

Synthesis of Thermostable Polyamideimides and Their Properties

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SYNOPSIS

Thermostable polyamideimides with inherent viscosity of 1.02–1.50 dL/g were synthesized from reacting of diamine-terminated aromatic amide prepolymer with various diisocyanate terminated imide prepolymers. The imide prepolymer was prepared by using 4,4'-diphenylmethane diisocyanate to react with 3,3',4,4' benzophenonetetracarboxylic dianhydride, 3,3',4,4'-sulfonyl diphthalic anhydride, or 4,4'-oxydiphthalic anhydride using the direct one-pot method to improve their solubility. Almost all of the polyamideimides were generally soluble in a wide range of organic solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, and pyridine at room temperature. Polymers with high imide content required high temperatures to dissolve. All polyamideimides had a glass transition temperature of 223–352°C and showed a 10% weight loss temperature of 415–575°C in air and 424–583°C in nitrogen atmosphere. The tensile strength, elongation at break, and initial modulus of polymer films ranged from 61 to 108 MPa, 5 to 10%, and 1.54 to 2.50 GPa, respectively. These copolymers were partly crystalline in structure as shown by X-ray patterns. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides are known as one of the best materials for use in high temperature applications.^{1–3} This is due to their aromatic and heterocyclic structure. Polyimides can resist 500°C for a few minutes or 300°C for several months. However, the rigid structure in the polyimide chain imparts good properties such as thermooxidative stability^{4–6} but makes the material hard to process due to its poor solubility.^{7–10} Here, we used the poly(*m*-phenylene isophthalamide) (PmIA) prepolymer to modify the polyimides. The purpose is to increase their molecular weight in polymerization, to promote their solubility for film formation, and also to improve the mechanical properties and processing characteristics of the copolymers. Noticeably, we synthesized the polyamideimides by using the one-pot instead of the two-pot method to simplify the polymerization process and also to improve their solvent solubility.

EXPERIMENTAL

Materials

Four kinds of commercially available dianhydrides, that is, 3,3',4,4' benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), 4,4'-oxydiphthalic anhydride (OPDA), and 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA), were dried under vacuum at –40°C for 4 h to remove possible moisture. The 4,4'-diphenylmethane diisocyanate (MDI) was used without further purification. *m*-Phenylenediamine (MPA) and isophthaloyl dichloride (IPC) that were used to synthesize PmIA prepolymer were of high purity and used as received from the manufacturers. Solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1,3-dimethyl-2-imidazolidone (DMI) were purified by vacuum distillation on calcium hydride. Triethylamine, which was used as a catalyst, was used without further purification.

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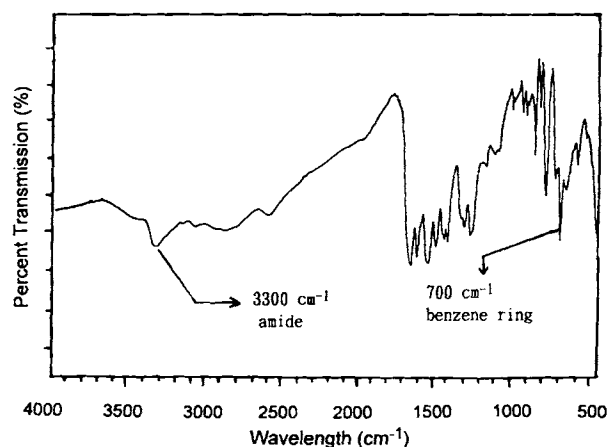


Figure 1 The IR spectrum of diamine-terminated No-mex prepolymer.

