

Synthesis and Characterization of Copolyimides with High Solubility

Tsu-Shang Leu,¹ Chun-Shan Wang²

¹Department of Chemical Engineering, Yung-Ta Junior College of Technology and Commerce, Ping-Tung, 900, Republic of China

²Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, 701, Republic of China

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ABSTRACT: A series of copolyimides were prepared from various diamines (polysiloxane and isophorone units) with aromatic tetracarboxylic dianhydrides via a two-step (thermal imidization) method. The monomers and polymers were produced in high yields, and the copolyimides containing Si—O—C bonds and asymmetric meta catenation in the polymer backbone exhibited good solubility. The glass-transition temperatures (T_g 's) of all the copolyimides were found to be 201–262 and 215–258°C by differential scanning calorimetry (DSC) and dynamic mechanical analysis, respec-

tively. Thermogravimetric analyses indicated that the polymers were fairly stable up to 502–578°C (10 wt % loss in N₂) and 490–574°C (10 wt % loss in air). The char yields at 800°C in N₂ and air atmospheres were 26–59 and 20–53%, respectively. The copolymerization results, determined with ¹H-NMR and DSC, indicated a random copolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1963–1970, 2003

Key words: polysiloxanes; copolymerization; differential scanning calorimetry (DSC); NMR

INTRODUCTION

Polyimides are among the most important groups of special polymers with high thermostability. Their uses, however, are limited because of their poor solubility. Besides the blending of polyimides with other polymers, the synthesis of copolyimides systems can be used to provide materials with increased processability. Recently, soluble polyimides with high molecular weights have been synthesized for various applications.^{1–3} Copolyimides can be prepared from an amine-terminated prepolymer with a dianhydride and from an anhydride-terminated one with a diamine.^{4–8} In general, silicone polyimides possess high thermal, hydrolytic, and oxidative stability and exhibit good adhesion and electrical properties. In this study, we synthesized copolyimides from a dianhydride [3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)] and three diamines [2,2'-bis(4-aminophenoxy phenyl)propane (BAPP); isophorone diamine (IPDA) or 5-amino-1,3,3-trimethylcyclohexanemethylamine; and amine-terminated polysiloxane (PSX) or poly(dimethyl siloxane), weight-average molecular weight (M_w) = 900]. This article explores the relationship between the structures and properties of these copolyimides.

EXPERIMENTAL

Materials

All the monomers, of high purity, were obtained from various commercial sources, including bisphenol A (Acros, Belgium), PSX (M_w = 900; Shin-Etsu, Taiwan), 5-amino-1,3,3-trimethylcyclohexanemethylamine or IPDA (Aldrich, USA), *p*-chloronitrobenzene (Acros), hydrazine monohydrate (Acros), anhydrous potassium carbonate (Showa, Tokyo, Japan), 10% palladium on activated charcoal (TCI, Tokyo, Japan), *N,N*-dimethylacetamide (DMAc; Tedia, USA), *N,N*-dimethylformamide (DMF; Fison, England), and *N*-methyl-2-pyrrolidone (NMP; Tedia). The dianhydride (BTDA) was recrystallized from acetic anhydride so that the required purity would be achieved. The solvent for polyimide synthesis (NMP) was dehydrated with CaH₂ and then distilled before being stored in 4-Å molecular sieves. The other reagents were used as received and without further purification.

Measurements

Fourier transform infrared spectra were recorded on a Nicolet Magna 550 spectrometer with KBr pellets or approximately 10- μ m film. Spectra in the optical range of 400–4000 cm⁻¹ were obtained by the averaging of 32 scans at a resolution of 4 cm⁻¹. ¹H-NMR spectra were registered with a Bruker Avance 600 spectrometer with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as a solvent. Elemental analyses were carried out with a Heraeus CHN rapid elemental analyzer. Electron-im-

Correspondence to: C.-S. Wang (cswang@mail.ncku.edu.tw).

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fact mass spectrometry analyses were performed on a VG 70-250S gas chromatography/mass spectrometry spectrometer with a solid inlet. Differential scanning calorimetry (DSC; PerkinElmer DSC-7) measurements were used in this study. Samples of approximately 10 mg were sealed in hermetic aluminum pans and scanned in the calorimeter at a heating rate of 20°C/min in the range of 30–350°C under an atmosphere of N₂, and the glass-transition temperature (*T_g*) values were taken as the change of the specific heat in the heat flow curves. Dynamic mechanical analysis (DMA) was performed on a PerkinElmer DMA-7 thermal analyzer system. A sample 10 mm long (i.e., the system display sample height from zero) and 5 mm wide was used. The modulus and tan δ were studied when the sample was subjected to the temperature scan mode with an extension measuring system (with a stainless steel extension kit) at a programmed heating rate of 20°C/min from 30 to 350°C at a frequency of 1 Hz. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA-7 thermal analyzer at a heating rate of 20°C/min in N₂ at a purge pressure of 25 psi within the temperature range of 60–820°C.

