

# Synthesis and Characterization of Homo- and Copolyimides Prepared From Two-Step Polymerization

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## SYNOPSIS

Homopolyamic acids and copolyamic acids were prepared from four dianhydrides and three diamines. Copolyimides could be arranged in sequence through different reaction processes, such as alternating, block, and random. Polyamic acids were subsequently converted into corresponding polyimides by the solid-phase imidization. Polyimide derivatives were characterized by viscosity, thermal stability, mechanical properties, and solubility. The extent of polymerization might be influenced by the nucleophilicity of a diamine and the electrophilicity of a dianhydride. In gel permeation chromatography, molecular weight distribution of polymers was 2.5–3.0. The thermal stability of polymers decreased with increasing the ratio of a more flexible component, and alternating copolyimides showed slightly better than corresponding random and block ones. The melting temperatures of all polyimide derivatives did not exist on the differential scanning calorimetry curves, and the results were proof that the X-ray diffraction curves. Polymers derived from bis[4-(3-amino phenoxy)phenyl]sulfone dissolved well in some polar solvents. Alternating copolymers represented a better solubility than the corresponding random and block ones. All polymers had good mechanical properties, both tensile and elongation. The kinetics of imide formation could be also dependent on the structure and reactivity of reagents. The kinetics of cyclodehydration was described by the first-order kinetics up to relatively high conversion but deviated from the first-order kinetics at high conversion followed by the second-order kinetics. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polyimides have been one of the most important classes of high-performance polymers because of their excellent electrical, thermal, and high-temperature mechanical properties.<sup>1,2</sup> Their uses, however, are limited because of their poor solubility. Most polyimide derivatives are processed in the form of polyamic acids, which are subsequently converted into the imide structures.

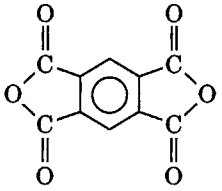
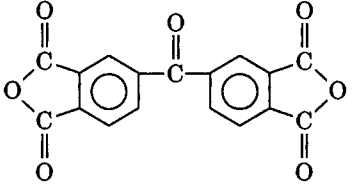
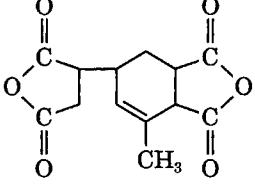
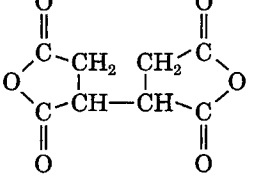
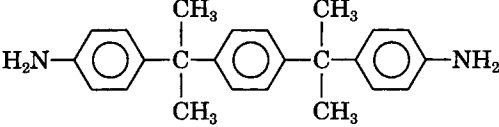
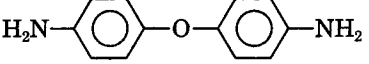
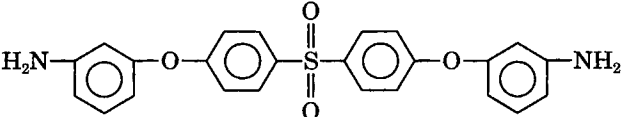
Recently, the soluble polyimides with large molecular weights have been synthesized for sufficient applications.<sup>3–5</sup> For enhancing processability, most approaches have involved the following factors<sup>3–5</sup>: the separation of the imide ring

along the backbone, that is, reducing the density of imide ring in the repeating structure; the introduction of bulky substituents along the backbone to enhance the free volume of the main chain; the incorporation of flexible or thermally stable linkages in the main chain, reducing the packing force; and the disruption of symmetry or recurrence regularity through copolymerization to reduce crystallinity.

In general, the polymers prepared from single diamine and single dianhydride were called homopolyimides, and polyimides synthesized from single diamine and two or more dianhydrides or from single dianhydride and two or more diamines were called copolyimides.<sup>6</sup> Copolyimides could be prepared from amine-terminated prepolymer with a dianhydride and anhydride-terminated one with a diamine.<sup>6–9</sup> However, the preparation of the anhydride-terminated prepolymer was actually very difficult because

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**Table I** Chemical Structures and Abbreviations of Monomers

Chemical Structure	Abbreviation	MW
	PMDA	218.1
	BTDA	322.2
	DMCA	264.2
	BTCA	198.0
	BADB	344.5
	ODA	200.2
	BAPS	432.5

the anhydride group was easily attacked by the moisture in the reaction medium.

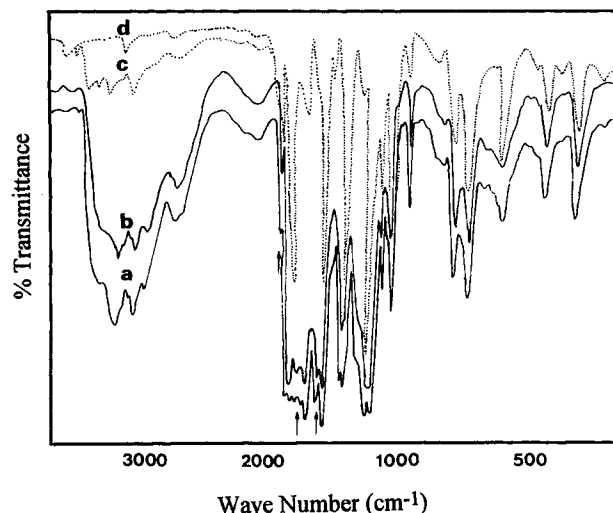
Our objectives were to relate characteristics of polyimide derivatives to their structures. In this article, four series of polyimide derivatives with different arrangement of molecular chain are prepared by two-step polymerization. The H series is homopolyimide, the A series is prepared from single dianhydride and two diamines, the B series is produced from a diamine and two dianhydrides, and the C

series results from reacting two dianhydrides and two diamines.