Synthesis of Aromatic Polyimide

Equimolar amounts of MDI and dianhydride were dissolved in solvent NMP with solid content of 15%, poured into the reaction flask of 250 mL, and heated at 60°C for 1.5 h. The triethylamine catalyst at 0.03 g/L was then added, and the temperature was raised to 80°C. The viscosity was found to be gradually increased and bubbles of gas (carbon dioxide) were evolved. The viscosity was adjusted by adding the solvent. The reaction was

completed after 1 h. A golden viscous solution of polyimide was obtained. The reaction scheme 1 is shown as follows:

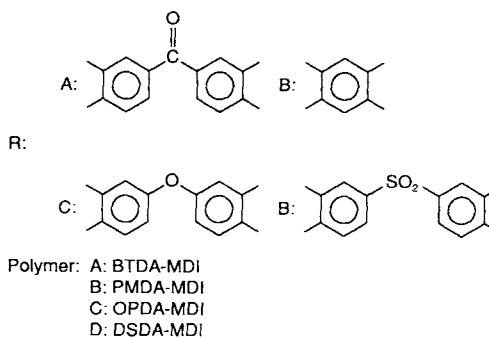
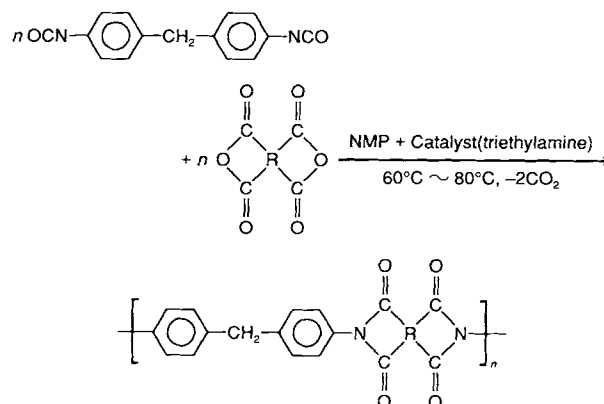


Table I Inherent Viscosity of Polymers

Symbol	Polymer	η_{inh} (dL/g)	Imide Content (%)	PmIA Content (%)	Urea Content (%)
A	BTDA-MDI	0.88	100	—	—
B	OPDA-MDI	0.52	100	—	—
C	PMDA-MDI	0.50	100	—	—
D	DSDA-MDI	0.87	100	—	—
A-a	PmIA-MDI-BTDA (1-2-1)*	1.02	49.3	41.9	8.8
A-b	PmIA-MDI-BTDA (1-3-2)	1.37	62.9	30.7	6.4
A-c	PmIA-MDI-BTDA (1-4-3)	1.08	70.8	24.1	5.1
A-d	PmIA-MDI-BTDA (1-5-4)	1.12	75.9	19.9	4.2
C-a	PmIA-MDI-PMDA (1-2-1)	1.42	46.3	44.4	9.3
C-b	PmIA-MDI-PMDA (1-3-2)	1.28	59.6	33.4	7.0
C-c	PmIA-MDI-PMDA (1-4-3)	1.21	67.6	26.8	5.6
C-d	PmIA-MDI-PMDA (1-5-4)	1.50	73.0	22.3	4.7

* The molar ratio of PmIA/MDI/BTDA is 1/2/1.

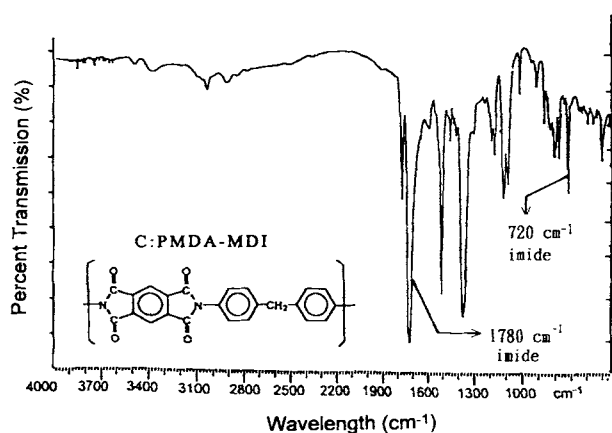
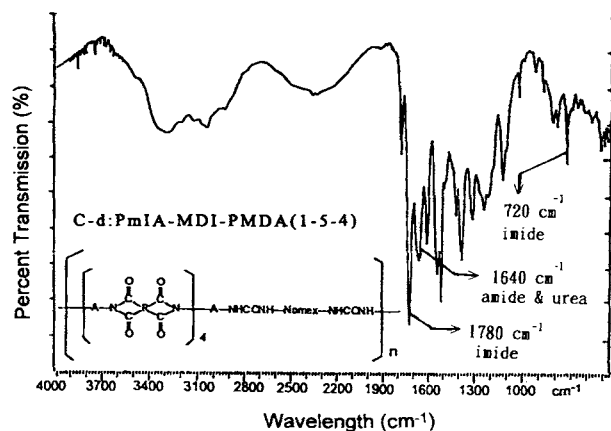
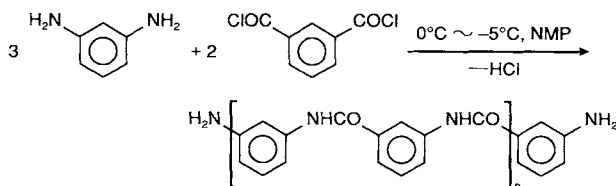