Monomer syntheses

2,2'-bis(4-nitrophenoxy phenyl) propane (BNPP)

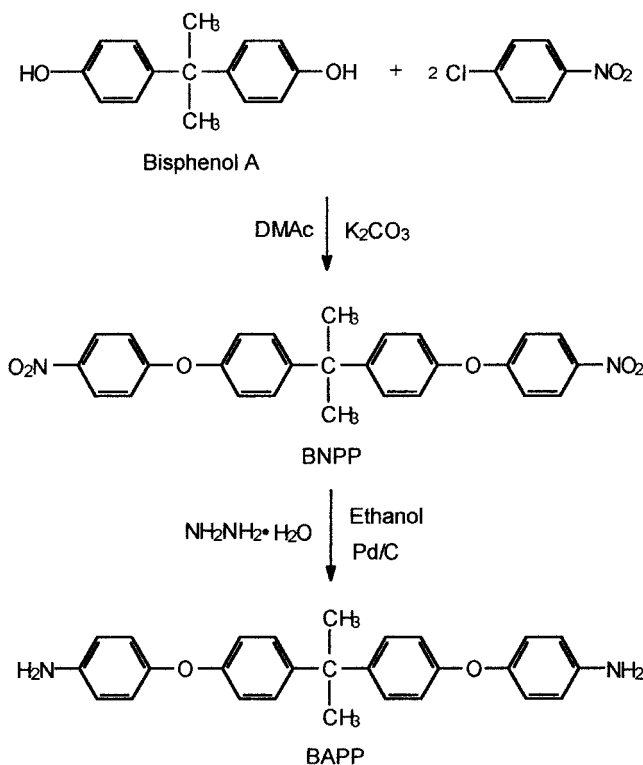
Into a reactor equipped with a stirrer, a reflux condenser, and a nitrogen inlet were charged 300 g of DMAc, 45.66 g (0.2 mol) of bisphenol A, 69.33 g (0.44 mol) of *p*-chloronitrobenzene, and 60.81 g (0.44 mol) of potassium carbonate. The reaction mixture was refluxed at 159 ± 1°C for 8 h under an atmosphere of N₂. After the completion of the reaction, the reaction mixture was poured into a methanol/water (1:1 v/v) mixture to yield the crude dinitro compound, and it was collected by filtration and was further recrystallized from acetic anhydride to produce 78.96 g (84%) of yellow crystals.

mp: 122–124°C. IR (KBr, cm⁻¹): 1300, 1510 (NO₂ stretching), 1230 (C—O—C stretching). Electron-impact mass spectrometry (*m/z*): 470 (M⁺, 20). ELEM. ANAL. Calcd. for C₂₇H₂₂N₂O₆: C, 68.94%; H, 4.68%; N, 5.96%. Found: C, 68.75%; H, 4.68%; N, 5.87%.

2,2'-bis(4-aminophenoxy phenyl) propane (BAPP)

To a dispersion of BNPP (47.00 g, 0.1 mol) in ethanol (300 g) was added 0.25 g of 10% Pd/C, and hydrazine monohydrate (80%, 100 g) was charged to the stirred mixture dropwise at 70°C over 1 h. After the addition was completed, the mixture was stirred at 85°C for another 12 h. The solution was filtered for the removal Pd/C and then dried *in vacuo* (80°C), yielding 36.08 g (88%) of a yellow powder.

mp: 127–130°C. IR (KBr, cm⁻¹): 3300–3400, 1610 (NH stretching and deformation), 1220 (C—O—C



Scheme 1

stretching). Electron-impact mass spectrometry (*m/z*): 410 (M⁺, 95). ¹H-NMR (600 MHz, DMSO-*d*₆): 1.60 (6H, CH₃, s), 4.69 (4H, NH₂ br, s), 6.58–7.14 ppm (16H, ph-H, m). ELEM. ANAL. Calcd. for C₂₇H₂₆N₂O₂: C, 79.02%; H, 6.34%; N, 6.83%. Found: C, 78.94%; H, 6.34%; N, 6.72%.

The reactions are shown in Scheme 1.

Polymer preparation and film casting

A three-necked flask equipped with an addition funnel and a high-purity N₂ inlet was charged with a solution of the diamine in NMP, and then dianhydride was added all at once. The molar ratio and solid content of the diamine/dianhydride mixture were 1:1 and 15 wt %, respectively. The reaction mixture (ca. 15 mL) was stirred at 5°C under an atmosphere of N₂, affording a viscous poly(amic acid) solution after 9–11 h. The solution was spread (with a film casting apparatus) on a heatproof glass plate and dried at 60°C for 12 h in a forced-air oven. The film on the glass was then converted into the polyimide via heating in air at 100, 200, and 300°C for 1 h each. The film was cooled to room temperature and stripped from the plate by being soaked in water.

