

Synthesis and Properties of Thermostable Naphthalate-Containing Copoly(amide-imide)s

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ABSTRACT: Thermostable naphthalate-containing copoly(amide-imide)s with inherent viscosity of 0.53–0.96 dL/g were synthesized by reacting diacid-terminated naphthalate monomers with various diisocyanate-terminated polyimide prepolymers. The polyimide prepolymers were prepared by using 4,4'-diphenylmethane diisocyanate to react with 3,3',4,4'-benzophenonetetracarboxylic dianhydride, pyromellitic dianhydride, or 3,3',4,4'-sulfonyl diphthalic anhydride using a direct one-pot method to improve their solubility without sacrificing their thermal properties. The copolymers, except the B-2 and P-2 series, can be dissolved in *N,N*-dimethylacetamide and 5% lithium chloride or dimethyl sulfoxide at high temperature but are not soluble in pyridine. The solubility of the copolymers is related to their chemical and crystalline structures. Those copolymers with sulfonyl or amorphous structures display good solubility. All the naphthalate-containing copoly(amide-imide)s have glass transition temperatures and melting points in the range of 223–312°C and 348–366°C, respectively, and show a 10% weight-loss temperature of 485–549°C in air and 465–564°C in a nitrogen atmosphere. The tensile strength, elongation at break, and initial modulus of polymer films range from 25–74 MPa, 4–9%, and 0.74–1.60 GPa, respectively. From the X-ray diffraction studies, copolymers of B-2, P-2, and D-2 with symmetrical 2,6-naphthalate amide structure are crystalline, but the others are amorphous. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1581–1593, 1997

Key words: copoly(amide-imide); polyamideimide; naphthalate-containing; thermostable

INTRODUCTION

Aromatic polyimide has been known as one of the best materials for use in high-temperature applications.^{1–3} Its imperviousness to heat is due to its aromatic and heterocyclic structure. Polyimides can resist temperatures of 500°C for a few minutes or 300°C for several months. The rigid structure in the polyimide chain imparts good properties, such as thermooxidative stability,^{4–6} but makes the material hard to process owing to its poor solubility.^{7–10} In our previous studies,^{11–13} we employed the diacid-terminated poly[*m*-phenylene isophthalamide (PmIA)] prepolymer (No-

mex prepolymer) to modify the polyimides. It improved the solubility, mechanical properties, and processing characteristics of the copolymers. This article addresses the use of diacid-terminated naphthalate monomers instead of a diacid-terminated PmIA prepolymer to modify the polyimide and the effect of naphthalate structure on the properties of copoly(amide-imide)s.

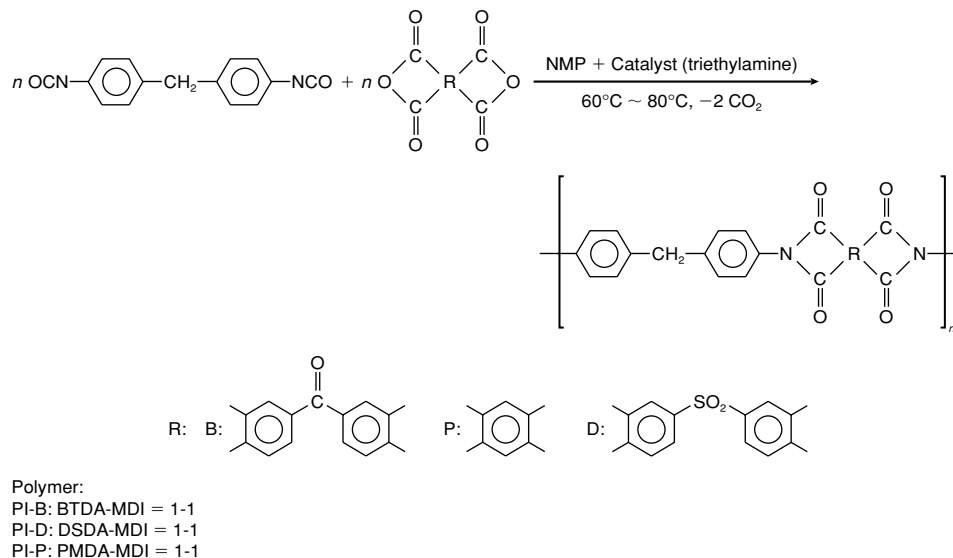
EXPERIMENTAL

Materials

Three kinds of commercially available dianhydrides, namely, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 3,3',4,4'-sulfonyl diph-

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Scheme 1

thalic 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. The 1,4-naphthalene dicarboxylic acid (1,4-NDA) and 2,6-naphthalene dicarboxylic acid (2,6-NDA) monomers 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 1,3-dimethyl-2-imidazolidone (DMI) were purified by vacuum distillation with calcium hydride. Triethylamine, which was employed as a catalyst, was used without purification.

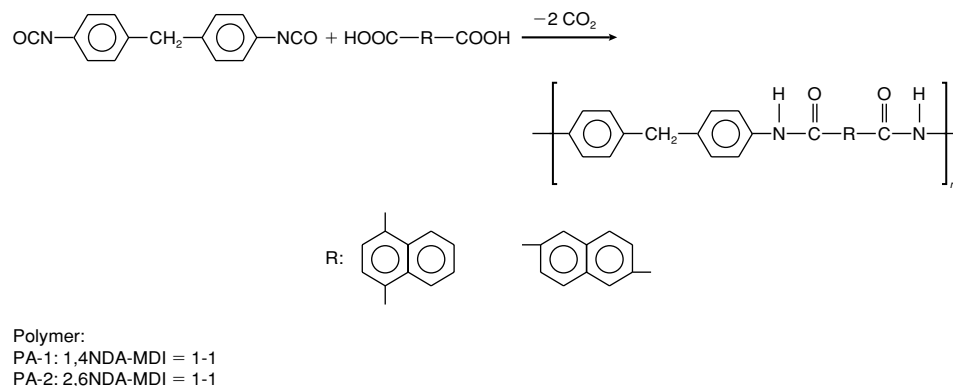
Synthesis of Aromatic Polyimide

Equimolar amounts of MDI and dianhydride were dissolved in the solvent NMP with a solid content

