Synthesis of Thermostable Nomex Copoly(amide–imide) and Their Properties

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SYNOPSIS

Thermostable Nomex copoly(amide–imide)s with inherent viscosity of 0.72–1.31 dL/g were synthesized by reacting diacid-terminated Nomex prepolymer with various diisocyanate-terminated polyimide prepolymers. The polyimide prepolymer was 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 in order to improve their solubility. The copolymers, except B-1, P-1, P-2, D-1, and D-2, could be dissolved in N,N-dimethylacetamide +5% lithium chloride at room temperature or dimethyl sulfoxide at high temperature but were not soluble in N,N-dimethylformamide or pyridine. The solubility is considered to be related to their crystallinity. Those copolymers with crystalline structure displayed poor solubility. All the Nomex copoly(amide–imide)s had glass transition temperatures in the range of 223–352°C and showed a 10% weight loss temperature of 438–574°C in air and 441–585°C in nitrogen atmosphere. The tensile strength, elongation at break, and initial modulus of polymer films ranged 63–118 MPa, 4–9% and 1.67–2.53 GPa, respectively. From the X-ray diffraction studies, copolymers of B-1, P-1, P-2, D-1, and D-2 with high content of PmIA showed a crystalline structure, but the others only displayed an amorphous morphology. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimide has been known as one of the best materials for use in high temperature application.[1-3] This is due to its aromatic and heterocyclic structure. Polyimides can resist 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 due to its poor solubility.[7-10] In our previous studies,[11,12] we employed the diamine-terminated poly(m-phenylene isophthalamide (PmIA) prepolymer (Nomex prepolymer) to modify the polyimides. It improved the solubility, mechanical properties, and processing characteristics of the copolymers; but, due to the urea linkage in the copolymer chain, it resulted in poor heat re-

sistance. In this paper, we used a diacid-terminated, instead of a diamine-terminated, PmIA prepolymer to modify the polyimide, and better thermal properties were therefore expected.
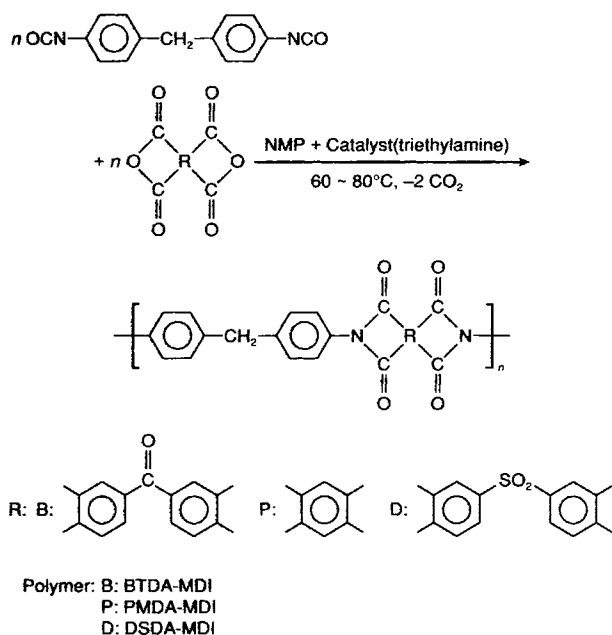
EXPERIMENTAL

Materials

Three kinds of commercially available dianhydrides, that is, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 3,3',4,4'-sulfonyl diphthalic anhydride (DSDA) were dried under vacuum at −40°C for 4 h in order to remove possible moisture. The 4,4'-diphenylmethane diisocyanate (MDI) was used without further purification. m-Aminobenzoic acid (MABA) and isophthaloyl dichloride (IPC), which were employed to synthesize a diacid-terminated PmIA prepolymer, were of high purity and used as received from the manufacturer. Sol-

vents 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.
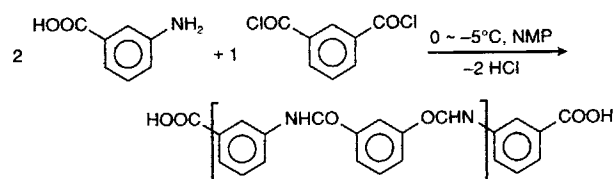
Synthesis of Aromatic Polyimide[13]

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 1.5 h. The catalyst, 0.03 g/L of triethylamine, was then added, and the temperature was raised to 80°C. The viscosity was found to gradually increase, and bubbles of gas (carbon dioxide) evolved. The viscosity was adjusted by adding solvent. The reaction was completed after 1 h. A golden viscous solution of polyimide was obtained. The reaction [1] is shown as follows:

$$n\ OCN\!-\!\!\bigcirc\!\!-\!CH_2\!-\!\!\bigcirc\!\!-\!NCO$$

$$+\ n\ \text{(dianhydride)}\quad \xrightarrow[\;60\sim80°C,\ -2\ CO_2\;]{\text{NMP + Catalyst(triethylamine)}}$$

(polyimide structure)

R: B: (benzophenone structure)   P: (phenyl structure)   D: (diphenyl sulfone structure)