Figure 2 The IR spectra of polymer C and copolymer C-d.

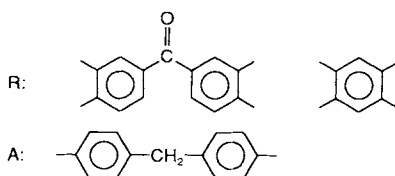
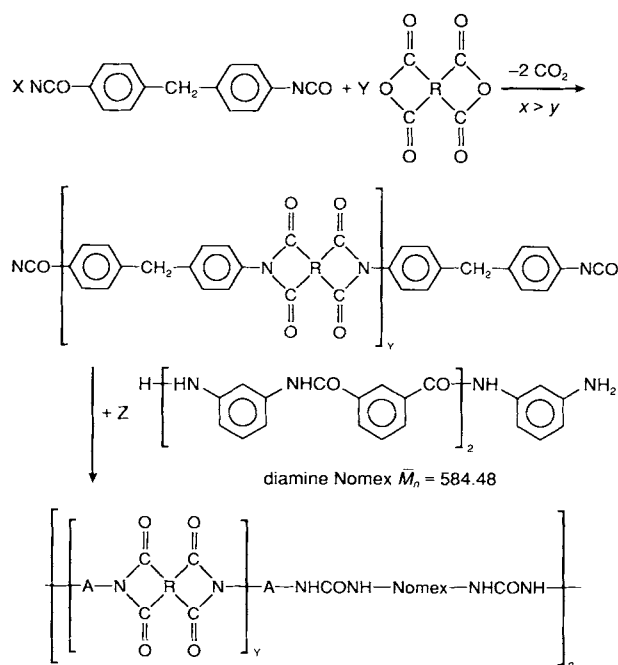
Synthesis of Diamine-Terminated PmIA Prepolymer

Low-molecular-weight diamine-terminated PmIA prepolymer^{11,12} was prepared by the low-temperature polymerization method. The MPA was firstly dissolved in NMP and cooled to the temperature of 0 to -5°C and IPC (molar ratio 3/2) was then added with vigorous stirring over a period of 2 h. The polymer solution was poured into water and washed with methanol and vacuum dried at 80°C for 8 h. The reaction scheme 2 is shown as follows:



Synthesis of Amideimide Copolymers

The amideimide copolymers were synthesized by first preparing a diisocyanate-terminated polyimide prepolymer with excess of MDI in Scheme 1. The diamine-terminated PmIA prepolymer was then added to a reaction flask that contained the diisocyanate polyimide prepolymer (theoretical mol wt of PmIA prepolymer is 584) at 60°C for 0.5 h, and then the temperature was gradually raised to 80°C and left to react for another 1 h. A pale golden viscous solution was obtained. The reaction scheme 3 is shown as follows:



Measurements

Infrared (IR) spectra of polyimides and Nomex-Polyimide copolymers were obtained by Hitachi Model 260-50 Type, over $250\text{--}4000\text{ cm}^{-1}$. The samples were in a form of film about $10\ \mu\text{m}$ thick. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 Analyzer.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Du Pont 9900 and Seiko SSC-5000 apparatuses at a heating rate of $20^{\circ}\text{C}/\text{min}$ under nitrogen at-