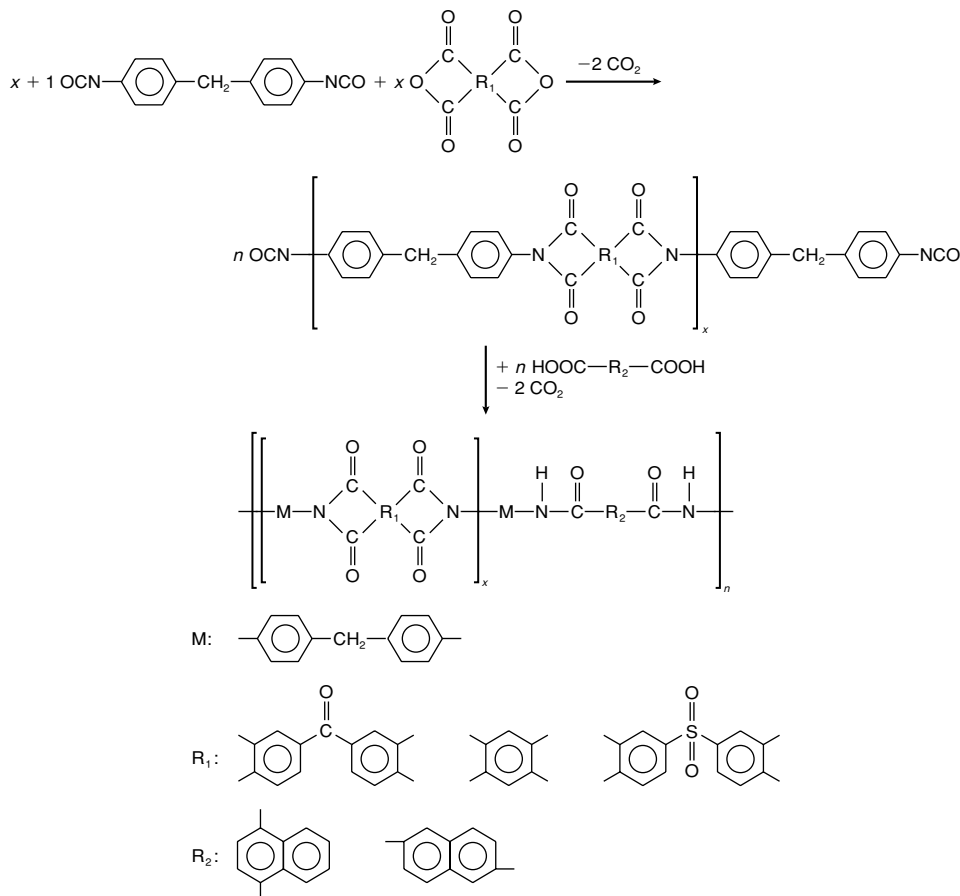
of 15%, poured into the 250-ml reaction flask, and heated at 60°C for 4 h.¹³ The catalyst, 0.03 g/l of triethylamine, was then added. The viscosity was found to gradually increase, and bubbles of gas (carbon dioxide) evolved. The viscosity was adjusted by adding solvent. After the solution was permitted to react 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 polyimide was obtained. The reaction is shown in Scheme 1.

Synthesis of Naphthalate-Containing Polyamide

High molecular weight naphthalate-containing polyamide was polymerized through a low-temperature solution polymerization method.¹⁴ Equimolar amounts of MDI and naphthalene dicarboxylic acid were dissolved in the solvent NMP with a solid content of 15%, poured into the 250-ml



Scheme 2

**Copolymer:**

B1-1: BTDA-MDI-1,4NDA = 1-2-1	B2-1: BTDA-MDI-2,6NDA = 1-2-1
B1-2: BTDA-MDI-1,4NDA = 2-3-1	B2-2: BTDA-MDI-2,6NDA = 2-3-1
B1-3: BTDA-MDI-1,4NDA = 3-4-1	B2-3: BTDA-MDI-2,6NDA = 3-4-1
B1-4: BTDA-MDI-1,4NDA = 4-5-1	B2-4: BTDA-MDI-2,6NDA = 4-5-1
P1-1: PMDA-MDI-1,4NDA = 1-2-1	P2-1: PMDA-MDI-2,6NDA = 1-2-1
P1-2: PMDA-MDI-1,4NDA = 2-3-1	P2-2: PMDA-MDI-2,6NDA = 2-3-1
P1-3: PMDA-MDI-1,4NDA = 3-4-1	P2-3: PMDA-MDI-2,6NDA = 3-4-1
P1-4: PMDA-MDI-1,4NDA = 4-5-1	P2-4: PMDA-MDI-2,6NDA = 4-5-1
D1-1: DSDA-MDI-1,4NDA = 1-2-1	D2-1: DSDA-MDI-2,6NDA = 1-2-1
D1-2: DSDA-MDI-1,4NDA = 2-3-1	D2-2: DSDA-MDI-2,6NDA = 2-3-1
D1-3: DSDA-MDI-1,4NDA = 3-4-1	D2-3: DSDA-MDI-2,6NDA = 3-4-1
D1-4: DSDA-MDI-1,4NDA = 4-5-1	D2-4: DSDA-MDI-2,6NDA = 4-5-1

Scheme 3

reaction flask, and heated at 80°C for 2 h. The catalyst, 0.03 g/l of triethylamine, was then added. The viscosity was found to gradually increase, and bubbles of gas (carbon dioxide) evolved. The viscosity was adjusted by adding solvent. After the solution was permitted to react for 4 h, the temperature was raised to 120°C for 2 h. The reaction was completed. A golden, viscous solution of naphthalate-containing polyamide was obtained. The reaction is shown in Scheme 2.

Synthesis of Naphthalate-Containing Copoly(amide-imide)

The naphthalate-containing copoly(amide-imide) was synthesized by initial preparation of

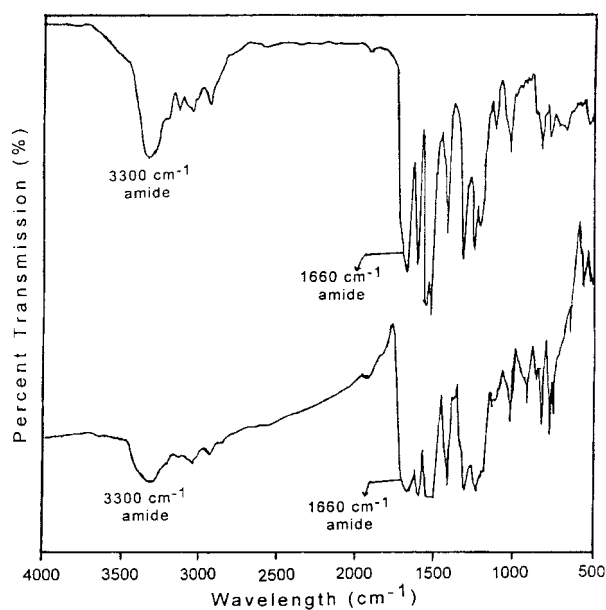
diisocyanate-terminated polyimide prepolymer with excess of MDI.^{1-3,15} The 1,4- or 2,6-naphthalene dicarboxylic acid was then poured into the reaction flask containing the diisocyanate polyimide prepolymer maintained at 60°C for 0.5 h; then, the catalyst, 0.03 g/l of triethylamine, was added. The temperature was gradually raised to 80°C and kept at that level for another hour to permit the solution to react. A pale golden, viscous solution was obtained. The reaction is shown in Scheme 3.