Determination of the degree of imidization (XID) by IR spectra

XID was analyzed by the band ratio method.^{9,10} The absorbance of the asymmetric carbonyl stretch at 1780

TABLE I
Sample Code and Molar Ratio of Diamine and Dianhydride

Sample code	Monomer (mol %)	BAPP (mol)	PSX (mol)	IPDA (mol)	BTDA (mol)
B ^a	BAPP (100)	0.01			0.01
BP-91	BAPP (90)/PSX (10)	0.009	0.001		0.01
BP-82	BAPP (80)/PSX (20)	0.008	0.002		0.01
BI-73	BAPP (70)/IPDA (30)	0.007		0.003	0.01
BI-55	BAPP (50)/IPDA (50)	0.005		0.005	0.01
BI-37	BAPP (30)/IPDA (70)	0.003		0.007	0.01
BI-28	BAPP (20)/IPDA (80)	0.002		0.008	0.01
BPI-118	BAPP (10)/PSX (10)/IPDA (80)	0.001	0.001	0.008	0.01
BPI-117	BAPP (15)/PSX (15)/IPDA (70)	0.0015	0.0015	0.007	0.01

^a The sample was a homopolyimide.

cm⁻¹ was ratioed with a reference aromatic stretch at 1500 cm⁻¹. The imidization percentage of the poly(amic acid) was calculated with the following equation:

$$X_{ID}\% = \frac{[Ai - Ar]_t}{[Ai - Ar]_\infty} \times 100 \quad (1)$$

where *Ai* is the absorbance of the imide peak at 1780 cm⁻¹, *Ar* is the absorbance of the imide peak at 1500 cm⁻¹, and *t* = ∞ is taken as the time beyond which no further changes in the imide peak can be observed at 300°C for 2 h.

Determination of the intrinsic viscosity ($[\eta]$)

The $[\eta]$ values of the copolyimides in concentrated DMAc or H₂SO₄ solutions (0.2–0.4 g/dL) were measured at 30°C with an Ubbelohde viscometer. The following algebraic expansion is useful:

$$\frac{\ln \eta_{rel}}{c} = \frac{1}{c} [(\eta_{rel} - 1) - \frac{1}{2}(\eta_{rel} - 1)^2 + \frac{1}{3}(\eta_{rel} - 1)^3 - \dots] \quad (0 < \eta_{rel} < 2) \quad (2)$$

where η_{rel} is the relative viscosity ($0 < \eta_{rel} < 2$). For dilute solutions, the logarithm of η_{rel} is divided by *c* (concentration) and, extrapolated to zero concentration, yields $[\eta]$; that is, $[\frac{\ln \eta_{rel}}{c}]_{c \rightarrow 0} = [\eta]$.

Sample code

The sample codes for the diamine (BAPP)-based copolyimides are designated BP (or BI)-XY and BPI-XYZ, respectively, as shown in Table I. B stands for BAPP, P (or I) stands for PSX (or IPDA), and the numbers XY and XYZ after the dashes are the molar percentages of the two diamines BAPP and PSX (or IPDA) and the three diamines BAPP, PSX, and IPDA,

respectively. For the systems, monomers of BAPP with PSX and IPDA were applied to the starting mixture, as shown in Scheme 2.