## EXPERIMENTAL

### Reagents

Pyromellitic dianhydride (PMDA, Aldrich Chemical Co.), 3,3',4,4'-benzophenone tetracarboxylic dian-



**Figure 1** IR spectra of H-2 polymers cured at (a) 80°C, (b) 150°C, (c) 250°C, and (d) 270°C.

hydride (BTDA, Aldrich Chemical Co.), and 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DMCA, Tokyo Kasei Co.) were recrystallized from 4-methyl-2-pentanone followed by vacuum drying and stored in a desiccator over  $\text{CaCl}_2$  and silicagel. 1,2,3,4-Butanetetracarboxylic dianhydride (BTCA) was prepared by dehydration of 1,2,3,4-butanetetracarboxylic acid (Aldrich Chemical Co.) in acetic anhydride and then was recrystallized by the same manner as in the preceding case.  $\alpha, \alpha'$ -Bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB, Tokyo Kasei Co.), 4,4'-oxydianiline (ODA, Aldrich Chemical Co.), and bis[4-(3-amino phenoxy)phenyl] sulfone (BAPS, Wakayama Seika Kogyo Co.) were purified by recrystallization in ethanol and followed by vacuum drying at 60°C for 4 h and stored in a drying oven. The chemical structures and abbreviations of all monomers are presented in Table I. *N,N'*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and *N,N'*-dimethylformamide (DMF) were obtained from Aldrich Chemical Co. All solvents were dehydrated with  $\text{CaH}_2$  and then distilled before being stored in 4 Å molecular sieves. Others laboratory-grade reagents were used without further purification, among them were acetic anhydride, methanol, ethanol, and 4-methyl-2-pentanone.

### Measurements

The viscosity of polyamic acid (PAA) solution was measured with an ubbelohde viscometer in 0.5 dL/g DMAc at 30°C. The molecular weight distribution was obtained from the gel permeation chromatog-

raphy (GPC, Water 150 C). IR spectrum was recorded in film using a Digilab-FTS-600 FT-TR.

The extent of imidization could be calculated according to eq. (1). The sample was made into a film and cured at different temperatures:

### Degree of Imidization

$$= \frac{[\{A(1)/A(s)_t\} - \{A(1)/A(s)_{t=0}\}]}{[\{A(1)/A(s)_\infty\} - \{A(1)/A(s)_{t=0}\}]} \quad (1)$$

where  $A(1)$  is the absorbance of imide peak at about  $1780 \text{ cm}^{-1}$ ,  $A(s)$  is the standard reference peak at about  $1500 \text{ cm}^{-1}$ , and  $t = \infty$  is taken as the time beyond which no further change in the imide peak is observed at 270°C, for 4 h.

The kinetics of imide formation could be evaluated according to the first- and second-order kinetic equation<sup>10</sup>:

$$\ln(1 - P) = -kt \quad (2)$$

$$1/(1 - P) = kt + 1 \quad (3)$$

where  $P$  is the extent of imidization and  $k$  is the rate constant.

The thermal properties were measured by using a differential scanning calorimetry (DSC, Dupont 2100) and a thermogravimetric analysis (TGA, Perkin-Elmer TGA7).

The tensile strength and elongation were measured at room temperature using an instron testing machine model TT-C. This test used the PI film with 150- $\mu\text{m}$  thickness, 10-mm width, and 50-mm length.

X-ray diffraction was recorded in film using a Rigaku model RAD-II A X-ray diffractometer.

**Table II** Effect of Solvent on the Viscosity and Yield of PAA<sup>a</sup>

Solvent	Polymer <sup>b</sup>	Viscosity <sup>c</sup> (dL/g)	Yield (%)
DMAc	H-2	1.35	> 95
	H-3	0.74	> 95
NMP	H-2	1.06	> 95
	H-3	0.67	> 95
DMF	H-2	0.79	> 95
	H-3	0.54	> 95

<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration at 20°C for 7 h under nitrogen.

<sup>b</sup> H-2 (PMDA/ODA polymer) and H-3 (PMDA/BAPS polymer).

<sup>c</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

**Table III** Effect of Monomer Concentration on the Viscosity and Yield of PAA<sup>a</sup>

Temperature (°C)	Concentration (%)	Viscosity <sup>b</sup> (dL/g)		Yield (%)	
		H-2	H-3	H-2	H-3
10	5	0.93	0.54	> 90	> 90
	10	1.35	0.65	> 95	> 90
	15	1.43	0.66	> 95	> 95
	20	1.41	0.59	> 95	> 90
	25	0.79	0.43	> 85	> 90
20	5	1.00	0.54	> 90	> 90
	10	1.30	0.72	> 95	> 90
	15	1.35	0.74	> 95	> 95
	20	1.31	0.71	> 95	> 95
	25	0.90	0.67	> 90	> 95
30	5	0.80	0.49	> 90	> 90
	10	0.86	0.71	> 90	> 90
	15	0.82	0.72	> 95	> 95
	20	0.79	0.70	> 95	> 95
	25	0.67	0.66	> 90	> 95
50	5	0.56	0.42	> 85	> 80
	10	0.60	0.43	> 85	> 80
	15	0.57	0.43	> 80	> 80
	20	0.45	0.41	> 80	> 80
	25	0.37	0.35	> 80	> 80

<sup>a</sup> Polymerization was carried out in DMAc for 7 h under nitrogen. H-2 (PMDA/ODA polyimide) and H-3 (PMDA/BAPS polyimide).

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

To determine solubility, polymer samples were immersed in the various solvents and allowed to shake for 7 days. If the sample was only partially dissolved or swelled, it was heated at 70°C for 24 h.