Polymer: B: BTDA-MDI
P: PMDA-MDI
D: DSDA-MDI

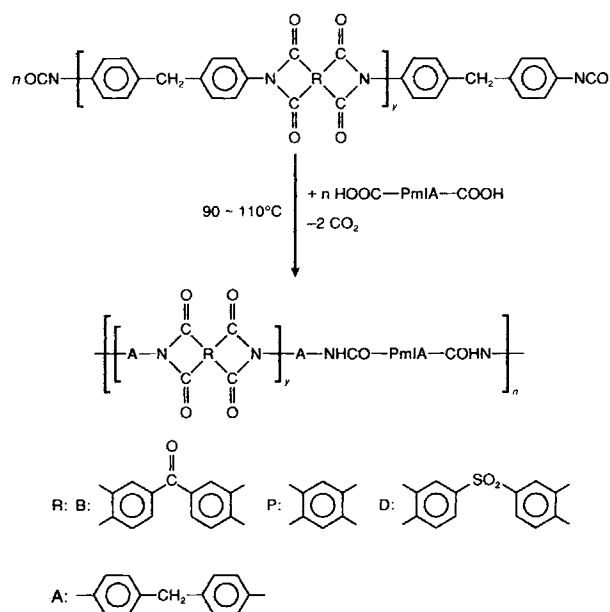### Synthesis of Diacid-terminated Nomex Prepolymer[14]

Low molecular weight of diacid-terminated Nomex prepolymer (PmIA) was prepared by a low-temperature polymerization method. The MABA was firstly dissolved in NMP, and the solution cooled to 0 ~ −5°C. The IPC (molar ratio MABA/IPC = 2/1) 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 [2] is shown as follows:

$$2\ HOOC\!-\!\!\bigcirc\!\!-\!NH_2\ +1\ ClOC\!-\!\!\bigcirc\!\!-\!COCl\ \xrightarrow[\;-2\ HCl\;]{0\sim-5°C,\ NMP}$$

$$HOOC\!-\!\Big[\bigcirc\!-\!NHCO\!-\!\bigcirc\!-\!OCHN\Big]\!-\!\bigcirc\!-\!COOH$$

Synthesis of Nomex Copoly(amide–imide)[15]

The Nomex copoly(amide–imide) was synthesized by initial preparation of diisocyanate-terminated polyimide prepolymer with excess of MDI in [1]. The diacid-terminated Nomex prepolymer was then added to the reaction flask, which contained the diisocyanate polyimide prepolymer (theoretical mol wt of Nomex prepolymer is 404) 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 there to react for another hour. A pale golden viscous solution was obtained. The reaction [3] is shown as follows:

$$n\ OCN\!-\!\Big[\bigcirc\!-\!CH_2\!-\!\bigcirc\!-\!N(\text{imide})N\!-\!\bigcirc\!-\!CH_2\!-\!\bigcirc\Big]_y\!-\!NCO$$

$$\xrightarrow[\;90\sim110°C\;]{+\ n\ HOOC-PmIA-COOH,\ -2\ CO_2}$$

(copoly(amide–imide) structure)

R: B: (benzophenone structure)   P: (phenyl structure)   D: (diphenyl sulfone structure)

A: $-\bigcirc\!-\!CH_2\!-\!\bigcirc-$

Measurements

Infrared (IR) spectra of polyimides and Nomex copoly(amide–imide) were obtained by a Hitachi Model 260-50 type, over a range of 250 to 4000 cm^{-1}. The samples were in a form of film about 10 μm
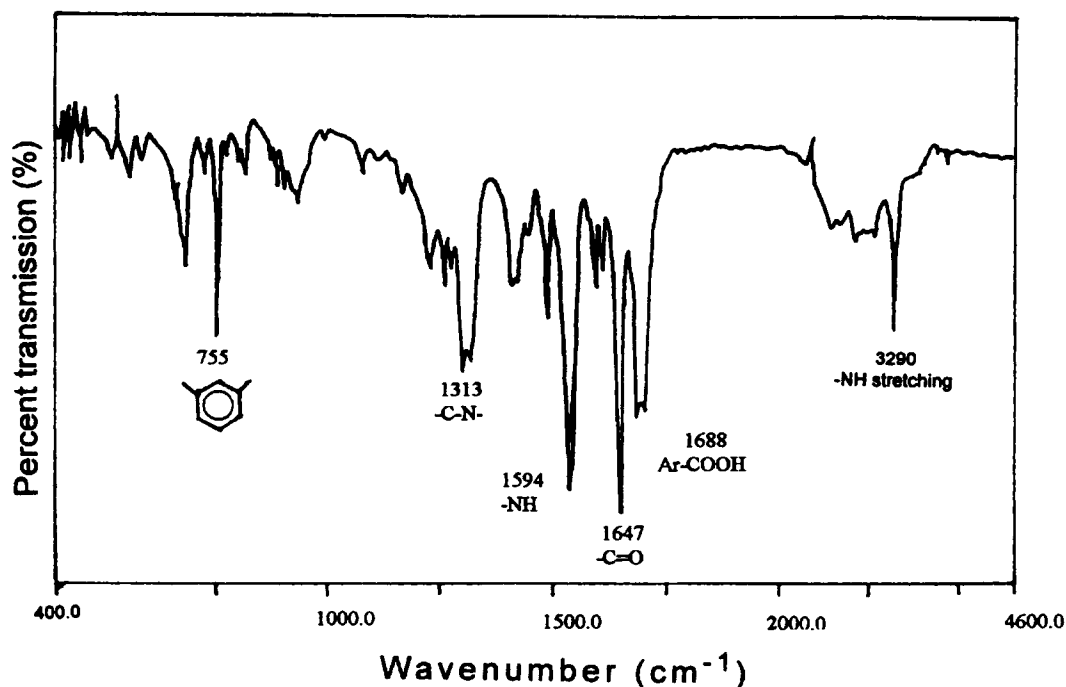
Figure 1 The IR spectrum of diacid-terminated Nomex prepolymer.