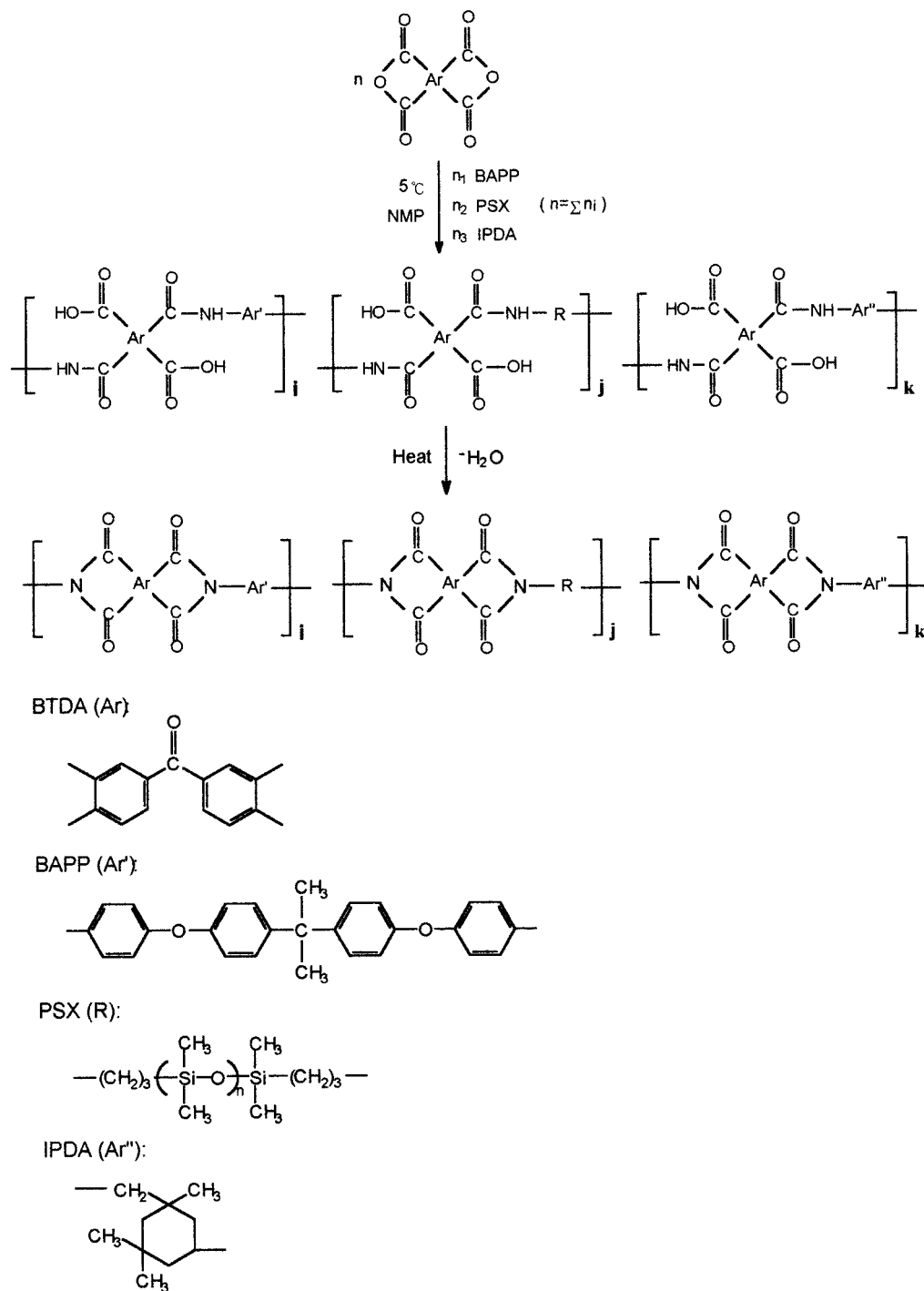
RESULTS AND DISCUSSION

Monomer syntheses

Scheme 1 shows the synthetic route to BAPP. A dinitro monomer was obtained in a high yield, and this can be attributed to the fact that the dipotassium salt of bisphenol A is a good nucleophile. In addition, the electron-withdrawing NO₂ group in *p*-chloronitrobenzene also increased its reactivity. In this work, hydrazine hydrate/Pd—C was used to reduce BNPP, and this resulted in a high yield (the reduction of the dinitro compound to an amino compound can be carried out in a number of ways¹¹) because the palladium on activated carbon had a higher activity and/or selectivity. The metal readily absorbed hydrogen into the interstices between metal atoms. The elemental analysis, mass spectrometry analysis, characteristic peaks in the ¹H-NMR spectra, and characteristic bands in the IR spectra correlated well with the proposed structures.

Preparation of the polymers

A series of copolyimides were synthesized by the conventional two-step method; the synthesis started with diamines and an aromatic tetracarboxylic dianhydride, and these were followed by ring-opening polyaddition and subsequent thermal cyclodehydration imidization. The formation of poly(amic acid) is actually a very complex situation that includes competition between propagation and hydrolysis.¹² The reaction is shown in Scheme 2. Although the structures of the copolymers are idealized, most of the copolymers contained a small percentage of triads (three mers) in their distributions because the thermodynamically and spatially preferred structure was usually the dyad configuration (two mers). The com-



Scheme 2

position of the repeat unit differed from that of the two mers (monomeric units) by the elements of water. The copolymers had sequence lengths of one, two, or at most several repeat units (see Scheme 2).