Measurements

Infrared (IR) spectra of polyimides and naphthalate-containing polyamide and copoly-

Table I Inherent Viscosity of Polymers

Code	Polymer	η_{inh}^a (dL/g)	Imide Content (%)	Amide Content (%)
PI-B	BTDA-MDI	0.88	100	—
PI-P	PMDA-MDI	0.50	100	—
PI-D	DSDA-MDI	0.87	100	—
PA-1	1,4NDA-MDI	0.38	—	100
PA-2	2,6NDA-MDI	0.35	—	100
B1-1	BTDA-MDI-1,4NDA (1-2-1)	0.90	56.2	43.8
B1-2	BTDA-MDI-1,4NDA (2-3-1)	0.89	71.9	28.1
B1-3	BTDA-MDI-1,4NDA (3-4-1)	0.83	79.3	20.7
B1-4	BTDA-MDI-1,4NDA (4-5-1)	0.79	83.7	16.3
B2-1	BTDA-MDI-2,6NDA (1-2-1)	0.75	56.2	43.8
B2-2	BTDA-MDI-2,6NDA (2-3-1)	0.78	71.9	28.1
B2-3	BTDA-MDI-2,6NDA (3-4-1)	0.60	79.3	20.7
B2-4	BTDA-MDI-2,6NDA (4-5-1)	0.66	83.7	16.3
P1-1	PMDA-MDI-1,4NDA (1-2-1)	0.61	50.1	49.9
P1-2	PMDA-MDI-1,4NDA (2-3-1)	0.55	66.8	33.2
P1-3	PMDA-MDI-1,4NDA (3-4-1)	0.53	75.1	24.9
P1-4	PMDA-MDI-1,4NDA (4-5-1)	0.58	80.1	19.9
P2-1	PMDA-MDI-2,6NDA (1-2-1)	0.63	50.1	49.9
P2-2	PMDA-MDI-2,6NDA (2-3-1)	0.62	66.8	33.2
P2-3	PMDA-MDI-2,6NDA (3-4-1)	0.68	75.1	24.9
P2-4	PMDA-MDI-2,6NDA (4-5-1)	0.70	80.1	19.9
D1-1	DSDA-MDI-1,4NDA (1-2-1)	0.96	57.9	42.1
D1-2	DSDA-MDI-1,4NDA (1-2-1)	0.90	73.3	26.7
D1-3	DSDA-MDI-1,4NDA (1-2-1)	0.92	80.5	19.5
D1-4	DSDA-MDI-1,4NDA (1-2-1)	0.89	84.6	15.4
D2-1	DSDA-MDI-2,6NDA (1-2-1)	0.74	57.9	42.1
D2-2	DSDA-MDI-2,6NDA (1-2-1)	0.71	73.3	26.7
D2-3	DSDA-MDI-2,6NDA (1-2-1)	0.65	80.5	19.5
D2-4	DSDA-MDI-2,6NDA (1-2-1)	0.68	84.6	15.4

^a Inherent solubility.**Figure 1** The infrared spectrum of naphthalate polyamides.

(amide-imide)s were obtained using a Hitachi Model 260-50 spectrometer over a range of 250 to 4000 cm^{-1} . The samples were in the form of a film about 10 μm thick. Elemental analysis (C, H, N) was performed using a Perkin-Elmer 2400 analyzer.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Du Pont 9900 differential scanning calorimeter and a Seiko SSC-5000 type thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere to obtain the glass transition temperature (T_g) and the weight loss, respectively.

Wide-angle X-ray photographs were taken with Ni-filtered $\text{CuK}\alpha$ radiation using a Rigaku D/max-II type X-ray diffractometer. All stress-strain data were obtained from an Instron 1122-type testing instrument at an extension rate of 10 mm/min using a specimen 50 mm long, 10 mm wide, and 0.5 mm thick.

RESULTS AND DISCUSSION

Synthesis of Polyimide, Naphthalate-Containing Polyamide, and Copoly(amide-imide)

4,4'-Diphenylmethane diisocyanate and three kinds of aromatic dianhydride (BTDA, PMDA, and DSDA) were used to prepare three polyimides. Two kinds of naphthalene diacids (1,4-NDA and 2,6-NDA) were also used to prepare two naphthalate-containing polyamides. Twenty-four copolymers were synthesized from four different molar ratios of MDI, three kinds of dianhydride, and two naphthalene dicarboxylic acids. The inherent viscosities of polyimide, naphthalate-containing polyamide, and copoly(amide-imide) are listed in Table I. The intrinsic viscosity of naphthalate-containing polyamide is relatively low.

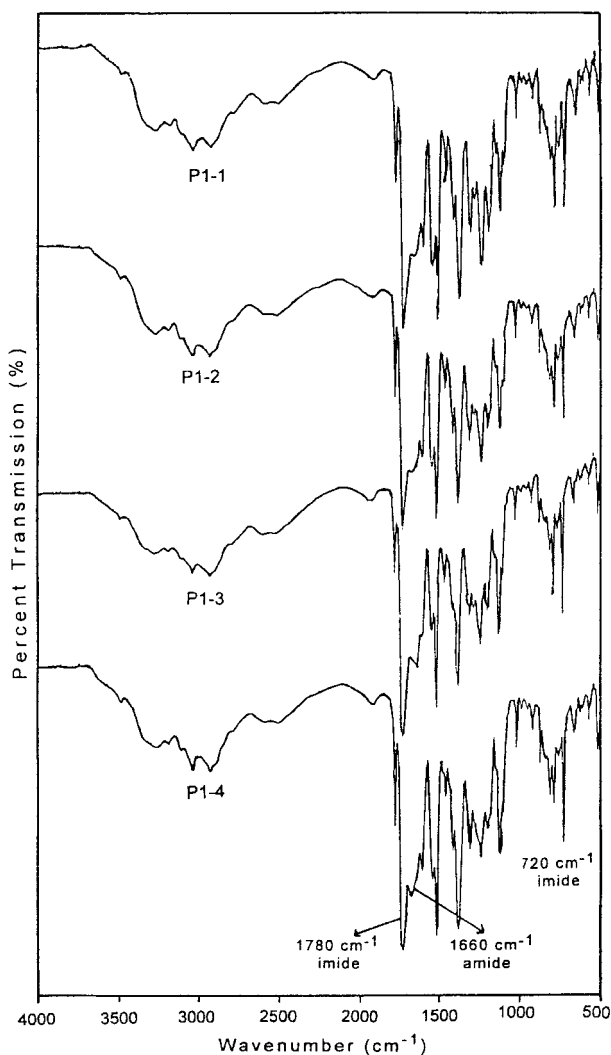


Figure 2 The infrared spectra of the copolymers (P1 series).