## Synthesis of Polyimide

### Homopolymers

A diamine was dissolved in solvent in a four-neck round flask equipped with a sealed Teflon agitator, nitrogen gas inlet-tube, reflux condenser with CaCl<sub>2</sub> guard tube, and thermometer. Under flow of nitrogen, equivalent dianhydride was added to the solution of diamine with a stirrer to obtain a PAA. The mixture was stirred until the reaction was complete. The next step was the transformation of the PAA into the corresponding PI. Viscous PAA solution was cast on the dry glass plate and then the major amount of solvent was removed in drying oven at 70°C for 1–2 h. The resulting film, which was only partially dried, could be peeled off the plate and clamped to a stainless steel frame. The film was then

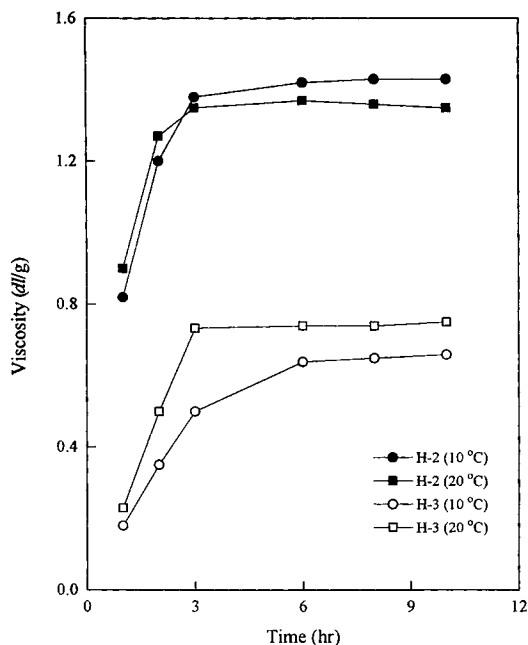
gradually heated in a forced draft oven up to 270°C over a period of 3–4 h.

### Block and Alternating Copolymers

The first step consisted of synthesis of prepolymer in the same flask as described above. Under nitrogen atmosphere, unequivalent dianhydride was added to the solution of diamine to yield a prepolymer terminated with anhydride or amine. If the reaction was complete, another diamine or dianhydride was added to the above mixture to complete the unbalanced stoichiometry. The reaction was continued until viscosity no longer increased, and the viscous polymer solution yielded was treated in the same manner as in the preceding case.

### Random Copolymers

In the same flask as described above, equivalent dianhydrides were added to the solution of mixed diamines to attain a highly viscous PAA. The reaction was continued until viscosity no longer increased. The resulting PAA was subsequently con-



**Figure 2** The viscosity of H-2 and H-3 PAA's against reaction time. (a) Polymerization was carried out with 15 wt % of monomer concentration in DMAc under nitrogen. (b) Viscosity was measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

verted into corresponding PI as in the preceding case.

## RESULTS AND DISCUSSION

### Identification of Polymer

Figure 1 represents the IR spectra of PMDA/ODA homopolymer. The spectrum of PAA exhibited characteristic absorption peaks around 1660, 1520, and 1300  $\text{cm}^{-1}$ , which are peculiar to amide I, II, and III bands, respectively. The band around 3300  $\text{cm}^{-1}$  was assigned to the stretching N—H linkage. A band peak, 2400–3200  $\text{cm}^{-1}$ , was due to the stretching of —O—H of carboxylic acid, but the absorption peaks due to imide groups showed only weak traces. On the other hand, in the spectra of the cured polymer, the intensity of the characteristic absorption peaks of PAA gradually decreased and ultimately disappeared with curing temperature and time, and new absorption peaks, as marked on the IR chart, appeared at about 1780, 1710, 1380, and 720  $\text{cm}^{-1}$ . The bands at 1710 and 1780  $\text{cm}^{-1}$  related to the stretching vibration of C=O linkages of imide ring and the bands at 1380 and 720  $\text{cm}^{-1}$  assigned to the C—N stretching vibration of cyclic imide groups. The spectra indicated that the product pre-

**Table IV** Effect of Dianhydride/Diamine Molar Ratio on the Viscosity and Yield<sup>a</sup>

Dianhydride/Diamine (mole ratio)	Viscosity <sup>b</sup> (dL/g)		Yield (%)	
	H-2	H-3	H-2	H-3
0.7/1.0	0.53	0.33	> 50	> 70
0.9/1.0	0.93	0.58	> 70	> 90
1.0/1.0	1.35	0.74	> 95	> 95
1.1/1.0	0.34	0.44	> 85	> 95
1.3/1.0	0.30	0.22	> 50	> 50

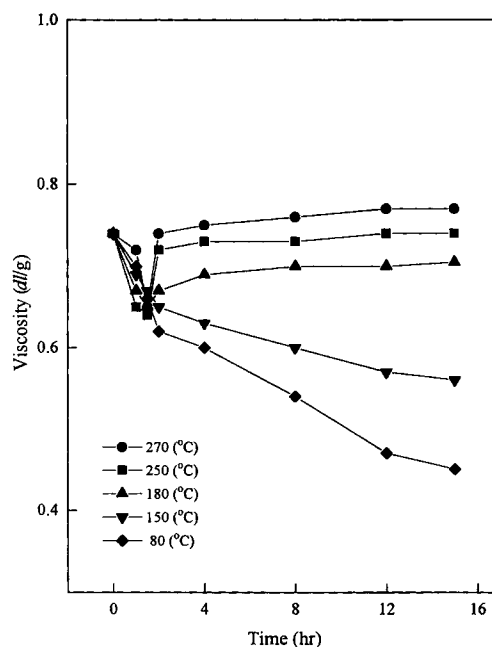
<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration in DMAc at 20°C for 7 h under nitrogen. H-2 (PMDA/ODA polyimide) and H-3 (PMDA/BAPS polyimide).

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

pared in the first step was mostly the PAA and the final product, obtained by heating at above 250°C, consisted purely of PI.