This section treats cases in which whole polymer chains are linked together to form larger polymer structures. The probability of finding a sequence $\cdots ABC \cdots$ of repeat units A, B, C, and so forth can be stated mathematically as follows:

$$P(\cdots ABC \cdots) = P(A)P(B)P(C) = \cdots \prod_i P(i) \quad (3)$$

$i = A, B, C, \dots$

where $P(A)$, $P(B)$, $P(C)$, and so forth are the unconditional probabilities of the occurrence of the various repeat units. If eq. (3) is considered, some of the possible copolymers can be represented as follows:

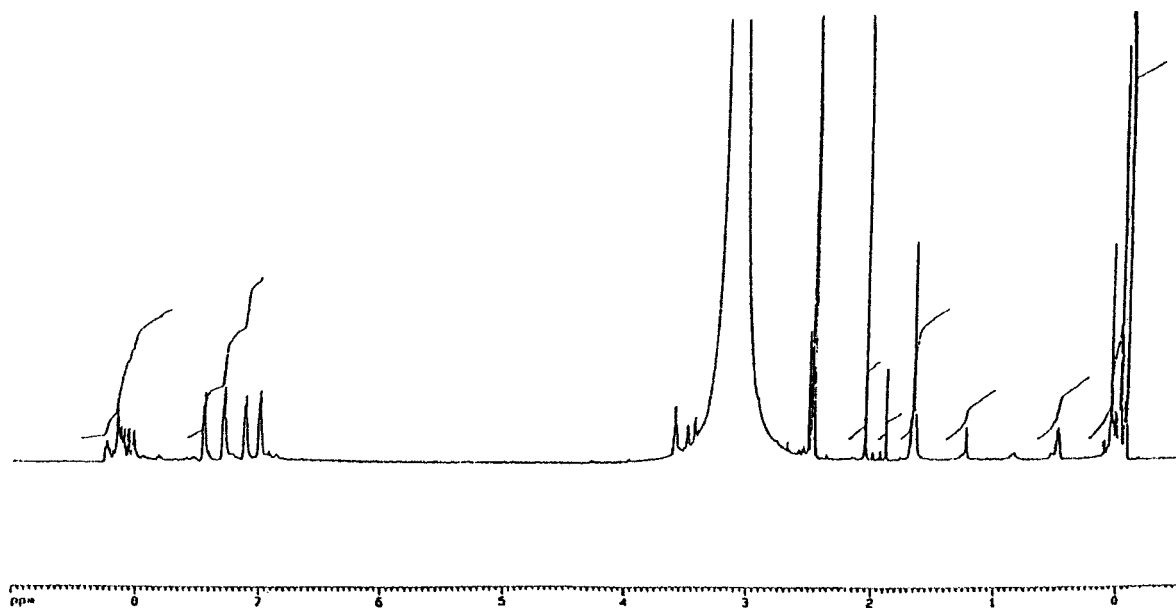


Figure 1 $^1\text{H-NMR}$ spectra of BP-82.

Long sequence: polyA-*block*-polyB-*block*-polyC

Short sequence: poly(A-*ran*-B-*ran*-C)

The term *ran* was used to indicate a random copolymer if the DSC scan of the copolymers showed only one T_g , which indicated that the various repeat units were randomly distributed along the polymer chain and formed a random copolymer structure.

The copolyimides resulting from BP-82 and BI-55 were dissolved in $\text{DMSO-}d_6$, and then their $^1\text{H-NMR}$ spectra were measured. Typical NMR spectra are

shown in Figures 1 and 2. The signals of the aromatic protons of the BTDA and BAPP residues were detected at 8.0–8.3 (12H) and 7.0–7.5 ppm (16H), respectively. The signals of the three-methylene groups of the PSX residue were observed at 0.5 [aliphatic H's ortho to $-\text{Si}(\text{CH}_3)_2-$], 1.3 (aliphatic H's ortho to $-\text{CH}_2-$), and 3.6 ppm [aliphatic H's ortho to $-\text{N}(\text{CO})_2$]. Figure 2 shows signals for the IPDA residue at 2. ppm (aliphatic H's ortho to $-\text{NH}_2-$), 2.8 (isophorone H's ortho to $-\text{NH}_2-$), and 0.8–1.7 ppm (other H's on the isophorone). These repeat unit parts,