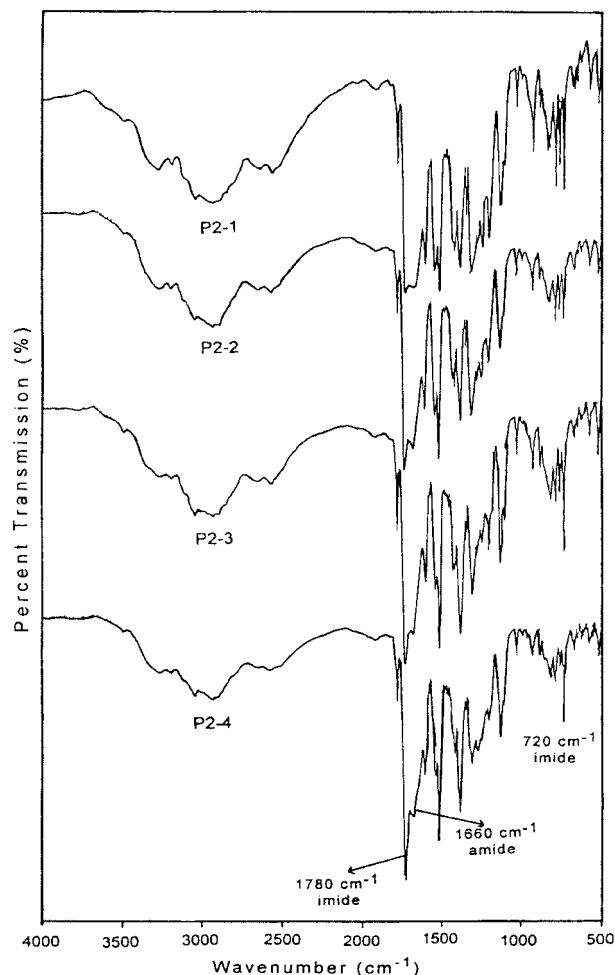


Figure 3 The infrared spectra of the copolymers (P2 series).

This is due to the slowness of naphthalene carboxylic acid to react with the isocyanate group. The intrinsic viscosity of the copolymers is higher than 0.53. Specifically, some of copolymers have the value of 0.96, possibly indicating that a high molecular weight copolymer has been obtained. In the table, the contents of imide and amide groups in the copolymer are also calculated. These polymers can be cast into transparent, tough, and flexible films. Figures 1–3 show the IR spectra of naphthalate-containing polyamides and copolymers of the P1, P2 series; the characteristic absorption at 1720, 1780, 1360, and 720 cm^{-1} , indicates the existence of the imide group in the P1 and P2 series. Moreover, the absorption peaks of 1660 cm^{-1} and 3300–3400 cm^{-1} demonstrate the —NH stretching vibration of the amide group. There is no absorption at 1680–1700 cm^{-1} , indicating the absence of a diacid group. From this, we could conclude that the naphthalate amide

Table II Elemental Analysis of Polymers

Code	Polymer	Elemental Analysis (%)			
			C %	H %	N %
PI-B	BTDA-MDI (1-1)	Calculated	74.38	3.33	5.78
		Found	74.21	3.72	6.22
PI-P	PMDA-MDI (1-1)	Calculated	72.25	3.69	7.33
		Found	71.88	4.18	7.88
PI-D	DSDA-MDI (1-1)	Calculated	66.92	3.10	5.38
		Found	66.84	4.41	6.85
PA-1	1,4-NDA-MDI (1-1)	Calculated	79.37	4.76	7.41
		Found	68.33	5.73	9.90
PA-2	2,6-NDA-MDI (1-1)	Calculated	79.37	4.76	7.41
		Found	66.11	5.06	5.94
B1-1	BTDA-MDI-1,4NDA (1-2-1)	Calculated	76.57	3.94	6.50
		Found	68.91	4.91	7.45
B1-2	BTDA-MDI-1,4NDA (2-3-1)	Calculated	75.78	3.37	6.63
		Found	70.27	4.42	6.90
B1-3	BTDA-MDI-1,4NDA (3-4-1)	Calculated	75.41	3.61	6.12
		Found	70.40	4.31	6.91
B1-4	BTDA-MDI-1,4NDA (4-5-1)	Calculated	75.19	3.54	6.05
		Found	67.86	4.74	7.16
B2-1	BTDA-MDI-2,6-NDA (1-2-1)	Calculated	76.57	3.94	6.50
		Found	70.07	4.38	6.94
B2-2	BTDA-MDI-2,6-NDA (2-3-1)	Calculated	75.78	3.37	6.63
		Found	68.56	4.57	6.87
B2-3	BTDA-MDI-2,6-DNA (3-4-1)	Calculated	75.41	3.61	6.12
		Found	69.37	4.46	6.90
B2-4	BTDA-MDI-2,6-NDA (4-5-1)	Calculated	75.19	3.54	6.05
		Found	69.44	4.47	6.69
P1-1	PMDA-MDI-1,4-NDA (1-2-1)	Calculated	75.99	3.96	7.39
		Found	68.63	4.85	7.66
P1-2	PMDA-MDI-1,4-NDA (2-3-1)	Calculated	74.87	3.69	7.38
		Found	67.63	4.72	7.72
P1-3	PMDA-MDI-1,4-NDA (3-4-1)	Calculated	74.31	3.56	7.38
		Found	67.71	4.69	7.86
P1-4	PMDA-MDI-1,4-NDA (4-5-1)	Calculated	73.97	3.48	7.38
		Found	68.75	4.35	7.67
P2-1	PMDA-MDI-2,6-NDA (1-2-1)	Calculated	75.99	3.96	7.39
		Found	67.69	4.71	7.41

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 empirical values agree well with the calculated ones.

The Solubility Properties of Polymers

Table III summarizes the solubilities of the polymers. As indicated in the table, the three polyimides can be dissolved in sulfuric acid at room temperature, or in NMP at 80°C, but are only partially dissolvable in DMAc, DMAc and 5% LiCl, and DMSO at high temperatures. In general, the copolymers have better solubility than the homo-

polyimides and naphthalate-containing polyamides. The copolymers, except B-2 and P-2 (not including D-2) can be dissolved in DMAc and 5% LiCl at room temperature or in DMSO at high temperatures but are not soluble in DMF or pyridine. The solubility of the copolymers is therefore considered to be related to their chemical and crystalline structures. Copolymers of B-2 and P-2 with a symmetric 2,6-naphthalate amide structure exhibiting a crystalline morphology as shown by X-ray diffraction displayed poor solubility. However, copolymer D-2 demonstrates good solubility despite its 2,6-naphthalate amide and crystalline structure. This finding can be explained by noting that copolymer D-2 contains the polar

Table II (Continued from the previous page)

Code	Polymer	Elemental Analysis (%)			
			C %	H %	N %
P2-2	PMDA-MDI-2,6-NDA (2-3-1)	Calculated	74.87	3.69	7.38
		Found	67.39	4.74	7.83
P2-3	PMDA-MDI-2,6-DNA (3-4-1)	Calculated	74.31	3.56	7.38
		Found	67.07	4.62	7.72
P2-4	PMDA-MDI-2,6-NDA (4-5-1)	Calculated	73.97	3.48	7.38
		Found	66.70	4.63	7.69
D1-1	DSDA-MDI-1,4-NDA (1-2-1)	Calculated	72.16	3.79	6.24
		Found	64.92	4.25	6.65
D1-2	DSDA-MDI-1,4-NDA (2-3-1)	Calculated	70.24	3.53	5.92
		Found	65.03	4.55	6.87
D1-3	DSDA-MDI-1,4-NDA (3-4-1)	Calculated	69.35	3.41	5.78
		Found	65.31	4.32	6.86
D1-4	DSDA-MDI-1,4-NDA (4-5-1)	Calculated	68.84	3.34	5.70
		Found	66.16	4.71	7.13
D2-1	DSDA-MDI-2,6-NDA (1-2-1)	Calculated	72.16	3.79	6.24
		Found	65.86	4.36	6.55
D2-2	DSDA-MDI-2,6-NDA (2-3-4)	Calculated	70.24	3.53	5.92
		Found	64.88	4.44	7.02
D2-3	DSDA-MDI-2,6-NDA (3-4-1)	Calculated	69.35	3.41	5.78
		Found	64.74	4.35	6.71
D2-4	DSDA-MDI-2,6-NDA (4-5-1)	Calculated	68.84	3.34	5.70
		Found	64.58	4.36	6.39

sulfonyl group in the copolymer chain, which can contribute to better interaction with the solvent, thus resulting in good solubility. From this, it can be concluded that the addition of naphthalate amide to the polyimide chain does increase the solubility of polymers with the exception of those copolymers having a 2,6-naphthalate amide and crystalline structure.