thickness. Elemental analysis (C, H, N) was performed by Perkin-Elmer 2400 Analyzer.

Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed using a Du Pont 9900 DSC and Seiko SSC-5000 type TGA at a heating rate of 20°C/min under 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 Cuk$_\alpha$ radiation using a Rigaku D/max-II type X-ray diffractometer. All stress–strain data were obtained on an Instron 1122 type testing in-

Table I   The Inherent Viscosity of Polymers

Code	Polymer	η_{inh} (dL/g)	Imide Content (%)	Amide Content (%)
B	BTDA-MDI	0.90	100	—
B-1	BTDA-MDI-PmIA (1-2-1)	1.12	61.9	38.1
B-2	BTDA-MDI-PmIA (2-3-1)	1.02	73.9	26.1
B-3	BTDA-MDI-PmIA (3-4-1)	1.08	80.2	19.8
B-4	BTDA-MDI-PmIA (4-5-1)	1.18	84.1	15.9
P	PMDA-MDI	0.72	100	—
P-1	PMDA-MDI-PmIA (1-2-1)	1.05	57.7	42.3
P-2	PMDA-MDI-PmIA (2-3-1)	0.98	69.8	30.2
P-3	PMDA-MDI-PmIA (3-4-1)	0.92	76.5	23.5
P-4	PMDA-MDI-PmIA (4-5-1)	1.23	80.8	19.2
D	DSDA-MDI	0.85	100	—
D-1	DSDA-MDI-PmIA (1-2-1)	1.21	63.2	36.8
D-2	DSDA-MDI-PmIA (2-3-1)	1.16	75.1	24.9
D-3	DSDA-MDI-PmIA (3-4-1)	1.11	81.2	18.8
D-4	DSDA-MDI-PmIA (4-5-1)	1.31	84.9	15.1
PI	Polyimide fiber	0.96	—	—

strument at an extension rate of 10 mm/min, with the specimen of 50 mm length, 10 mm width, and 0.5 mm thickness.

RESULTS AND DISCUSSION

Nomex Prepolymer Syntheses

Diacid-terminated poly(m-phenylene isophthalamide) (Nomex) prepolymer was prepared from m-aminobenzoic acid and isophthaloyl dichloride (IPC) (molar ratio 2/1). The molecular weight of PmIA prepolymer was theoretically 404. From the results of elemental analysis, it showed that the found values were in good agreement with the calculated ones. The IR spectrum of diacid-terminated Nomex prepolymer (Fig. 1) exhibited the — NH stretching vibrations of amide group at 3290 cm^{-1}, the characteristic benzoic acid group absorption (Ar-COOH) at 1688 cm^{-1}, and the benzene ring absorption at
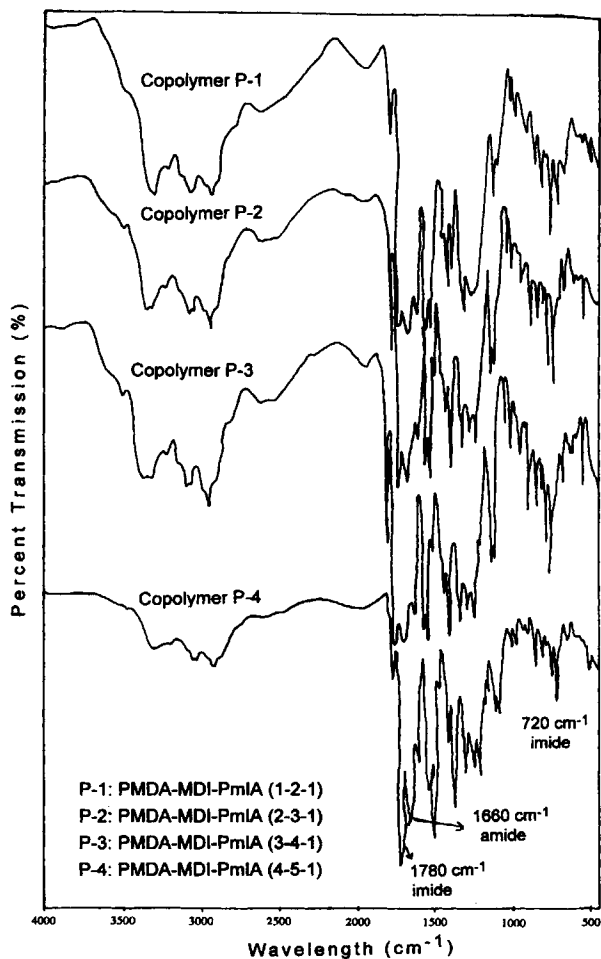

Figure 2 The IR spectra of P series copolymers.