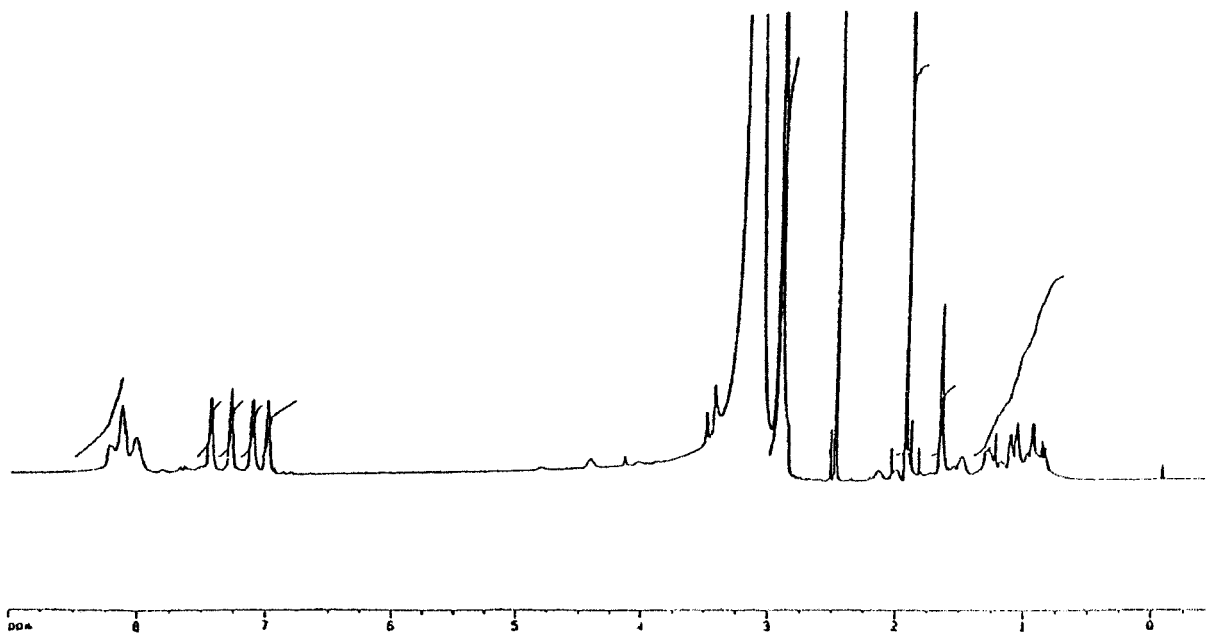


Figure 2 $^1\text{H-NMR}$ spectra of BI-55.

TABLE II
Synthesis of Copolyimides from Various Diamines and Aromatic Tetracarboxylic Dianhydride

Polymer code	η_{rel}	C (g/dL)	$[\eta]_{exp}^a$ (dL/g)	$[\eta]_{cal}^b$ (dL/g)	X_{ID}^c (%)	M_n^d
B	1.111	0.2120	0.50	0.49	→100	—
BP-91	1.110	0.1112	0.95	0.93	98.5	58357
BP-82	1.170	0.1860	0.86	0.84	98.0	43550
BI-73	1.126	0.0688	1.71	1.72	99.6	126500
BI-55	1.101	0.1056	0.92	0.91	99.2	63250
BI-37	1.081	0.1124	0.69	0.69	98.3	29854
BI-28	1.061	0.1228	0.48	0.48	98.0	25300
BPI-118	1.050	0.1240	0.40	0.39	97.5	28360
BPI-117	1.103	0.0668	1.44	1.46	97.0	23397

^a The solutions (polymer B in concentrated H_2SO_4 , and other polymers in concentrated DMAc, 0.2–0.4 g/dL) were measured at 30°C, by extrapolation to zero concentration, yielding $[\eta]_{exp}$, that is, $[\frac{\ln \eta_{rel}}{c}]_{c \rightarrow 0} = [\eta]_{exp}$.

^b Calculated from eq. (2). For dilute solutions, the full equation may be written (taking two terms) as $\frac{\ln \eta_{rel}}{c} = \frac{1}{c}[(\eta_{rel} - 1) - \frac{1}{2}(\eta_{rel} - 1)^2] = \frac{1}{2c}(\eta_{rel} - 1)(3 - \eta_{rel}) \eta_{rel} \cong [\eta]_{cal}$.

^c Calculated from eq. (1).

^d Calculated from eq. (6) and (7).

combined with one another, were in good agreement with the copolyimide structure.

X_n is defined as the average degree of polymerization for the polymer chain or is simply given as the concentration of poly(amic acid) (C) initially present divided by the concentration of poly(amic acid) present at time t :

$$X_n = \frac{C_0}{C} \quad (4)$$

C at time t is given by

$$C = C_0(1 - X_{ID}) \quad (5)$$

Combining eqs. (4) and (5), one obtains

$$X_n = \frac{1}{1 - X_{ID}} \quad (6)$$

Equation (6), also from Carother's equation, can be written as follows:

$$X_n = \frac{1 + r}{1 + r - 2rX_{ID}}$$

Because $r = \text{dianhydride/diamine (molar ratio)} = 1$, these two equations are equivalent.

The number-average molecular weight (M_n) is

$$M_n = X_n \cdot M_0 \quad (7)$$

where M_0 is the average molecular weight of the repeating units.