The Thermal Properties of Polymers

The thermal properties of all polymers were evaluated by DSC and TGA, and the data derived are presented in Table IV. The copolymers of B-2, P-2, and D-2 exhibit an endothermic melting point absorption T_m between 348 and 366°C, whereas other copolymers do not. This demonstrates that, with a symmetric 2,6-naphthalate amide structure in the polyimide, the fine structure of the copolymer becomes tighter than that encountered with a nonsymmetric 1,4-naphthalate amide structure and therefore easily assumes a crystalline morphology. Besides, given the benzoic and heterocyclic ring structure of polyimide, or the naphthalate and amide-imide structure of copolymers, these polymers have excellent thermooxidative stability and also show high glass transi-

tion temperatures. The glass transition temperatures of the three polyimides *B*, *P*, *D* range from 308 to 347°C. Polyimide *P* has the highest glass transition temperature (T_g) among these three polyimides. Also, polyimide *D* has a higher T_g than *B* owing to its polar sulfonyl structure. The glass transition temperatures of copolymers are in the range of 223 to 312°C and decrease as the amide content increases, since the incorporation of amide into the polyimide backbone can increase the flexibility of the copolymer chain and, hence, decrease the glass transition temperatures of copolymers. The relationship between glass transition temperatures and imide content is shown in Figure 4.

Additionally, the copolymer with the symmetric 2,6-naphthalate amide structure has a higher T_g than the one with the 1,4-naphthalate amide structure. It is believed that the copolymer with the 1,4-naphthalate amide structure is nonsymmetric (i.e., it possesses more free volume), which means that its molecular chain is more easily rotated, resulting in a lower T_g .

Figures 5–8 show the heat-weight loss of copolymers in the P-1 and P-2 series, and Table V summarizes the thermogravimetric data for all of the polymers. As indicated in the table, all

Table III Solubility of Polymers

Solubility of Polymer ^a									
Polymer			Solvent ^b						
Code	Imide Content (%)	Amide Content (%)	Concentrated Sulfuric Acid	NMP	DMF	DMAc	DMAc + 5% LiCl	DMSO	Py
PI-B	100	—	++	+	—	—	+—	+—	—
PI-P	100	—	++	+	—	—	—	—	—
PI-D	100	—	++	++	+—	+—	+	+—	—
PA-1	—	100	++	++	++	++	++	++	+
PA-2	—	100	++	++	++	++	++	++	+—
B1-1	56.2	43.8	++	++	+	++	++	++	+—
B1-2	71.9	28.1	++	++	+	+	+	++	—
B1-3	79.3	20.7	++	++	+	+—	+	++	—
B1-4	83.7	16.3	++	++	+—	—	+	++	—
B2-1	56.2	43.8	++	++	+—	+—	+—	+	—
B2-2	71.9	28.1	++	+	—	—	+—	+—	—
B2-3	79.3	20.7	++	+	—	—	—	+—	—
B2-4	83.7	16.3	++	+	—	—	—	—	—
P1-1	50.1	49.9	++	++	+	+—	+	+	—
P1-2	66.8	33.2	++	++	+—	+—	+	+	—
P1-3	75.1	24.9	++	++	+—	—	—	+	—
P1-4	80.1	19.9	++	+	+—	—	—	+—	—
P2-1	50.1	49.9	++	+	—	—	+—	+	—
P2-2	66.8	33.2	++	+	—	—	+—	+—	—
P2-3	75.1	24.9	++	+	—	—	+—	+—	—
P2-4	80.1	19.9	++	+	—	—	+—	—	—
D1-1	57.9	42.1	++	++	+	+	++	++	+
D1-2	73.34	26.7	++	++	+	+	++	++	—
D1-3	80.5	19.5	++	++	+	+	+	+	—
D1-4	84.6	15.4	++	++	+	+	+	+	—
D2-1	57.9	42.1	++	++	+	+	+	++	—
D2-2	73.3	26.7	++	++	+—	+	+	+	—
D2-3	80.5	19.5	++	++	+—	+—	+	+	—
D2-4	84.6	15.4	++	++	+—	+—	+	+	—

^a Solubility: (++) Soluble at room temperature; (+) 80°C soluble; (+—) 80°C partially soluble; (—) 80°C insoluble.

^b DMF (*N,N*-dimethylformamide); DMAc (*N,N*-dimethylacetamide); NMP (*N*-methyl-2-pyrrolidone); DMSO (dimethyl sulfoxide); Py (pyridine).

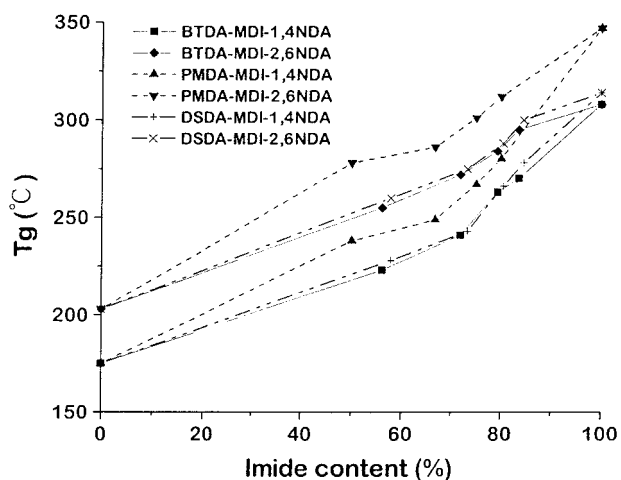
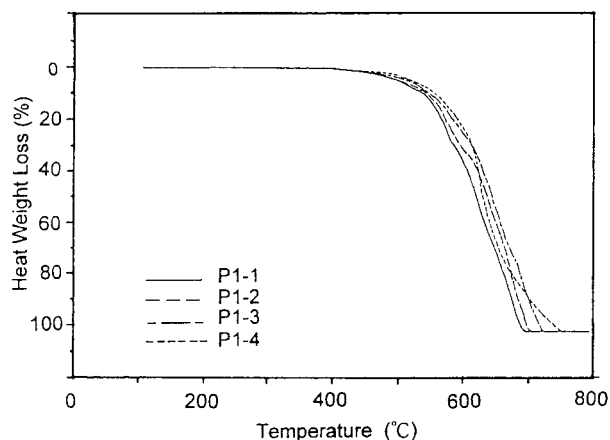
the polymers possess good thermal and thermo-oxidative stability, with no significant weight loss up to temperatures of about 360°C in nitrogen and in air atmospheres. Moreover, the polyimides *P* and *B* have the best thermal stability and 10% weight loss properties: 585 and 576°C, respectively. The decomposition temperatures at 10% weight loss of these copolymers range from 485 to 549°C in air and from 465 to 564°C in nitrogen. With increasing amide content, the 10% weight loss temperature is lowered. This suggests that the amide linkage contributes less thermooxidative stability than that of imide. In addition, copolymers with symmetric 2,6-naphthalate amide structures do not manifest better

