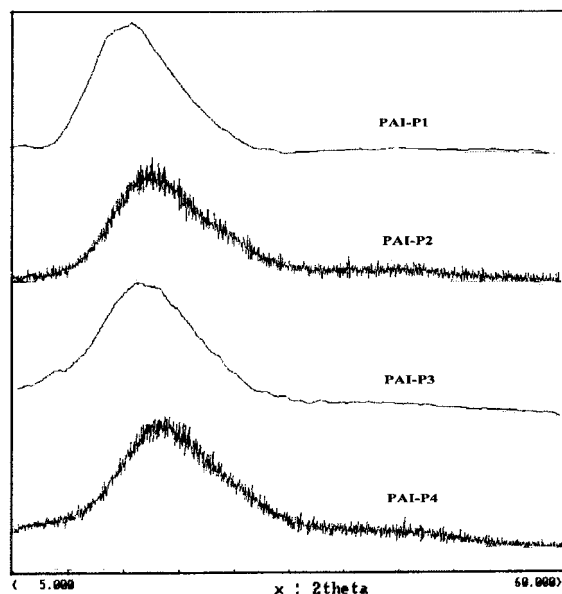


Figure 15 X-ray diffraction curves of the PAI-PMDA series.

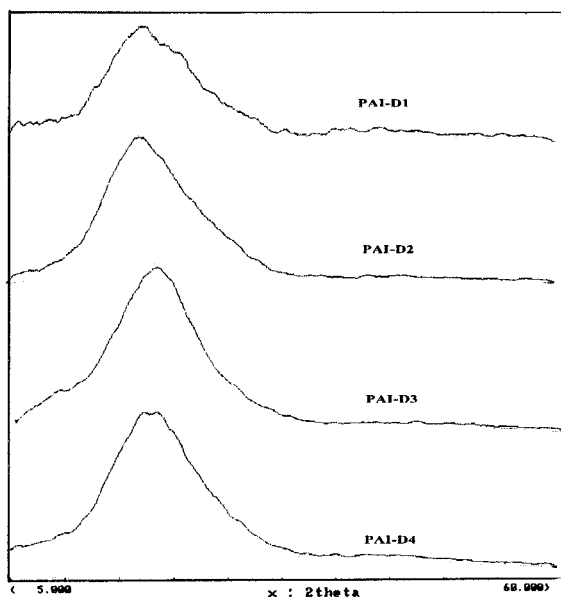


Figure 16 X-ray diffraction curves of the PAI-DSDA series.

and, therefore, the thermal degradation properties of the copolymers were promoted, even close to those of the homopolyimide.

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

The X-ray diffraction curves of the copolymers were measured with the Rigaku diffractometer and are shown in Figures 15–18. All the PAI series copolymers were amorphous. This might have been caused by the presence of heterocyclic imide groups and aromatic structures in the polymer chain. Moreover, all the PBI

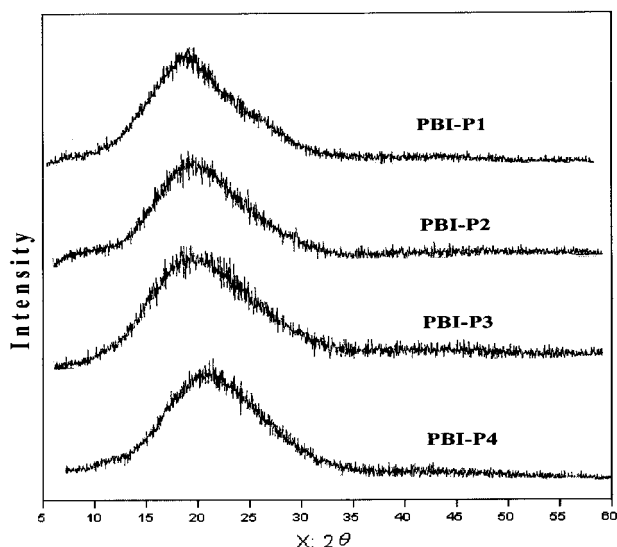


Figure 17 X-ray diffraction curves of the PBI-PMDA series.