In general, X_n is both a function of the bifunctional monomer molar ratio, given by r , and a function of the extent of reaction, given by X_{ID} . The highest X_n value should be obtained when r is adjusted to 113 and X_{ID} is equal to 1. The values obtained for the BI system are summarized in Table II. For most polyimide systems, these conservative reaction conditions are employed to ensure that quantitative step polymerization and possible molecular weight redistribution to a most probable value ($M_w/M_n \cong 2$) are achieved.^{12,14–17} For $[\eta]$, the resulting $[\eta]_{exp}$ and $[\eta]_{cal}$ values with these methods yielded very little deviation (within 2.5%). With the Mark–Houwink equation ($[\eta] = KM_n^a$),

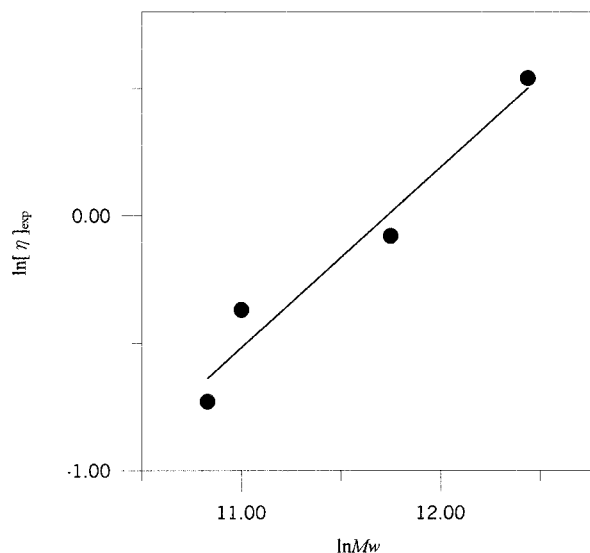


Figure 3 Double logarithmic plots of $[\eta]_{exp}$ versus M_w for the BI (BAPP/IPDA) system.

TABLE III
Solubility of Copolyimides^a

Polymer code	Solvent						
	NMP	DMAc	DMF	cyclohexane	<i>m</i> -cresol	chloroform	H ₂ SO ₄
B	h-	h-	--	--	h-	--	++
BP-91	h+	--	h-	h+	--	++	
BP-82	h+	h-	h-	h+	h+	--	++
BI-73	h+	h+	h+	h-	h+	--	++
BI-55	h+	h+	h+	h+	h+	h-	++
BI-37	h+	h+	h+	h+	h+	h-	++
BI-28	h+	h+	h+	h+	h+	h-	++
BPI-118	h+	h+	h+	h+	h+	h-	++
BPI-117	h+	h+	h+	h-	h+	h-	++

++ = soluble at room temperature, h+ = soluble in hot solvent (hot solvent at 60°C); h- = swelled, slightly soluble in hot solvent; -- = insoluble.

^a Measured at a concentration of 0.5g/dL in solvent.

Mw's of sharp fractions or narrow molecular weight distributions are usually used to determine *K* and *a*. When $Mv \cong Mw$ and the dispersity is 2, the resulting $[\eta]$ expression can be formulated as follows (see Fig. 3):

$$[\eta] = 2.46 \times 10^{-4} Mw^{0.71}$$

Properties of the polyimides

The solubilities of the polyimides in various solvents were investigated, and the results are summarized in Table III. All the polymers were soluble in concentrated sulfuric acid at room temperature. In polar aprotic and common organic solvents, they exhibited somewhat limited solubility, whereas the copolyimides showed better solubility than the homopolyimide because the second law of thermodynamics had to be obeyed (i.e., $\Delta S > 0$ and $\Delta G < 0$). In addition, the copolyimides had a relatively longer distance between the imide groups [containing flexible (PSX) and/or asymmetric meta position (IPDA) catenation in the polymer backbone]. The introduction of isophorone (or cycloalkane18) groups (IPDA) into the polymers,

resulting in a larger molecular space, also led to an increase in solubility.

The thermal properties of the copolyimides were investigated by TGA, DSC, and DMA, as shown in Table IV. The *Tg*'s of the polyimides were found to be 201–262 and 215–258°C by DSC and DMA, respectively. These results of the thermal analysis indicated the high thermal stability of the synthesized polyimides. In many cases, the copolymer *Tg* was only slightly lower or higher than that of the homopolymer, and this indicated good microphase separation (PSX) or a rigid structure (IPDA). In addition, the curing (thermal imidization) reaction for all the samples could be safely completed below 300°C without decomposition during curing. The DSC scan of the copolyimides showed only one *Tg* (see Fig. 4), indicating that the various repeat units were randomly distributed along the polymer chain and formed a random copolymer structure. The 10 wt % degradation temperature (*Td*) ranged from 502 to 578°C in N₂ and from 490 to 574°C in air. The char yields at 800°C were 26–59% in an atmosphere of N₂ and 20–53% in an air atmosphere.

TABLE IV
Thermal Properties of Copolyimides

Polymer code	<i>T_g</i> (°C)		<i>T_d</i> (°C) 10 wt % loss in		Char yield at 800°C (%)	
	DSC	DMA	N ₂	Air	N ₂	Air
B	242	246	578	574	59	53
BP-91	218	228	564	570	55	51
BP-82	201	215	543	574	49	50
BI-73	239	248	564	553	51	50
BI-55	248	258	537	531	41	41
BI-37	259	ND	515	527	36	36
BI-28	262	ND	512	516	34	28
BPI-118	225	ND	512	490	26	20
BPI-117	211	ND	502	502	27	27

ND = not detected.