### Effect of the Solvents

Table II shows the viscosity and yield of the polymers prepared with various solvents. As it could be deduced from the result, DMAc and NMP were more suitable solvents than DMF. The reasons probably



**Figure 3** Relation between the viscosity of H-3 polymer and time as a function of cured temperature. Viscosity was measured at concentration of 0.5 dL/g polymer in DMAc at 30°C.

**Table V Viscosity and Yield of Homopolyamic Acid Prepared From Various Reagents<sup>a</sup>**

Polymer No.	Dianhydride	Diamine	Viscosity <sup>b</sup> (dL/g)	Yield (%)	Remark <sup>c</sup>
H-1	PMDA	BADB	1.42	> 95	IS
H-2		ODA	1.35	> 95	IS
H-3		BAPS	0.74	> 95	S
H-4		BADB	1.10	> 95	IS
H-5	BTDA	ODA	1.02	> 95	IS
H-6		BAPS	0.55	> 95	S
H-7	DMCA	BADB	0.42	< 70	S
H-8		ODA	0.30	< 60	S
H-9		BAPS	0.15	< 60	S
H-10		BADB	0.60	> 85	SW
H-11	BTCA	ODA	0.49	> 85	S
H-12		BAPS	0.20	> 80	S

<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration in DMAc at 20°C for 7 h under nitrogen.

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

<sup>c</sup> Where S is soluble, PS is partially soluble, SW is swell, and IS is insoluble PI in NMP.

related to the change of the reactivity of reagents and propagating PAA by the solvent effect.<sup>3,11,12</sup> The aprotic polar solvents acting as a Lewis base might enhance the nucleophilicity of the dissolved diamine to easily attack the anhydride carbonyl carbon, and the complex between prepolymer and solvent also formed. The solvent activity in the complex and the diamine depended on its basicity,<sup>3,6,12</sup> which increased as DMF < NMP < DMAc. From the result, the extent of polymerization enhanced with increasing basicity of the applied solvents.

#### Effect of the Monomer Concentration at Various Temperatures

Table III explains the effects of monomer concentration and temperature. The value of viscosity increased with increasing monomer contents, reaching a maximum value, whereas the value diminished in proportion to increasing temperature. The lower value at a higher reactant concentration attributed to reduced reactant mobility due to the onset of gelation, which took place before the viscosity reached a higher value. The reaction was reversible between PAA and reagents.<sup>3,13</sup> The important observation to be made concerning the equilibrium was that the forward reaction was exothermic; therefore, the equilibrium might shift to the depolymerization and the molecular weight of product reduced when the reaction temperature increased. Generally, the synthesis of PIs using the two-step method performed in the temperature range of 10–75°C.<sup>1</sup> A rapid in-

crease in temperature up to about 40°C occurred as soon as dianhydride was first added into the diamine solution in this reaction; therefore, the optimal reaction temperature was below 30°C.

#### Effect of the Reaction Time

Figure 2 represents the consequence of the reaction time influence. The extent of polymerization increased until 4 h, but after that time, the value of viscosity remained nearly unchanged. Those results might relate to the equilibrium between propagating reaction and depolymerization. When the rates of polymerization and depolymerization became equal, the value was maintained after that state. The reaction went on step by step, and the viscosity of propagating polymer gradually increased as time went by, reaching an equilibrium state. From the result, the reaction time was a significant factor to yield high-molecular-weight PI.

#### Effect of Ratio Between the Dianhydride and the Diamine

Table IV represents the result of different mole ratio between dianhydride and diamine. When the dianhydride and the diamine were in stoichiometric balance, the viscosity was the largest value; on the other hand, if a nonstoichiometric ratio was used, the polymer possessed a lower molecular weight. Those results were similar to that observed by other authors.<sup>12,14</sup>

Table VI Preparation of A-Series Copolyimides Yielded From One Dianhydride and Two Diamines<sup>a</sup>

Polymer No.	Dianhydride	Diamines (mol ratio)	Viscosity <sup>b</sup> (dL/g)	Yield (%)	Remarks <sup>c</sup>
		BADB/BAPS			
		2/1			
A-1	PMDA	Random	1.27	> 95	IS
A-2		Block	0.90	> 90	IS
A-3		Alternating	0.55	> 90	IS
		1/1			
A-4	PMDA	Random	1.02	> 95	IS
A-5		Block	0.90	> 90	IS
A-6		Alternating	0.47	> 85	PS
		1/2			
A-7	PMDA	Random	0.66	> 95	SW
A-8		Block	0.45	> 95	PS
A-9		Alternating	0.45	> 85	S
		ODA/BAPS			
		2/1			
A-10	PMDA	Random	1.10	> 95	IS
A-11		Block	0.97	> 90	IS
A-12		Alternating	0.60	> 80	IS
		1/1			
A-13	PMDA	Random	0.82	> 95	IS
A-14		Block	0.73	> 85	IS
A-15		Alternating	0.36	> 85	PS
		1/2			
A-16	PMDA	Random	0.68	> 95	IS
A-17		Block	0.28	> 80	PS
A-18		Alternating	0.39	> 80	S (heating)
		BADB/BAPS			
		2/1			
A-19	BTDA	Random	0.87	> 90	IS
A-20		Block	0.54	> 90	IS
A-21		Alternating	0.38	> 85	IS
		1/1			
A-22	BTDA	Random	0.67	> 90	IS
A-23		Block	0.67	> 90	SW
A-24		Alternating	0.49	> 85	SW
		1/2			
A-25	BTDA	Random	0.57	> 85	IS
A-26		Block	0.53	> 85	SW
A-27		Alternating	0.37	> 80	PS
		BADB/BAPS			
		1/1			
A-28	DMCA	Random	0.34	< 70	S
A-29		Alternating	0.23	< 70	S
		1/2			
A-30	DMCA	Random	0.26	< 70	S
A-31		Block	0.24	< 65	S
A-32		Alternating	0.24	< 50	S
		BADB/BAPS			
		1/1			
A-33	BTCA	Random	0.35	> 80	IS
A-34		Alternating	0.27	> 80	S
		1/2			
A-35	BTCA	Random	0.25	> 80	S
A-36		Block	0.25	> 80	S

<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration in DMAc at 20°C for 7 h under nitrogen.