Table II   Elemental Analysis of Polymers

| | Elemental Analysis (%) | | |
Code	C%	H%	N%
B			
Calcd.	74.38	3.33	5.78
Found	74.05	3.64	6.11
B-1			
Calcd.	74.28	4.03	7.99
Found	73.15	4.63	8.54
B-2			
Calcd.	74.31	3.81	7.30
Found	74.08	4.12	8.03
B-3			
Calcd.	74.32	3.69	6.93
Found	72.91	4.21	8.03
B-4			
Calcd.	74.33	3.62	6.71
Found	73.12	4.01	7.53
P			
Calcd.	72.25	3.79	7.33
Found	72.01	4.15	7.89
P-1			
Calcd.	73.56	4.04	8.88
Found	72.84	4.82	9.51
P-2			
Calcd.	73.30	3.80	8.44
Found	72.44	4.73	9.02
P-3			
Calcd.	73.15	3.66	8.20
Found	71.63	4.12	8.12
P-4			
Calcd.	73.05	3.57	8.05
Found	71.89	4.01	8.31
D			
Calcd.	66.92	3.10	5.38
Found	66.84	4.11	6.22
D-1			
Calcd.	70.71	3.89	7.73
Calcd.	69.49	4.84	7.80
D-2			
Found	69.48	3.64	6.97
Calcd.	69.01	4.31	7.13
D-3			
Found	68.85	3.50	6.58
Calcd.	67.12	4.05	7.01
D-4			
Found	68.47	3.43	6.35
Found	67.98	3.98	7.29

755 cm^{-1}. These supported the formation of diacid-terminated Nomex prepolymer.

EXP: $C_{22}H_{16}N_2O_6$: Calcd: C:65.34%; H:3.99%; N: 6.96%

Found: C:64.74%; H:4.41%; N:7.08%

Synthesis of Polyimide and Nomex Copoly(amide–imide)

4,4'-Diphenylmethane diisocyanate and three kinds of aromatic dianhydride were used to prepare three polyimides. Twelve copolymers were synthesized from four different molar ratios of MDI, three kinds of dianhydride, and diacid-terminated Nomex prepolymer. The inherent viscosities of polyimide and Nomex copoly(amide–imide) are listed in Table I. It was found that the intrinsic viscosity of polymers was higher than 0.72. Specifically, the copolymers had the value of more than 0.92, indicating a high molecular weight copolymer obtained. In the table, the content of the imide and amide groups in the copolymer was also calculated. These polymers could be cast into transparent, tough, and flexible films. Figure 2 shows the IR spectra of copolymer P series; the characteristic absorption at 1720, 1780, 1360, and 720 cm^{-1}, indicates the existence of the imide group. Moreover, the absorption peak of 1660 and 3300–3400 cm^{-1} demonstrates the —NH stretching vibration of amide group. Besides, there is no further absorption at 1680–1700 cm^{-1}, indicating no existence of benzoic acid group. From that, we could conclude 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.

The Solubility Properties of Polymers

Table III summarizes the solubility of the polymers. As indicated in the table, the three polyimides could be dissolved in sulfuric acid at room temperature, or in NMP at 80°C, but only partially dissolved in DMAc, DMAc + 5% LiCl, and DMSO at heated temperature. In general, the copolymers had better solubility than the homopolyimides. The copolymers, except B-1, P-1, P-2, D-1, and D-2, could be dissolved in DMAc +5% LiCl at room temperature or DMSO at heated temperature but were not soluble in DMF or pyridine. The solubility is therefore considered to be related to their crystallinity. Copolymers of B-1, P-1, P-2, D-1, and D-2 with crystalline structure as shown by X-ray diffraction pattern displayed poor solubility. It is believed that the crystalline region of the copolymer is structurally so tight that the solvent molecules are not able to penetrate into the region; thus, the solubility is poor. From that, it could be concluded that the addition of PmIA in the polyimide chain did increase their solubility, except those copolymers with crystalline structure.