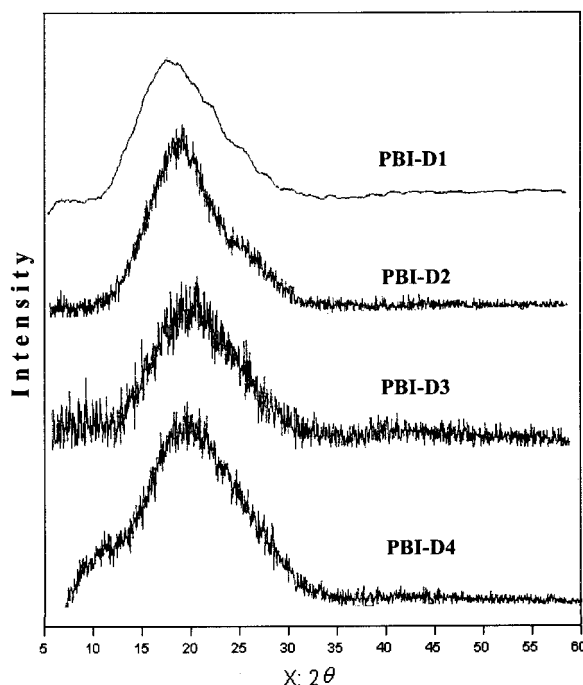


Figure 18 X-ray diffraction curves of the PBI-DSDA series.

series copolymers were also amorphous because the presence of imide and benzimidazole groups in the main chain constrained the molecular mobility of the polymers, which, therefore, hardly formed crystal structures. Meanwhile, the presence of benzimidazole groups further hindered and reduced the formation of hydrogen bonding. These results agreed with the results of DSC measurements.

CONCLUSIONS

In this study, we used a one-step method to form poly-imide prepolymers and a low-temperature method to convert the amide into a benzimidazole structure. The poly(imide amide benzimidazole) copolymers were soluble in sulfuric acid and poly(phosphoric acid) at room temperature and in sulfolane or NMP under heating to 100°C with 5% lithium chloride. With WAXD, it was found that all of these copolymers were amorphous. The conversion of amide groups into benzimidazole groups reduced the amide group content, and this promoted the rigidity and T_g of the copolymers. All the polymers had good thermal and thermooxidative stability. Also, because most of the amide groups were converted into benzimidazole, the thermal properties were close to those of the homopolyimide.

References

1. Sroog, C. E. *J Polym Sci Part D: Macromol Rev* 1976, 11, 161.
2. Hergenrother, P. M.; Havens, S. J. *J Polym Sci Part A: Polym Chem* 1989, 27, 1161.

3. Avadhani, C. V.; Wadgaonkar, P. P.; Vernekar, S. P. *J Appl Polym Sci* 1990, 40, 1325.
4. Ghatge, N. D.; Shinde, B. M.; Mulik, U. P. *J Polym Sci Polym Chem Ed* 1984, 22, 3359.
5. Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. *J Polym Sci Part A: Polym Chem* 1992, 30, 1027.
6. Kakimoto, M.; Akiyama, R.; Negi, Y. S.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1988, 26, 99.
7. Alvino, W. M.; Edelman, L. E. *J Appl Polym Sci* 1975, 19, 2961.
8. Khune, G. D. *J Macromol Sci Chem* 1980, 14, 687.
9. Masiulonis, B.; Hrouz, J.; Baldrian, J.; Ilavsky, M.; Dusek, K. *J Appl Polym Sci* 1987, 34, 1941.
10. Avadhani, C. V.; Wadgaonkar, P. P.; Vernekar, S. P. *J Appl Polym Sci* 1992, 45, 1335.
11. Plummer, L.; Marvel, C. S. *J Polym Sci Part A: Gen Pap* 1964, 2, 2559.
12. Mitsuhashi, K.; Marvel, C. S. *J Polym Sci Part A: Gen Pap* 1965, 3, 4.
13. Coffin, D. R.; Serad, G. A.; Hicks, H. L.; Montgomery, R. T. *Text Res J* 1982, 52, 466.