heat resistance than those with 1,4-naphthalate amide structures. This unanticipated finding implies that heat resistance is not greatly related to crystallinity.

Although, in general, the decomposition temperature of the polymers is higher in nitrogen than in air, some copolymers (Table V) have higher decomposition temperatures in air. It is believed that some copolymers chemically combine with oxygen molecules during the heat-treating process, which results in increased weight rather than degradation, therefore, the degradation temperature is higher. Nevertheless, from the TGA, the degradation rate is faster in air, especially at higher temperature.

Table IV Thermal Properties of Polymers

Code	Polymer	T_g^a (°C)	T_m^b (°C)	Imide Content (%)	Amide Content (%)
PI-B	BTDA-MDI	308		100	—
PI-P	PMDA-MDI	347		100	—
PI-D	DSDA-MDI	314		100	—
PA-1	1,4-NDA-MDI	175		—	100
PA-2	2,6-NDA-MDI	203	324	—	100
B1-1	BTDA-MDI-1,4NDA (1-2-1)	223		56.2	43.8
B1-2	BTDA-MDI-1,4NDA (2-3-1)	241		71.9	28.1
B1-3	BTDA-MDI-1,4NDA (3-4-1)	263		79.3	20.7
B1-4	BTDA-MDI-1,4NDA (4-5-1)	270		83.7	16.3
B2-1	BTDA-MDI-2,6NDA (1-2-1)	255	358	56.2	43.8
B2-2	BTDA-MDI-2,6NDA (2-3-1)	272	350	71.9	28.1
B2-3	BTDA-MDI-2,6NDA (3-4-1)	284	355	79.3	20.7
B2-4	BTDA-MDI-2,6NDA (4-5-1)	295	353	83.7	16.3
P1-1	PMDA-MDI-1,4NDA (1-2-1)	238		50.1	49.9
P1-2	PMDA-MDI-1,4NDA (2-3-1)	249		66.8	33.2
P1-3	PMDA-MDI-1,4NDA (3-4-1)	267		75.1	24.9
P1-4	PMDA-MDI-1,4NDA (4-5-1)	280		80.1	19.9
P2-1	PMDA-MDI-2,6NDA (1-2-1)	278	360	50.1	49.9
P2-2	PMDA-MDI-2,6NDA (2-3-1)	286	363	66.8	33.2
P2-3	PMDA-MDI-2,6NDA (3-4-1)	301	362	75.1	24.9
P2-4	PMDA-MDI-2,6NDA (4-5-1)	312	366	80.1	19.9
D1-1	DSDA-MDI-1,4NDA (1-2-1)	228		57.9	42.1
D1-2	DSDA-MDI-1,4NDA (1-2-1)	243		73.3	26.7
D1-3	DSDA-MDI-1,4NDA (1-2-1)	266		80.5	19.5
D1-4	DSDA-MDI-1,4NDA (1-2-1)	278		84.6	15.4
D2-1	DSDA-MDI-2,6NDA (1-2-1)	260	348	57.9	42.1
D2-2	DSDA-MDI-2,6NDA (1-2-1)	275	351	73.3	26.7
D2-3	DSDA-MDI-2,6NDA (1-2-1)	288	356	80.5	19.5
D2-4	DSDA-MDI-2,6NDA (1-2-1)	300	354	84.6	15.4

^a Glass transition temperature.^b Endothermic melting point absorption.**Figure 4** The relationship between glass transition temperatures and imide content.**Figure 5** The heat-weight loss of copolymers (P1 series) in air.

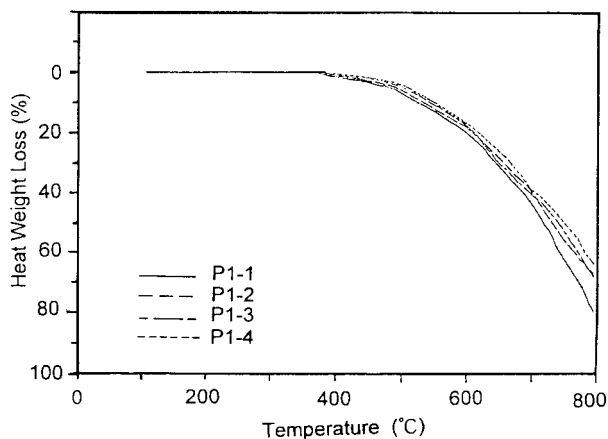


Figure 6 The heat-weight loss of copolymers (P1 series) in nitrogen.

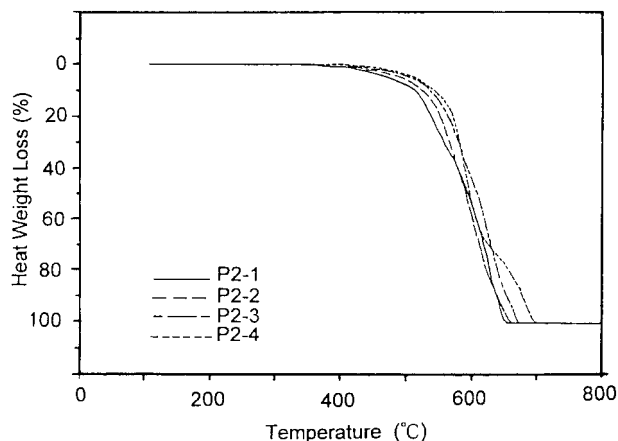


Figure 7 The heat-weight loss of copolymers (P2 series) in air.