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

<sup>c</sup> Where S is soluble, PS is partially soluble, SW is swell, and IS is insoluble PI in NMP.

**Table VII Preparation of B-Series Copolyimides Yielded From Two Dianhydrides and One Diamine<sup>a</sup>**

Polymer No.	Diamine	Dianhydride (mol ratio)	Viscosity <sup>b</sup> (dL/g)	Yield (%)	Remarks <sup>c</sup>
		PMDA/BTCA 1/1			
B-1	BADB	Random	1.35	> 95	IS
B-2		Alternating	1.32	> 95	IS
		1/2			
B-3	BADB	Random	1.33	> 95	IS
B-4		Alternating	1.29	> 95	IS
		2/1			
B-5	BAPS	Random	0.80	> 95	S (heating)
B-6		Alternating	0.76	> 95	S
		1/1			
B-7	BAPS	Random	0.70	> 95	PS
B-8		Alternating	0.70	> 95	S
		1/2			
B-9	BAPS	Random	0.69	> 95	IS
		Alternating	0.62	> 95	PS
		PMDA/DMCA 2/1			
B-10		Random			
B-11	BAPS	Random	0.28	> 80	S
B-12		Alternating	0.26	> 80	S
		1/1			
B-13	BAPS	Random	0.34	> 85	S
B-14		Alternating	0.33	> 85	S
		1/2			
B-15		Random	0.19	> 80	S

<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration in DMAc at 20°C for 7 h under nitrogen.

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

<sup>c</sup> Where S is soluble, PS is partially soluble, SW is swell, and IS is insoluble PI in NMP.

**Table VIII Preparation of C-Series Copolyimides Yielded From Two Dianhydrides and Two Diamines<sup>a</sup>**

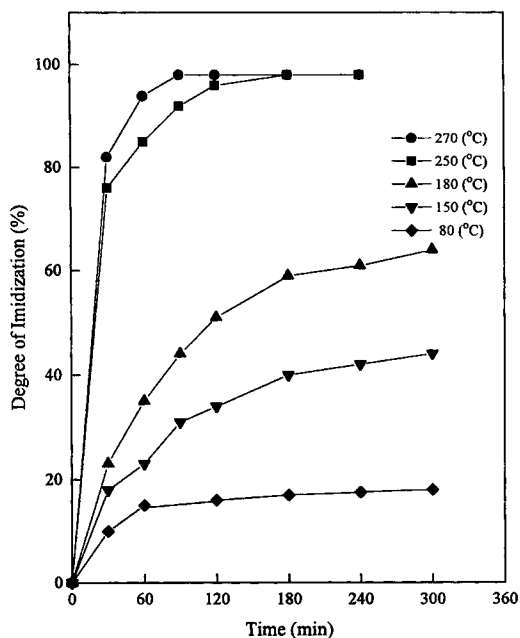
Polymer No.	Dianhydride (mol ratio)	Diamine (mol ratio)	Viscosity <sup>b</sup> (dL/g)	Remarks <sup>c</sup>
	PMDA/BTDA	BADB/BAPS		
C-1	1/1	2/1	0.40	IS
C-2	1/1	1/1	0.49	SW
C-3	1/1	1/2	0.28	IS
C-4	2/1	1/1	0.37	PS
C-5	2/1	1/2	0.27	PS
	PMDA/DMCA	BADB/BAPS		
C-6	1/1	1/1	0.19	S
C-7	1/2	1/1	0.17	S
C-8	2/1	1/1	0.22	S
C-9	2/1	1/2	0.26	S
C-10	1/2	1/2	0.20	S

<sup>a</sup> Polymerization was carried out with 15 wt % of monomer concentration at in DMAc 20°C for 7 h under nitrogen.

<sup>b</sup> Measured at concentration of 0.5 dL/g PAA in DMAc at 30°C.

<sup>c</sup> Where S is soluble, PS is partially soluble, SW is swell, and IS is insoluble PI in NMP.

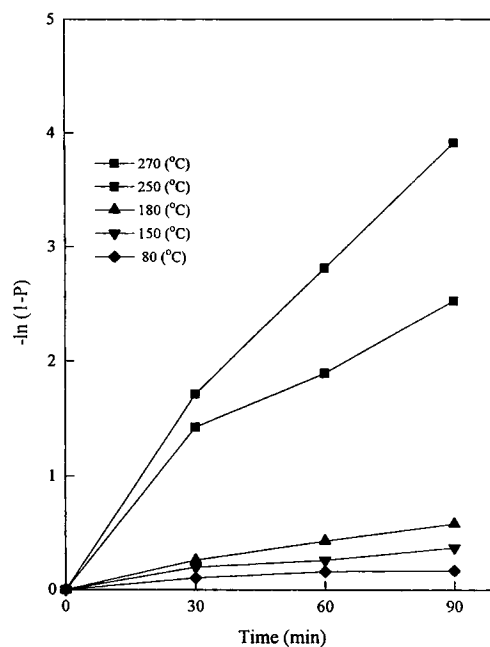




**Figure 4** Time dependence of degree of imidization of H-3 polymer as a function of cured temperature.

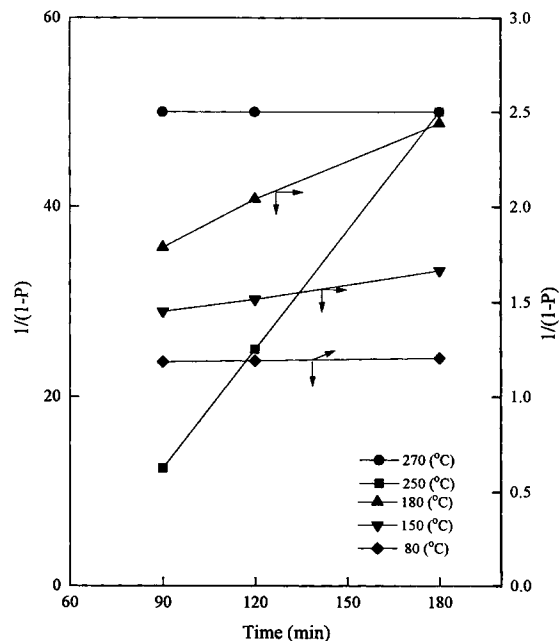
#### Fluctuation of the Viscosity During Thermal Imidization