Table III   Solubility of Polymers^a

Code	Polymer	Concentrated Sulfuric Acid	NMP	DMF	DMAc	DMAc+ 5% LiCl	DMSO	Pyridine
B	BTDA-MDI	++	+	−	+−	+−	+−	−
B-1	BTDA-MDI-PmIA (1-2-1)	++	++	−	+−	+	+−	−
B-2	BTDA-MDI-PmIA (2-3-1)	++	++	+−	+	++	+−	+−
B-3	BTDA-MDI-PmIA (3-4-1)	++	++	−	+	+	+	−
B-4	BTDA-MDI-PmIA (4-5-1)	++	++	−	+−	+	+−	−
P	PMDA-MDI	++	+	−	−	+−	−	−
P-1	PMDA-MDI-PmIA (1-2-1)	++	+	−	+−	+−	−	−
P-2	PMDA-MDI-PmIA (2-3-1)	++	+	−	−	+−	+−	−
P-3	PMDA-MDI-PmIA (3-4-1)	++	++	+−	+−	+	+−	−
P-4	PMDA-MDI-PmIA (4-5-1)	++	++	−	+−	+	+−	−
D	DSDA-MDI	++	++	+−	+−	+	+−	−
D-1	DSDA-MDI-PmIA (1-2-1)	++	++	+−	+−	+	+−	−
D-2	DSDA-MDI-PmIA (2-3-1)	++	++	+−	+−	+	+−	−
D-3	DSDA-MDI-PmIA (3-4-1)	++	++	+−	+	++	+	+−
D-4	DSDA-MDI-PmIA (4-5-1)	++	++	+−	+	+	+	−

^{a} Solubility: ++, Soluble in room temperature; +−, 80°C partially soluble; +, 80°C soluble; −, 80°C insoluble.
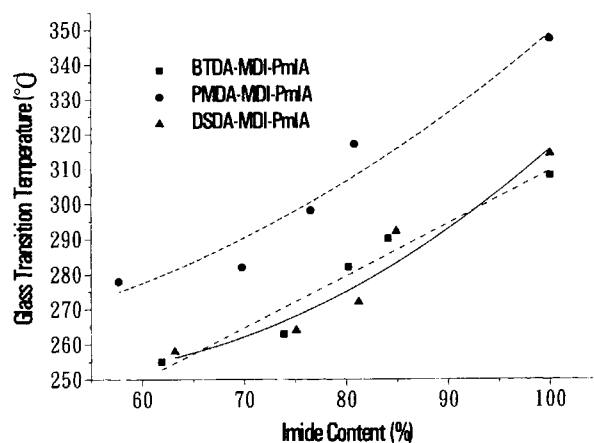^{b} NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; DMSO: Dimethyl sulfoxide, Py: Pyridine.
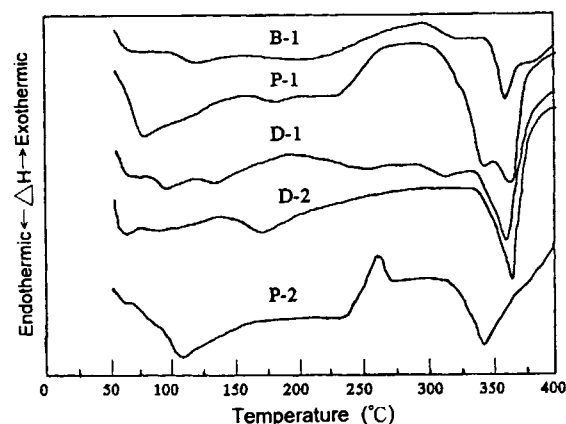
Figure 3 The first heating cycle DSC curves of some copolymers.

Figure 4 The relationship between T_g and imide content.

The Thermal Properties of Polymers

The thermal properties of all polymers were evaluated by DSC and TGA. The first heating cycles of DSC of some copolymers (B-1, P-1, P-2, D-1, and D-2) are shown in Figure 3, and the thermal behavior of all polymers are listed in Table IV. In Figure 3, it was found that copolymers of B-1, P-1, P-2, D-1, and D-2 exhibited an endothermic melting point absorption between 334–366°C. Nevertheless, other copolymers did not. This demonstrates that, with the PmIA present in the polyimide, the fine structure of copolymer becomes more tight and therefore easily forms a crystalline structure. Besides, with the presence of benzoic and heterocyclic ring structure

of polyimide, or the benzoic ring and amide group of PmIA in copolymers, these polymers had excellent thermooxidative stability and also showed high glass transition temperatures (T_g). The T_g of three polyimides (B, P, D) ranged from 308 to 347°C. Polyimide P had highest T_g among these three polyimides. Also, Polyimide D had a higher T_g than B due to its polar sulfonyl structure. The T_g of copolymers was in the range of 255–317°C and decreased with the increase amount of PmIA. This can be explained in that the incorporation of PmIA into the polyimide backbone could increase the flexibility of copolymer chain and, hence, decrease the T_g of copolymers. The relationship between T_g and imide content is shown in Figure 4.