Table II Elemental Analysis of Polymers

Code		Elemental Analysis (%)		
		C%	H%	N%
A	Calcd	74.38	3.33	5.78
	Found	74.21	3.72	6.22
B	Calcd	73.03	3.41	5.93
	Found	72.10	4.55	7.30
C	Calcd	72.25	3.69	7.33
	Found	71.88	4.18	7.88
D	Calcd	66.92	3.10	5.38
	Found	66.84	4.41	6.85
A-a	Calcd	72.08	4.28	10.35
	Found	71.38	5.10	9.87
A-b	Calcd	72.70	4.11	8.92
	Found	71.91	4.84	8.83
A-c	Calcd	73.02	4.02	8.17
	Found	72.43	4.78	8.20
A-d	Calcd	73.22	3.96	7.71
	Found	72.49	4.60	7.81
C-a	Calcd	71.16	4.32	11.45
	Found	69.20	5.15	10.40
C-b	Calcd	71.46	4.15	10.29
	Found	68.95	4.91	9.67
C-c	Calcd	71.63	4.05	9.64
	Found	69.29	4.75	9.30
C-d	Calcd	71.74	3.98	9.22
	Found	69.65	4.61	9.32

mosphere to obtain the glass transition temperature (T_g) and the weight loss, respectively.

Wide-angle X-ray photography was taken with Ni-filtered CuK_α radiation using Rigaku D/max-II Type X-ray diffractometer. All stress-strain data

Table IV Mechanical Properties of Polymers

Code	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
B	83	10	1.57
D	77	7	1.54
A	76	6	2.08
A-a	95	8	1.75
A-b	95	7	1.84
A-c	96	6	1.84
A-d	86	6	1.98
C	61	5	2.50
C-a	103	8	1.72
C-b	104	7	2.09
C-c	108	6	2.21
C-d	83	6	2.26

were obtained on an Instron 1122 Type testing instrument at an extension rate of 10 mm/min with a specimen of 50 mm length, 10 mm width, and 0.5 mm thick.

RESULTS AND DISCUSSION

PmIA Prepolymer Syntheses

Diamine-terminated PmIA prepolymer was prepared from MPA and IPC (molar ratio 3/2). The molecular weight of PmIA prepolymer was theoretically 584. From the results of elemental analysis, it showed that the found values were in good agreement with the calculated ones. The IR spectrum of

Table III Solubility of Polymers

Code	H_2SO_4	DMF	DMAc	DMAC + 5%				
				LiCl	NMP	DMSO	Py	DMI
A	+	-	-	-	+	-	-	○
A-a	+	△	○	+	+	○	△	+
A-b	+	-	○	+	+	○	△	+
A-c	+	-	△	○	+	△	△	+
A-d	+	-	-	△	+	-	-	△
B	+	○	+	+	+	○	○	+
C	+	-	-	△	○	-	△	-
C-a	+	△	○	+	+	○	△	+
C-b	+	△	△	○	+	○	△	○
C-c	+	-	△	○	+	△	△	○
C-d	+	-	△	○	+	-	△	○
D	+	-	-	△	+	△	-	-

+, Soluble in room temperature; ○, 70°C soluble; △, partially soluble; -, completely insoluble; Py, pyridine.

Table V The Thermal Properties of Polymers

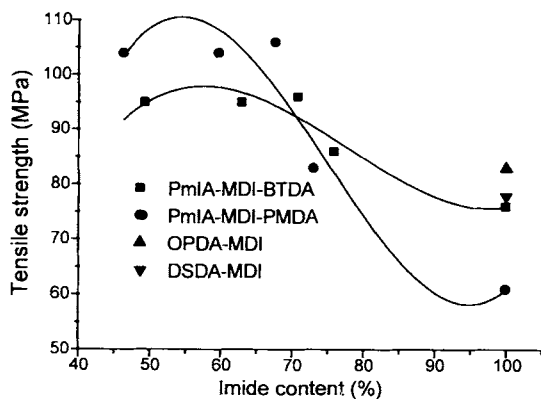
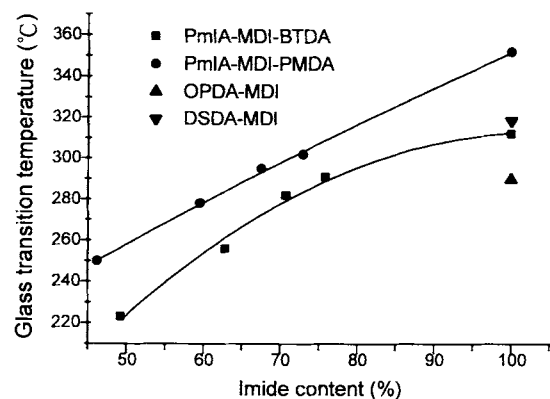
Code	T_g	Degradation Temperature*	
		In Nitrogen (°C)	In Air (°C)
A-a	223	424	418
A-b	256	490	507
A-c	282	516	524
A-d	291	535	536
A	312	577	570
C-a	250	430	414
C-b	278	491	503
C-c	295	538	516
C-d	302	551	523
C	352	583	575
B	290	—	—
D	319	—	—