Table V Decomposition Temperature of Polymers

Code	Polymer	Degradation Temperature		Imide Content (%)	Amide Content (%)
		Air (°C)	N ₂ (°C)		
PI-B	BTDA-MDI	570	577	100	—
PI-P	PMDA-MDI	575	583	100	—
PI-D	DSDA-MDI	552	560	100	—
PA-1	1,4NDA-MDI	373	413	—	100
PA-2	2,6NDA-MDI	380	407	—	100
B1-1	BTDA-MDI-1,4NDA (1-2-1)	519	555	56.2	43.8
B1-2	BTDA-MDI-1,4NDA (2-3-1)	523	557	71.9	28.1
B1-3	BTDA-MDI-1,4NDA (3-4-1)	530	560	79.3	20.7
B1-4	BTDA-MDI-1,4NDA (4-5-1)	534	564	83.7	16.3
B2-1	BTDA-MDI-2,6NDA (1-2-1)	515	520	56.2	43.8
B2-2	BTDA-MDI-2,6NDA (2-3-1)	518	538	71.9	28.1
B2-3	BTDA-MDI-2,6NDA (3-4-1)	532	545	79.3	20.7
B2-4	BTDA-MDI-2,6NDA (4-5-1)	549	562	83.7	16.3
P1-1	PMDA-MDI-1,4NDA (1-2-1)	522	525	50.1	49.9
P1-2	PMDA-MDI-1,4NDA (2-3-1)	526	530	66.8	33.2
P1-3	PMDA-MDI-1,4NDA (3-4-1)	531	537	75.1	24.9
P1-4	PMDA-MDI-1,4NDA (4-5-1)	536	539	80.1	19.9
P2-1	PMDA-MDI-2,6NDA (1-2-1)	513	518	50.1	49.9
P2-2	PMDA-MDI-2,6NDA (2-3-1)	519	526	66.8	33.2
P2-3	PMDA-MDI-2,6NDA (3-4-1)	528	534	75.1	24.9
P2-4	PMDA-MDI-2,6NDA (4-5-1)	537	553	80.1	19.9
D1-1	DSDA-MDI-1,4NDA (1-2-1)	485	465	57.9	42.1
D1-2	DSDA-MDI-1,4NDA (1-2-1)	487	467	73.3	26.7
D1-3	DSDA-MDI-1,4NDA (1-2-1)	492	468	80.5	19.5
D1-4	DSDA-MDI-1,4NDA (1-2-1)	496	472	84.6	15.4
D2-1	DSDA-MDI-2,6NDA (1-2-1)	501	466	57.9	42.1
D2-2	DSDA-MDI-2,6NDA (1-2-1)	505	475	73.3	26.7
D2-3	DSDA-MDI-2,6NDA (1-2-1)	508	483	80.5	19.5
D2-4	DSDA-MDI-2,6NDA (1-2-1)	517	485	84.6	15.4

^a Heating rate equals 20°C/min measured by TGA (10% weight loss temperature).

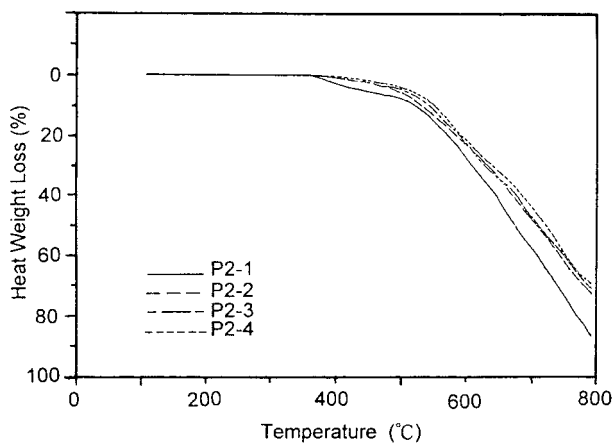


Figure 8 The heat-weight loss of copolymers (P2 series) in nitrogen.

Wide-Angle X-ray Diffraction of Polymers

The X-ray patterns of some representative P1 and P2 copolymer series are shown in Figures 9 and 10. Diffraction patterns of copolymers in the B-2, P-2, and D-2 series with symmetric 2,6-naphthalate amide structures reveal a partial crystalline structure; others with a nonsymmetric 1,4-naphthalate amide structure do not. The P-2 co-

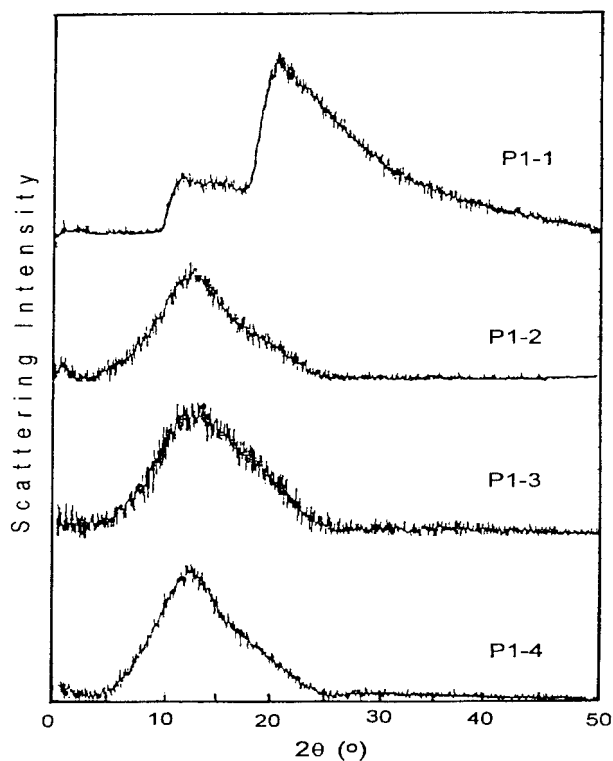


Figure 9 X-ray patterns of copolymers (P1 series).

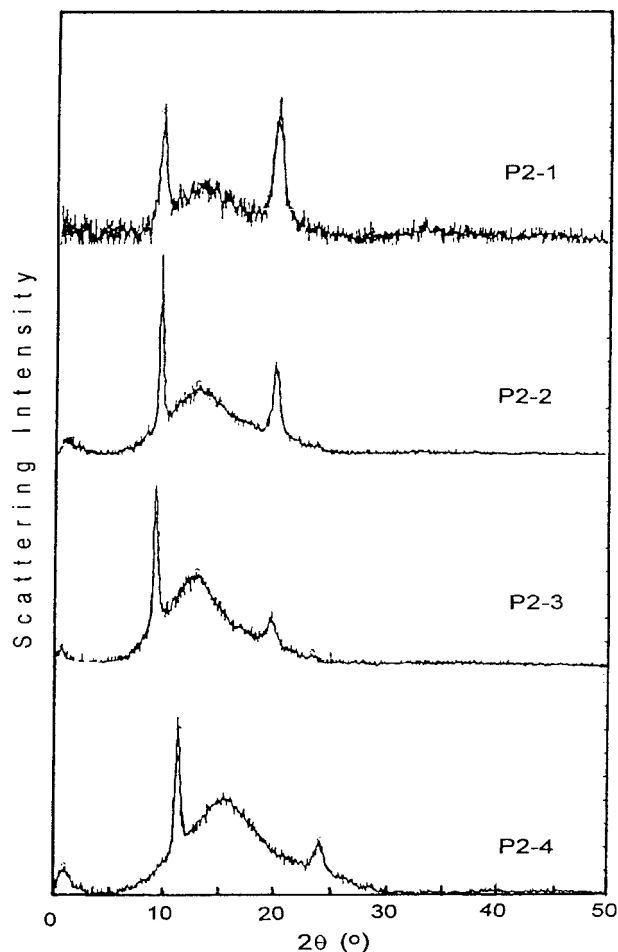


Figure 10 X-ray patterns of copolymers (P2 series).

polymer exhibits a scattering peak at $2\theta = 12^\circ$, 21° . Since the diffraction peaks of these copolymers are more pronounced as the amide content increases, these peaks are believed to represent the scattering of the amide chain in the copolymer. These results seem to be consistent with those found in the DSC melting point measurements.