Table IV The Thermal Properties of Polymers

Code	Polymer	T_g (°C)	T_m (°C)	Imide Content (%)	Amide Content (%)
B	BTDA-MDI	308	—	100	—
B-1	BTDA-MDI-PmIA (1-2-1)	255	355	61.9	38.1
B-2	BTDA-MDI-PmIA (2-3-1)	263	—	73.9	26.1
B-3	BTDA-MDI-PmIA (3-4-1)	282	—	80.2	19.8
B-4	BTDA-MDI-PmIA (4-5-1)	290	—	84.1	15.9
P	PMDA-MDI	347	—	100	—
P-1	PMDA-MDI-PmIA (1-2-1)	278	360	57.7	42.3
P-2	PMDA-MDI-PmIA (2-3-1)	282	334	69.8	30.2
P-3	PMDA-MDI-PmIA (3-4-1)	298	—	76.5	23.5
P-4	PMDA-MDI-PmIA (4-5-1)	317	—	80.8	19.2
D	DSDA-MDI	314	—	100	—
D-1	DSDA-MDI-PmIA (1-2-1)	258	355	63.2	36.8
D-2	DSDA-MDI-PmIA (2-3-1)	264	366	75.1	24.9
D-3	DSDA-MDI-PmIA (3-4-1)	272	—	81.2	18.8
D-4	DSDA-MDI-PmIA (4-5-1)	292	—	84.9	15.1
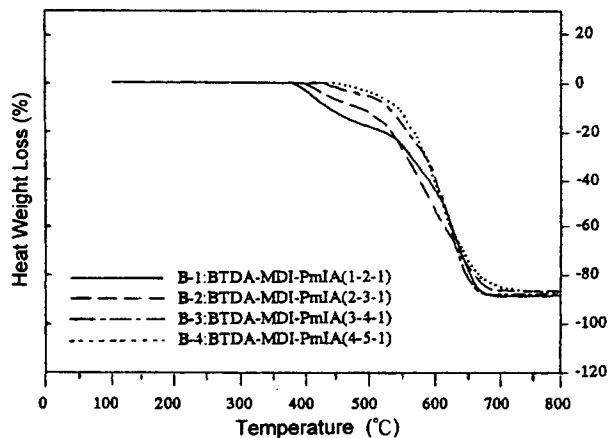
Figure 5 The heat weight loss of B series copolymers in air.
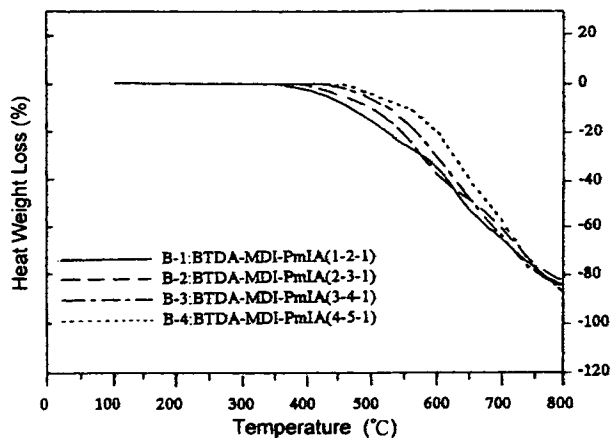
Figure 6 The heat weight loss of B series copolymers in nitrogen.

Figures 5 and 6 show the heat weight loss of the B series copolymer, and Table V also summarizes the thermogravimetric data of all polymers. As indicated in the table, all the polymers possessed good thermal and thermooxidation stability, with no significant weight loss up to temperature of approximate 360°C in nitrogen and in air atmosphere. Moreover, it was found that the polyimides P and B had the best thermal stability and 10% weight loss properties. They were 585 and 576°C, respectively. The decomposition temperatures at 10%

weight loss of these copolymers ranged 438–554°C in air and 441–578°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, comparing with our previous data of diamine-terminated PmIA modified polyimide, which contained urea linkage,[12] the 10% weight heat loss at P-1 (PMDA-MDI-PmIA = 1 : 2 : 1) was 473 and 430°C, respectively. This demonstrated that the copolymer without urea linkage did

Table V   The Decomposition Temperature of Polymers

| Code | Polymer | Decomposition Temperature[a] | | Imide Content (%) | Amide Content (%) |
		In Air (%)	In Nitrogen (%)		
B	BTDA-MDI	571	576	100	—
B-1	BTDA-MDI-PmIA (1-2-1)	445	462	61.9	38.1
B-2	BTDA-MDI-PmIA (2-3-1)	491	510	73.9	26.1
B-3	BTDA-MDI-PmIA (3-4-1)	529	538	80.2	19.8
B-4	BTDA-MDI-PmIA (4-5-1)	542	554	84.1	15.9
P	PMDA-MDI	574	585	100	—
P-1	PMDA-MDI-PmIA (1-2-1)	461	473	57.7	42.3
P-2	PMDA-MDI-PmIA (2-3-1)	511	506	69.8	30.2
P-3	PMDA-MDI-PmIA (3-4-1)	542	559	76.5	23.5
P-4	PMDA-MDI-PmIA (4-5-1)	554	578	80.8	19.2
D	DSDA-MDI	553	562	100	—
D-1	DSDA-MDI-PmIA (1-2-1)	438	441	63.2	36.8
D-2	DSDA-MDI-PmIA (2-3-1)	483	481	75.1	24.9
D-3	DSDA-MDI-PmIA (3-4-1)	528	523	81.2	18.8
D-4	DSDA-MDI-PmIA (4-5-1)	532	545	84.9	15.1

[a] Heating rate = 20°C/min, measured by TGA (10% weight loss temperature).

display a better heat resistance, i.e., the urea linkage in the copolymer could be the reason for the deterioration of the thermal stability.