Figure 3 shows the variation of viscosity as a function of curing time at 80, 150, 180, 250, and 270°C. Although a direct comparison of the value of viscosity was not possible because the molecular structure changed from an amic acid form to an imide one, the influence of curing temperature and time in the viscosity was possible to investigate. As a result, at relatively low curing temperature, below 150°C, the decrease of viscosity was rapid at first and slowed down with time, and the polymer films were flexible at the initial stage, brittle, and ultimately crumbly with the curing process. Although at higher temperatures, above 150°C, the value of viscosity also diminished at the initial stage, the value rapidly increased to initial value and/or to the limiting value and slowed up. The polymer films nearly retained its initial flexibility throughout the curing process. The fluctuation of viscosity was caused by the dissociation effect,<sup>13</sup> because the depolymerization and dehydrocyclization probably coexisted during thermal treatment. When the dehydrocyclization was more dominant than depolymerization, the value of viscosity maintained and/or slightly increased to its initial value and the mechanical property nearly unchanged from that of the prepolymer to that of the corresponding PI; on the other hand, if the depolymerization reaction was the dominant factor, the value of viscosity might de-



**Figure 5** First-order kinetic plot of  $-\ln(1 - P)$  versus time for H-3 polymer as functions of time and temperature in solid-phase imidization.

crease and the polymer films were getting brittle. Those results were confirmed in Figure 1, where a polymer thermal treated at below 150°C showed the characterized absorption peaks of reagents and PAA at around 3300, 1660, 1520, and 1300  $\text{cm}^{-1}$ . The



**Figure 6** Second-order kinetic plot of  $1/(1 - P)$  versus time for H-3 polymer. The slope gives rate constant ( $k$ ).

**Table IX Kinetic Parameters Derived From the First- and Second-Order Kinetics for PI Derivatives<sup>a</sup>**

Polymer	$k$ ( $\times 10^{-3}$ min <sup>-1</sup> )					ln $A$ (min <sup>-1</sup> )
	80°C	150°C	180°C	250°C	270°C	
H-1						
First	3.8	12.8	21.7	40.8	52.2	1.8
Second		3.7	8.1	0.4	0.6	18.4
H-2						
First	3.7	8.0	13.9	36.5	48.5	3.3
Second		3.3	7.3	0.4	0.6	19.4
H-3						
First	3.6	4.8	7.4	34.0	48.5	5.5
Second		1.6	4.8	0.4	0.6	22.0
B-8						
First	3.6	4.0	6.5	34.0	48.5	6.2
Second		1.3	4.1	0.4	0.6	22.8

<sup>a</sup> Where  $k$  is a rate constant and  $A$  is the Arrhenius frequency factor.

presence of those peaks indicated the incomplete imidization and/or depolymerization of prepolymer. The intensity of the absorption peaks, which are characterized as PI, increased with curing temperature and the absorption peaks of PAA nearly disappeared from the chart at above 150°C. Based on the results, the change of molecular weight during thermal treatment was significantly influenced by the rates of dehydrocyclization and depolymerization. The rate was dependent on curing temperature and the proper imidization conditions required to ensure dehydrocyclization.

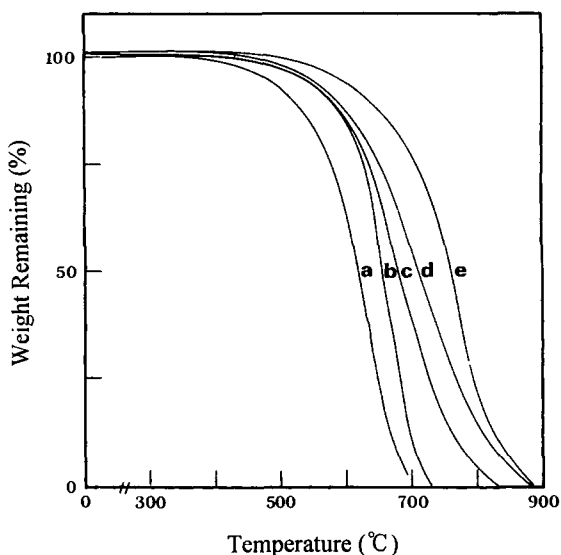
#### PI Derivatives From Various Monomers

The results of H-series PI are summarized in Table V. The value of viscosity increased with the following orders of dianhydrides, PMDA, BTDA, DMCA, BTCA, and diamines, BADB, ODA, BAPS. The results might relate to the chemical structures of reagents. PAA was conformed by the nucleophilic substitution at the carbonyl carbon atom of anhydride.<sup>2,6,13,15</sup> Thus, the extent of polymerization reaction was strongly dependent on the electron affinity of carbonyl carbon atom of dianhydride and the

**Table X Activation Parameters for the Solid-Phase Imidization of PI Derivatives at 453 K<sup>a</sup>**

Polymer	$E_a$ (kJ mol <sup>-1</sup> )	ln $A$ (min <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (kJ mol <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
H-1					
First	6.3	1.8	2.5	-280.4	129.5
Second	84.8	18.4	81.0	-142.2	149.2
H-2					
First	11.5	3.3	7.7	-268.1	129.2
Second	89.0	19.4	85.2	-133.9	149.7
H-3					
First	19.1	5.5	15.3	-250.0	128.5
Second	100.6	22.0	96.8	-112.3	151.5
B-8					
First	21.1	6.2	17.3	-243.9	127.4
Second	104.0	22.8	100.2	-105.6	151.9

<sup>a</sup>  $E_a$  is the activation energy,  $\Delta H^*$  is the activation enthalpy,  $\Delta S^*$  is the activation entropy, and  $\Delta G^*$  is the activation Gibbs free energy.