* 10% weight loss temperature at heating rate of 20°C/min with TGA measurement.

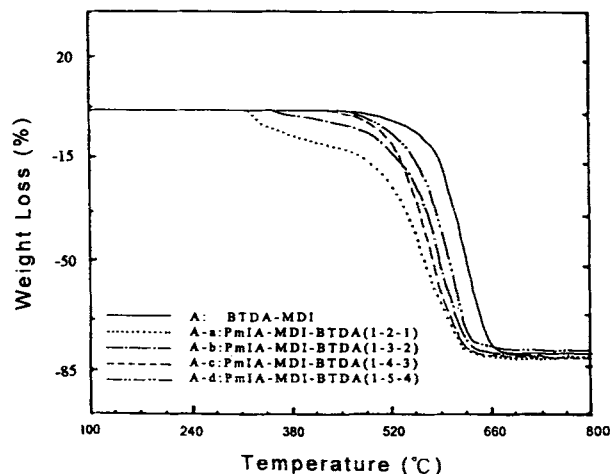
diamine-terminated Nomex prepolymer (Fig. 1) exhibited the —NH stretching vibrations of amide group at 3300 cm^{-1} and the characteristic benzene ring absorption at 700 cm^{-1} . These supported the formation of diamine-terminated PmIA prepolymer.

Synthesis of Polyimides and Polyamideimides

MDI and four kinds of aromatic dianhydride (BTDA, PMDA, OPDA, DSDA) were used to prepare four polyimides. Eight copolymers were synthesized from four different molar ratios of MDI, two kinds of dianhydride (BTDA, PMDA), and diamine-terminated PmIA prepolymer. The inherent viscosity of polyimides and polyamideimides is listed in Table I. It was found that the intrinsic viscosity of polymers was higher than 1.00. Especially, the

**Figure 3** The relationship between tensile strength and imide content.**Figure 4** The relationship between T_g s and imide content.

copolymer had the value of more than 1.00, indicating a high-molecular-weight copolymer obtained. In Table I, the content of imide group, PmIA, and urea in the copolymer was also calculated. These polymers could be cast into transparent, tough, and flexible films. Figure 2 shows the IR spectra of polymer C and copolymer C-d, and it was found that the characteristic absorption at 1720, 1780, 1360, and 720 cm^{-1} indicated an existence of imide group. In the copolymer, the absorption peak of 1640 and 3300–3400 cm^{-1} demonstrated the presence of urea group and —NH stretching vibration of amide group, respectively. From that, it could be concluded that the PmIA molecule was introduced into the main chain of polyimide. The results of elemental analysis of all polymers are listed in Table II. From the results, the found values agreed well with the calculated ones.

**Figure 5** The weight loss of A series polymers.

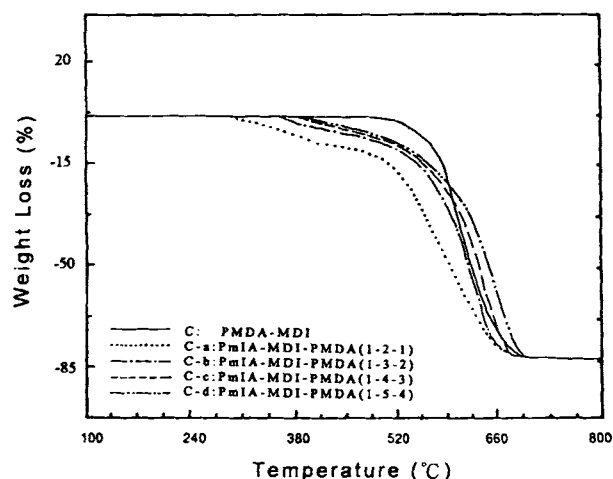


Figure 6 The weight loss of B series polymers.