Mechanical Properties

The mechanical properties of all copolymers are shown in Figures 11 and 12 and listed in Table VI. The tensile strength, the breaking elongation, and the initial modulus of the polymers are 25–74 MPa, 4–9% and 0.74–1.60 GPa, respectively. Most of the polymers have high strength and modulus but medium elongation. This indicates that

Table VI Mechanical Properties of Polymers

Polymer Code	Imide Content (%)	Amide Content (%)	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
PI-B	100	—	53	7	1.14
PI-P	100	—	59	5	1.40
PI-D	100	—	57	8	1.01
PA-1	—	100	44	11	0.65
PA-2	—	100	15	9	0.79
B1-1	56.2	43.8	48	9	0.86
B1-2	71.9	28.1	58	9	0.89
B1-3	79.3	20.7	65	7	1.05
B1-4	83.7	16.3	59	6	1.14
B2-1	56.2	43.8	35	9	0.88
B2-2	71.9	28.1	42	8	0.98
B2-3	79.3	20.7	57	7	1.08
B2-4	83.7	16.3	47	5	1.40
P1-1	50.1	49.9	45	8	0.74
P1-2	66.8	33.2	46	8	0.75
P1-3	75.1	24.9	48	7	0.94
P1-4	80.1	19.9	62	4	1.47
P2-1	50.1	49.9	40	7	0.92
P2-2	66.8	33.2	42	7	0.95
P2-3	75.1	24.9	47	6	1.21
P2-4	80.1	19.9	43	5	1.57
D1-1	57.9	42.1	58	9	0.74
D1-2	73.3	26.7	69	7	0.95
D1-3	80.5	19.5	74	6	1.17
D1-4	84.6	15.4	70	5	1.41
D2-1	57.9	42.1	25	7	1.11
D2-2	73.3	26.7	50	5	1.50
D2-3	80.5	19.5	55	5	1.57
D2-4	84.6	15.4	54	4	1.60

the polymers form tough material. Figure 11 shows the relationship between tensile strength and imide content. The tensile strength of copolymers is higher than that of polyimides at low amide content, but the strength drops sharply as the amide content increases. It is believed that, although the introduction of the naphthalate amide structure into the polyimide chain can increase the solubility of copolymers during polymerization, the molecular weight is not greatly increased because of the lessened reactivity of naphthalene dicarboxylic acid with the isocyanate group. The mechanical properties are relatively poor as compared with our previous polyamide-imide modified by poly[*m*-phenylene isophthalamide (PmIA)] prepolymer.¹³ Nevertheless, the hydrogen bonding of the naphthalate amide group in imide can enhance the intermolecular force of a copolymer and thus increase its tensile strength initially. But, as the amide content increases, the formation of a crystalline structure in the copoly-

mer can cause a weak point in the material, which can easily propagate and reduce the tensile strength sharply. In addition, copolymers with symmetric 2,6-naphthalate amide structures appear to have higher modulus but less strength and elongation. These copolymers of B-2, P-2, and D-2 are therefore brittle materials.

The breaking elongation of copolymers increases with the amount of amide but decreases with the presence of a symmetric, partial crystalline structure. In contrast, the initial modulus of all copolymers decreases with the amide content but increases with the degree of crystallinity. This indicates that the introduction of symmetric naphthalate amide into polyimide by copolymerization promotes the formation of crystalline structure and therefore increases the modulus.

CONCLUSIONS

In this article, we described one-step method to synthesize 3 polyimides, 2 naphthalate-con-

taining polyamides, and 24 naphthalate-containing copoly(amide-imide)s. The copoly(amide-imide)s show an improvement in solubility but only a small increase in molecular weight owing to the limited reactivity of naphthalene dicarboxylic acid with the isocyanate group. The inherent viscosity of these polymers is 0.53–0.96 dL/g, and the polymers can be cast into a transparent and flexible film. The tensile strength and breaking elongation of these copolymer films are better than those of polyimides, except for those copoly(amide-imide)s with symmetric, partially crystalline structures. In contrast, the modulus of crystalline copolymers is higher than that of polyimides because of their tight morphological structure. During thermal analysis, copolymers of B-2, P-2, and D-2 demonstrated an endothermic melting point absorption, but other copolymers did not. The glass transition temperatures of copolymers are lower than those of pure polyimides in view of the less stable amide linkage. On the basis of X-ray diffraction patterns, some copolymers with symmetric 2,6-naphthalate amide structures appear to have crystalline morphologies, which is a finding consistent with the results obtained through DSC melting point measurements.

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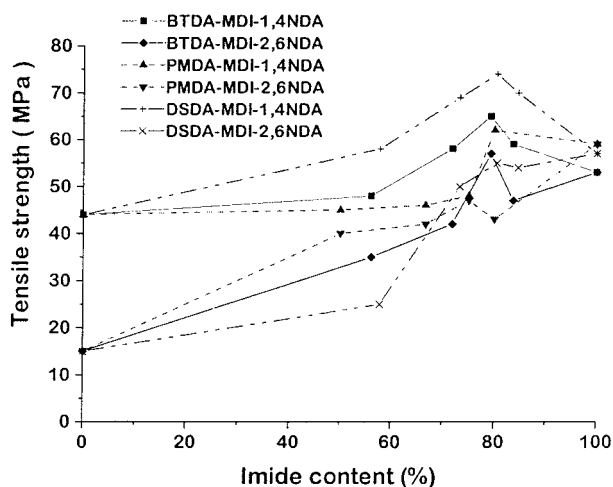


Figure 11 The relationship between tensile strength and the imide content of the copolymers.

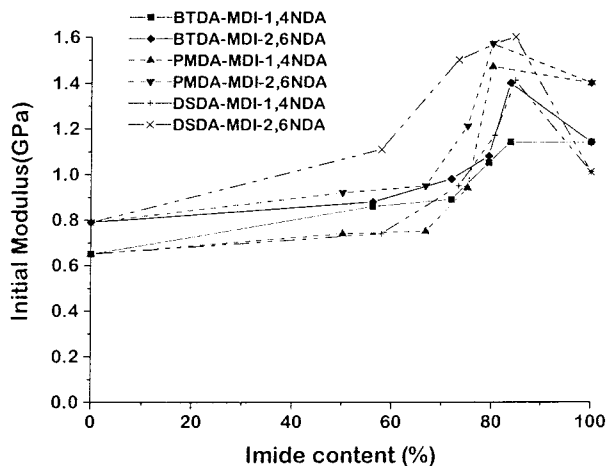


Figure 12 The relationship between tensile modulus and the imide content of the copolymers.

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