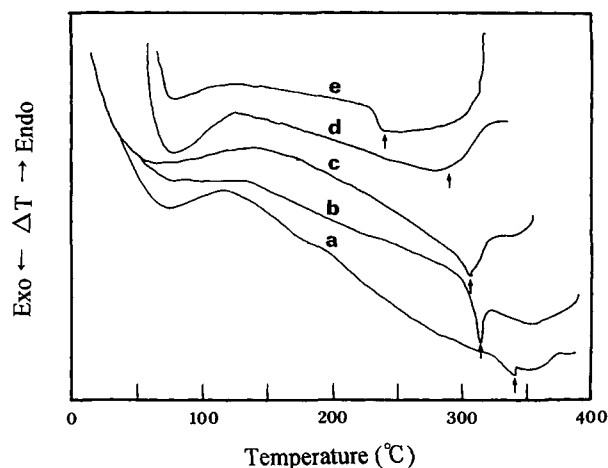
**Figure 7** TGA thermograms of (a) H-3, (b) A-12, (c) A-8, (d) A-4, and (e) H-2 PI derivatives.

nucleophilicity of nitrogen atom of diamine. The strong electron-withdrawing anhydride moieties probably were active toward nucleophilic attack. A nature of bridge group and its position in dianhydride strongly affected electrophilicity of dianhydride.<sup>11,12,16</sup> From the published data,<sup>2,3,13,15</sup> the electron affinity increased as BTCA < DMCA < BTDA < PMDA. The reactivity of diamines also influenced the extent of polymerization.<sup>11,12</sup> That was a function

**Table XI Thermal Behavior of PI Derivatives Prepared From Two-Step Polymerization in TGA Traces<sup>a</sup>**

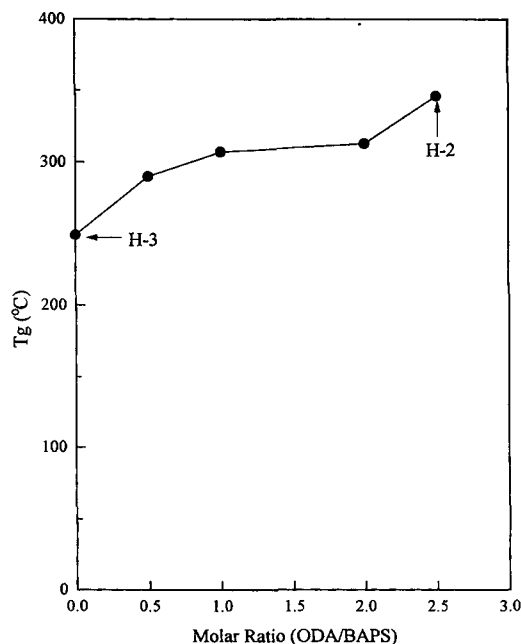
Polymer No.	$T_i$ (°C)	$T_{10}$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)
H-1	490	580	690	770
H-2	530	645	770	810
H-3	425	545	663	717
H-7	410	520	620	690
A-3	420	550	659	755
A-6	420	540	653	725
A-9	420	545	650	720
A-12	450	610	770	810
A-15	450	600	674	800
A-18	425	585	679	720
B-6	430	520	640	700
B-8	420	490	600	720
B-10	400	470	605	690

<sup>a</sup> Measured at heating rate 20°C/min under flowing air,  $T_i$  is initial decomposition temperature,  $T_{10}$  is 10% weight loss temperature,  $T_{max}$  is the maximum rate of weight loss, and  $T_f$  is final decomposition temperature.

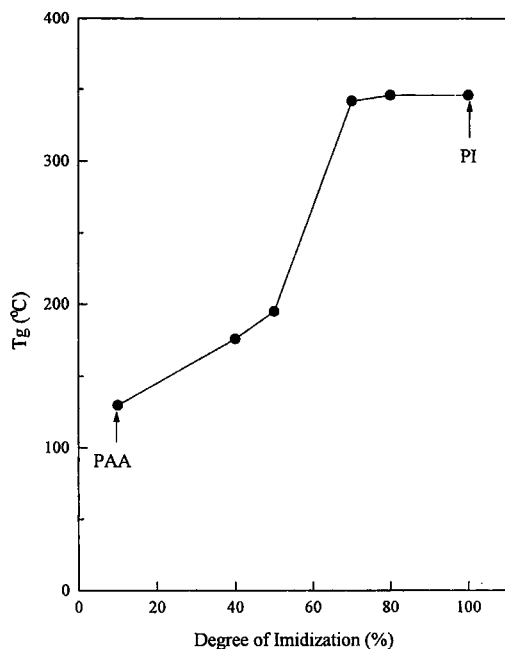


**Figure 8** DSC traces of (a) H-2, (b) A-4, (c) A-8, (d) A-12, and (e) H-3 PI derivatives.

of the chemical structure.<sup>12</sup> The nucleophilicity of diamines depended on the inductive and resonance effects<sup>12</sup>; amino group by induction is an electron-withdrawing one and by resonance is an electron-donor one. If the electron density of carbon carrying the amino group increased, the nucleophilicity of diamine, consequently, increased. For a bridged diamine, the nucleophilicity decreased as the electron-withdrawing ability of the bridge group increased. That was the inductive effect. The group position to the amine also influences the electron density of