Solubility Properties of Polymers

Table III indicates the solubility of the polymers. As indicated, the polyimide from monomer BTDA was only soluble in NMP and sulfuric acid at room temperature. Nevertheless, the copolymers of polyimide from BTDA such as A-a, A-b were soluble at room temperature in DMAc + 5% LiCl, DMI, NMP, or sulfuric acid. The copolymer A-c could even be soluble in DMI or NMP at room temperature or dissolved in DMAc + 5% LiCl at heated temperature. From that, it was manifested that the addition of PmIA in the polyimide chain did increase their solubility.

The solubility of copolymer from PMDA was inferior than that from BTDA, but with high content of PmIA, it could still be soluble in DMAc + 5% LiCl, DMI, DMSO at 70°C.

Mechanical Properties

The mechanical properties of polymers are shown in Table IV. It is shown that the tensile strength, the breaking elongation, and the initial modulus of polymer are 61–108 MPa, 5–10%, and 1.54–2.50 GPa, respectively. Most of the polymers had high strength and modulus but medium elongation. This indicated that the polymer was a medium tough material. Figure 3 shows the relationship between tensile strength and imide content. The tensile strength of copolymers was higher than that of polyimides and increased with PmIA content. Thus, the use of PmIA to modify the polyimide could intensify the tensile strength of copolymers. It was believed that the introduction of the metastructure of PmIA to the polyimide chain could increase the solubility of

copolymers in the polymerization and consequently increase their molecular weight. In addition, the hydrogen bonding of the amide group in PmIA could promote the intermolecular force in copolymer and therefore increase their tensile strength.

The copolymers A-d and C-d were found to be less reinforced due to their low PmIA content. The breaking elongation of copolymers was increased by the presence of PmIA but not obviously so. Nevertheless, initial modulus of copolymers was decreased with the increase of PmIA content. This indicated that the introduction of PmIA into polyimide by copolymerization could reduce the stiffness of copolymer chain and consequently lower the copolymer modulus.

Thermal Properties of Polymers

The thermal properties of all polymers were evaluated by DSC and TGA. The thermal behavior of all polymers is listed in Table V. With the presence of

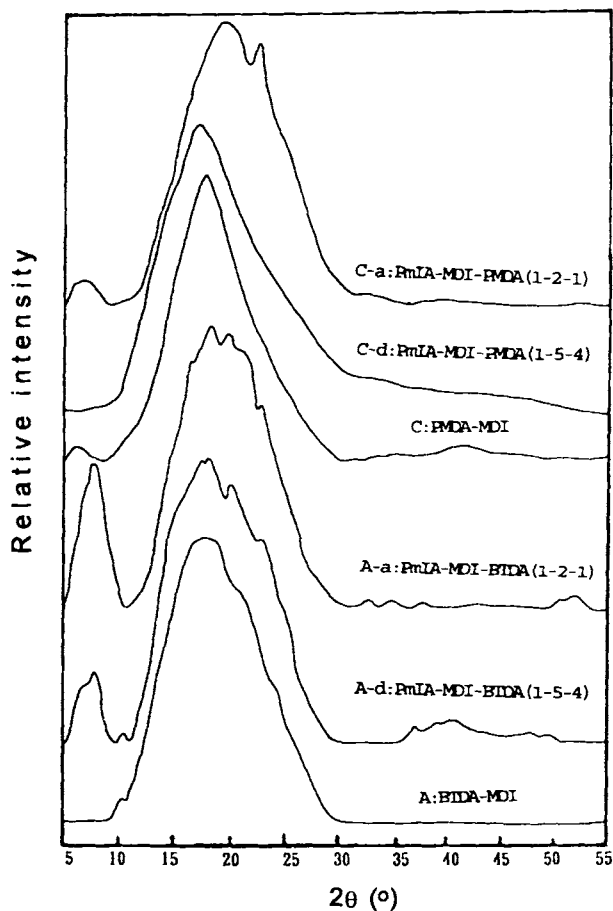


Figure 7 X-ray patterns of polyimides and their copolymers.