Wide-angle X-ray Diffraction of Polymers

The X-ray patterns of some representative P series copolymers are shown in Figure 7. Diffraction of copolymers P-1 or P-2 appeared to be a partial crystalline structure; others did not. The P-1 copolymer exhibited a scattering peak at $2\theta = 18, 20, 24, 28$ degrees; and P-2 at $2\theta = 7, 13,$ and 20 degrees. Since the diffraction peaks of these copolymers were more pronounced as the content of PmIA increased, these peaks were believed to be the scattering of PmIA chain in the copolymer. Moreover, as shown in Figures 8 and 9, copolymers of B-1, D-1, and D-2 also exhibited partial crystalline structure. These results seemed to be consistent with those found in the DSC melting point measurements.

Mechanical Properties

The mechanical properties of the P copolymers are shown in Figure 10, and all the mechanical properties of polymers are listed in Table VI. It was found that the tensile strength, the breaking elongation, and the initial modulus of polymer was 61–118 MPa, 4–9%, and 1.67–2.53 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 11 showed the
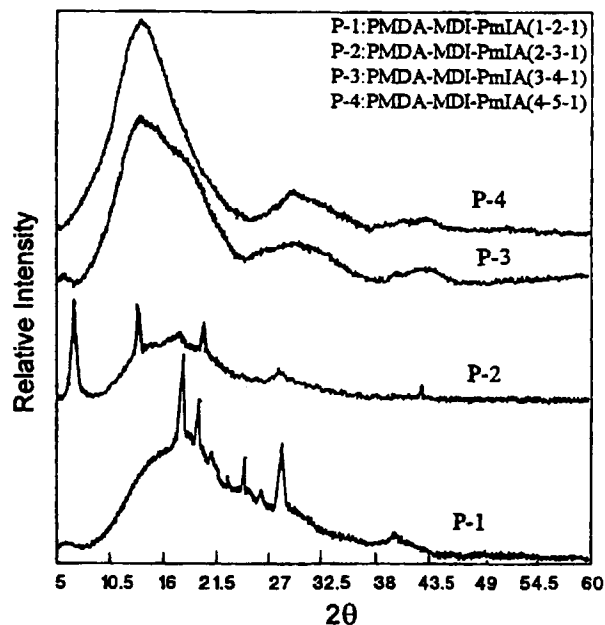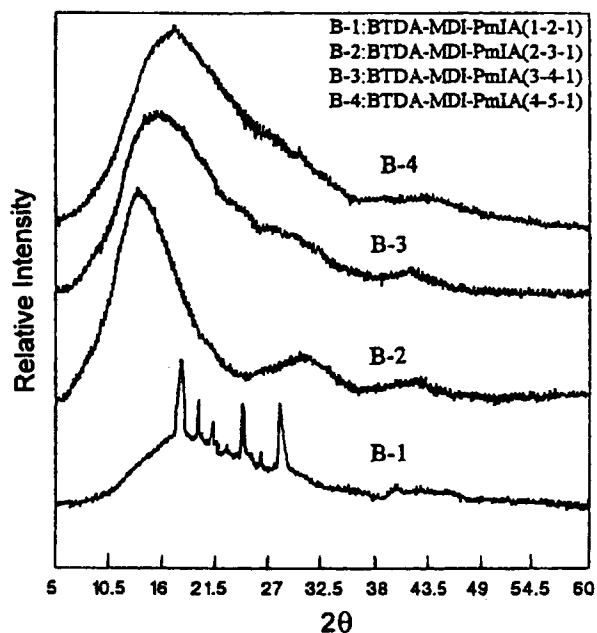

Figure 8   X-ray patterns of B series copolymers.

relationship between tensile strength and imide content. The tensile strength of copolymers were higher than that of polyimides at low PmIA content, but with more of PmIA present, the strength dropped. It was explained by the presence of a partial crystalline structure in the copolymer, as the PmIA content increased. Thus, it was believed that the introduction of meta-substitution pattern of PmIA into the polyimide chain increased the solubility of
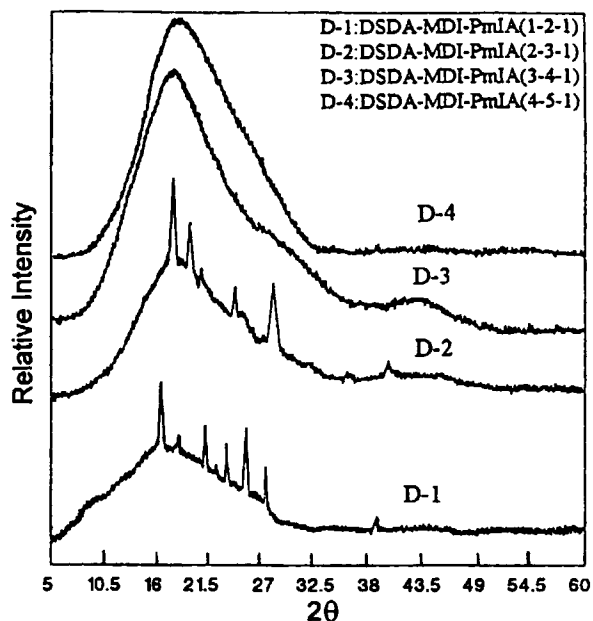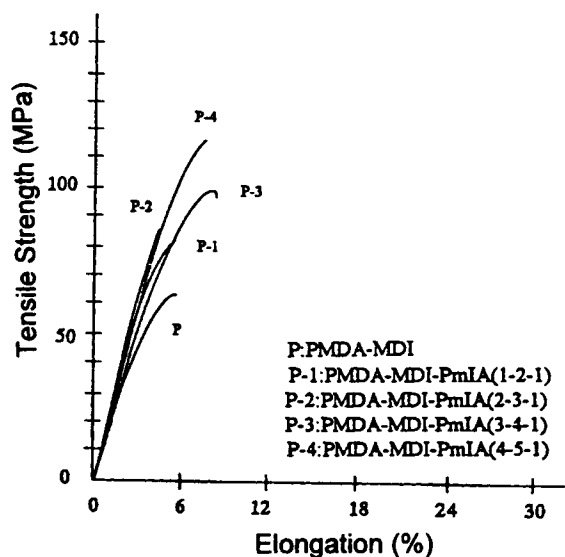