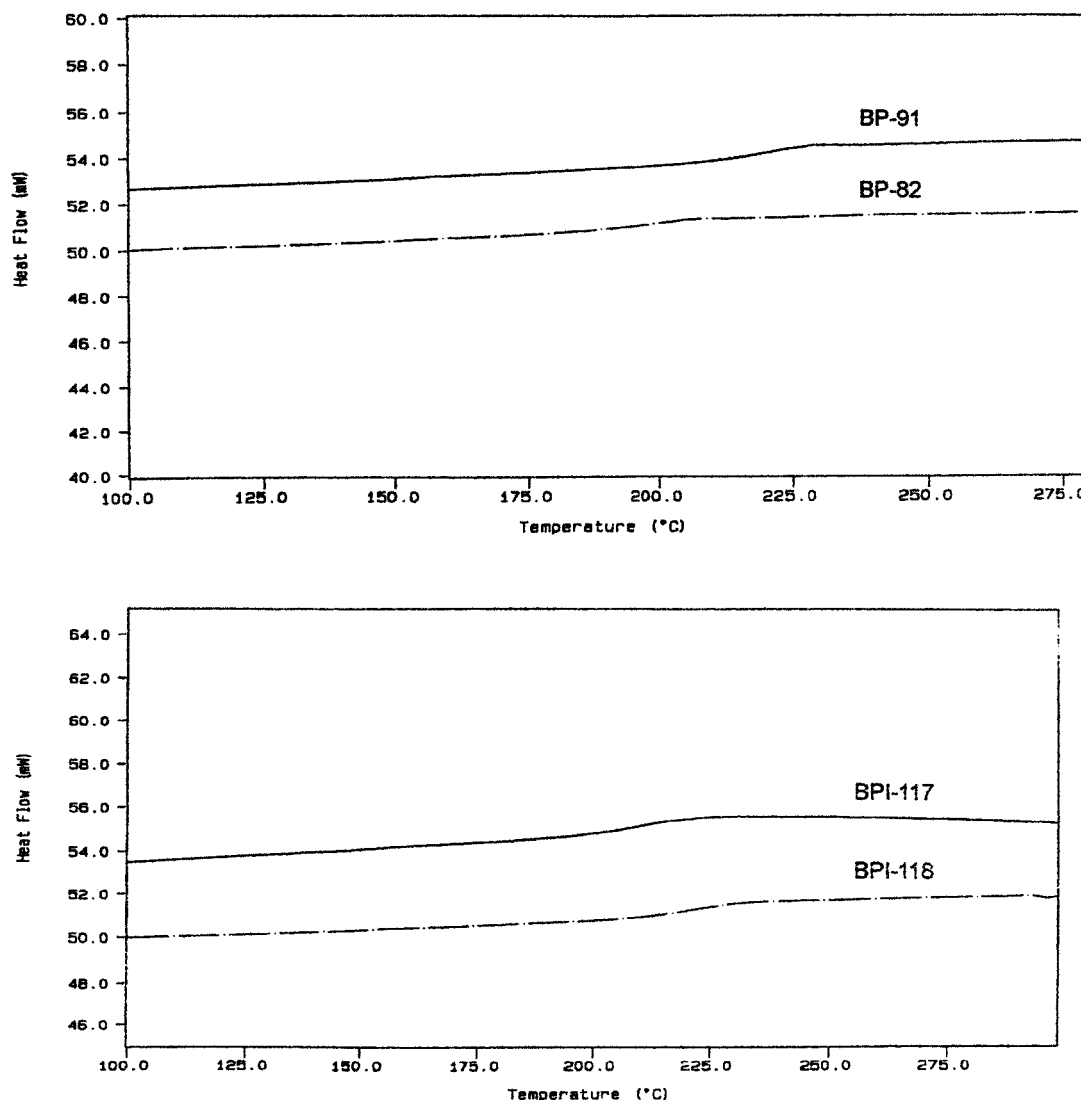


Figure 4 DSC scans for copolyimides BP-91, BP-82, BPI-117, and BPI-118.

CONCLUSIONS

Copolyimides were prepared from aryl ether linkages containing a diamine, BTDA with PSX, and isophorone so that the relationship could be studied between the structures and properties. A two-step method was used to prepare the polymers. The copolyimides were expected to obey second-order kinetics as ordinary aromatic polyimides, even though the copolymer systems contained two different imide units.¹³ The solubility and thermal properties of the copolyimides were greatly influenced by siloxane (flexible) and isophorone (stiffness) in the polymer main chain.

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