benzoic and heterocyclic ring structures of polyimide or benzoic ring and amide group of PmIA, these polymers had an excellent thermooxidative stability and also showed a high glass transition temperature. The T_g s of four polyimides, A, B, C, and D, ranged from 290 to 352°C. Among A, B, and D, the polyimide D had a higher T_g due to its polar sulfonyl structure. The T_g s of copolymers was 223–302°C and decreased with the increase amount of PmIA. It was explained that the incorporation of PmIA into the polyimide backbone could increase the flexibility of copolymer chain and hence decrease the T_g s of copolymers. The relationship between T_g s and imide content is shown in Figure 4.

Table V summarized the thermogravimetric data of all polymers. As indicated, all polymers possessed a good thermal and thermooxidation stability, with no significant weight loss up to a temperature of approximately 320°C in nitrogen and in air atmosphere. Moreover, it was found that the polyimides A and C (Figs. 5 and 6) had the best thermal stability and 10% weight loss properties, at 577 and 583°C, respectively. The decomposition temperatures at 10% weight loss of these copolymers were 414–536°C in air and 424–551°C in nitrogen. With the increase of PmIA content, the 10% weight loss temperature was lowered. This suggested that the amide linkage did contribute less thermooxidative stability than that of imide. In addition, the presence of urea group in the copolymer chain also gave a less thermal stability due to its poor heat resistance of urea linkage.

Wide-Angle X-Ray Diffraction of Polymers

X-ray pattern of some representative polymers are shown in Figure 7. All polymers exhibited a scattering peak at $2\theta=18^\circ$. However, the copolymer showed another peak at $2\theta=8^\circ$, which was more pronounced as the content of PmIA increased. This peak was believed to be the scattering of PmIA chain in the copolymer. As shown in Figure 7, these copolymers were partly crystalline in structure.

Conclusions

In this experiment, we used a one-step method to synthesize four polyimides and eight Nomex-polyimide copolymers. The copolyimide showed an in-

crease of their molecular weight and an improvement of their solubility. The inherent viscosity of these polymers was found to be 0.5–1.5 dL/g and could be cast into a transparent and flexible film. The tensile strength and breaking elongation of these copolymer films were better than those of polyimides. However, the modulus of copolymer was less than that of polyimide due to lower stiffness of amide chain. From the thermal analysis, the glass transition temperature of copolymer was less than that of pure polyimides. The presence of urea linkage in the copolymer was considered to be a deteriorating factor to its thermooxidative property. From X-ray diffraction patterns, these copolymers were a partly crystalline in structure.

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REFERENCES

1. C. E. Sroog, *J. Polym. Sci. Macromol. Rev.*, **11**, 161 (1976).
2. P. M. Hergenrother and S. J. Havens, *J. Polym. Sci. Part A: Polym. Chem.*, **27**, 1161 (1989).
3. C. V. Avadhani, P. P. Wadgaonkar, and S. P. Vernekar, *J. Appl. Polym. Sci.*, **40**, 1325 (1990).
4. N. D. Ghatge, B. M. Shinde, and U. P. Mulik, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3359 (1984).
5. Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 1027 (1992).
6. M. Kakimoto, R. Akiyama, Y. S. Negi, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **26**, 99 (1988).
7. W. M. Alvino, and L. E. Edelman, *J. Appl. Polym. Sci.*, **19**, 2961 (1975).
8. G. D. Khune, *J. Macro. Sci. Chem.*, **A14**, 687 (1980).
9. B. Masiulonis, J. Hrouz, J. Baldrian, M. Ilavsky, and K. Dusek, *J. Appl. Polym. Sci.*, **34**, 1941 (1987).
10. C. V. Avadhani, P. P. Wadgaonkar, and S. P. Vernekar, *J. Appl. Polym. Sci.*, **45**, 1335 (1992).
11. H. H. Wang and M. F. Lin, *Chin. J. Mater. Sci.*, **22**, 223 (1990).
12. H. H. Wang and M. F. Lin, *J. Polym. Sci.*, **43**, 259 (1991).

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