Figure 7   X-ray patterns of P series copolymers.

Figure 9   X-ray patterns of D series copolymers.

Figure 10 The relationship between tensile strength and elongation of P series polymers.

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

copolymers in the polymerization and consequently increased their molecular weight. In addition, the hydrogen bonding of amide group in PmIA could also promote the intermolecular force of copolymer and thus increase their tensile strength initially. Nevertheless, as the amide content increased, the formation of crystalline structure in the copolymer could cause a weak point in the material, which could easily propagate and therefore reduce the tensile strength. The partial crystalline copolymers of B-1, P-1, P-2, D-1, and D-2 were therefore hard and brittle materials.
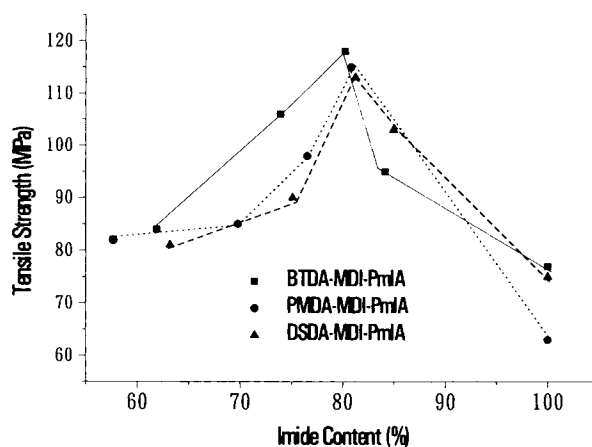
The breaking elongation of copolymers increased with the presence of PmIA, except for those of partial crystalline copolymers. In contrast, the initial modulus of those crystalline copolymers was increased with the increase of PmIA content. This indicated that the introduction of PmIA into polyimide by copolymerization could promote the formation of crystalline structure and therefore increase the modulus.

CONCLUSIONS

In this experiment, we used an one-step method to synthesize three polyimides and twelve Nomex copoly(amide–imide)s. The copoly(amide–imide)

Table VI   The Mechanical Properties of Polymers

Code	Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
B	BTDA-MDI	77	6	1.92
B-1	BTDA-MDI-PmIA (1-2-1)	84	4	2.31
B-2	BTDA-MDI-PmIA (2-3-1)	106	8	1.88
B-3	BTDA-MDI-PmIA (3-4-1)	118	7	1.92
B-4	BTDA-MDI-PmIA (4-5-1)	95	7	1.71
P	PMDA-MDI	63	5	2.13
P-1	PMDA-MDI-PmIA (1-2-1)	82	5	2.40
P-2	PMDA-MDI-PmIA (2-3-1)	85	4	2.53
P-3	PMDA-MDI-PmIA (3-4-1)	98	8	2.01
P-4	PMDA-MDI-PmIA (4-5-1)	115	7	2.12
D	DSDA-MDI	75	7	1.67
D-1	DSDA-MDI-PmIA (1-2-1)	81	6	2.02
D-2	DSDA-MDI-PmIA (2-3-1)	90	6	2.11
D-3	DSDA-MDI-PmIA (3-4-1)	113	9	1.78
D-4	DSDA-MDI-PmIA (4-5-1)	103	8	1.89

showed an increase in molecular weight and an improvement of their solubility. The inherent viscosity of these polymers was found to be 0.72–1.31 dL/g, and the polymers 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, except for those copoly(amide–imide)s with a partially crystalline structure. In contrast, the modulus of those crystalline copolymers was higher than that of polyimides due to their tight morphological structure. From the thermal analysis, copolymers of B-1, P-1, P-2, D-1, and D-2 demonstrated an endothermic melting point absorption, but other copolymers did not. The glass transition temperature of copolymers was lower than that of pure polyimides due to the less stable amide linkage. From X-ray diffraction patterns, some copolymers with high PmIA content exhibited a crystalline structure, which seemed consistent with the results found by DSC melting point measurement.

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