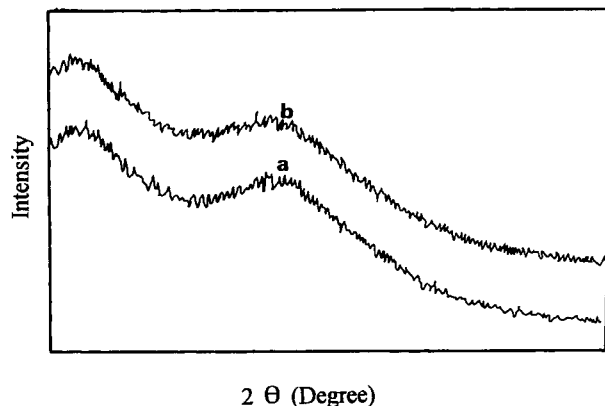
**Figure 9** Evaluation of the  $T_g$  versus the BAPS contents in the PMDA/(ODA/BAPS) PI derivatives.



**Figure 10** Relation between the  $T_g$  and the degree of imidization of the H-2 polymer in solid-phase conversion.

carbon with amino group. On the basis of the chemical structure, BADB appeared to be the most nucleophilic diamine and the nucleophilicity of diamines seemed to be in the following order: BADB, ODA, BAPS. From the result, the extent of this reaction was significantly affected by the electron deficiency of carbonyl carbon atom of the dianhydride and the electron sufficiency of amino nitrogen one of the diamine.

The results of the A-series copolymers are summarized in Table VI. The viscosity of block and/or alternating polymers was lower than that of the corresponding random one. The result was similar to



**Figure 11** X-ray diffraction intensity curves for H-2 and H-3 PI.

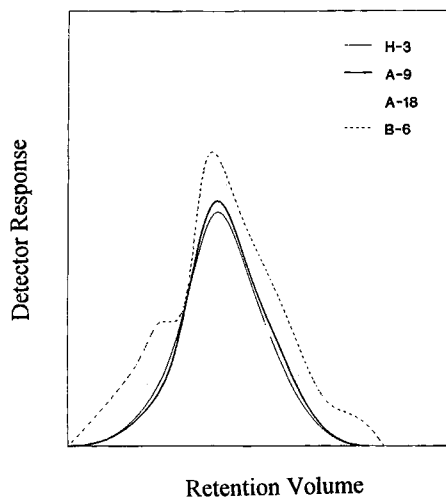
**Table XII** Tensile Strength and Elongation of PI Derivatives<sup>a</sup>

Polymer No.	Tensile Strength (kg/mm <sup>2</sup> )	Elongation (%)
H-1	3.6	8.0
H-2	10.5	8.0
H-3	7.4	8.3
A-3	8.9	11.6
A-9	9.5	10.3
A-12	5.1	9.0
A-15	5.1	15.6
B-2	6.4	11.3
B-4	8.9	9.7
B-8	8.7	7.6
C-12	3.1	5.9
Ultem -1000 <sup>b</sup>	5.6	6.7

<sup>a</sup> Measured at room temperature.

<sup>b</sup> Purchased from General Electric Specialty Plastics.

the result observed by Yang and Hsiao,<sup>6</sup> but was different from that investigated by Babu and Samant.<sup>9</sup> The anhydride group belonging to the block and/or alternating prepolymer might be destroyed by the residual water in the reaction medium; therefore, the next reaction probably did not proceed smoothly. On the other hand, the random copolymer, which was synthesized by simultaneously mixed diamines and a dianhydride, was not subjected to the influence of the terminated-anhydride groups. Thus, the viscosity of the random copolymer was higher than that of corresponding block or the alternating



**Figure 12** GPC of the H-3, A-12, A-22, and B-6 PI derivatives. (a) Evaluation conditions; column,  $\mu$ -styragel 10<sup>4</sup>-10<sup>6</sup> Å; solvent, DMF; temperature, 85°C; and calibration standard, polystyrene.

**Table XIII Solubility of PMDA/BAPS Homopolyimide Prepared From Two-Step Polymerization<sup>a</sup>**

No.	Solvent	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_t$	Remarks <sup>b</sup>
1	Acetic acid	7.1	3.9	6.6	10.5	IS
2	Acetic anhydride	7.8	5.7	5.0	10.9	IS
3	Acetone	7.6	5.1	3.4	9.8	IS
4	Benzene			2.2	9.2	IS
5	1-Butanol	7.8	2.8	7.7	11.3	IS
6	Chlorobenzene	9.3	2.1	1.0	9.6	IS
7	Chloroform	8.7	1.5	2.8	9.3	IS
8	<i>m</i> -Cresol	8.8	2.5	6.3	11.1	S
9	Diethyl ether	7.1	1.4	2.5	7.7	IS
10	<i>N,N</i> -Dimethylacetamide	8.2	5.6	5.0	11.1	S
11	<i>N,N</i> -Dimethylformamide	8.5	6.7	5.5	12.1	S
12	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	S
13	1,4-Dioxane	9.3	0.9	3.6	10.0	IS
14	Ethanol	7.7	4.3	9.5	13.0	IS
15	Formamide	8.4	12.8	9.3	17.9	IS
16	Formic acid	7.0	5.8	8.1	12.2	SW
17	Glycerol	8.5	5.9	14.3	17.6	IS
18	Methanol	7.4	6.0	10.9	14.5	IS
19	<i>N</i> -Methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	S
20	Nitrobenzene	9.8	4.2	2.0	10.9	S
21	1-Propanol	7.8	3.3	8.5	12.0	IS
22	Pyridine	9.3	4.3	2.9	10.7	SW
23	Tetrahydrofuran	8.2	2.8	3.9	9.5	IS
24	Toluene	8.8	0.7	1.0	9.1	IS

<sup>a</sup> Heated continuously at 25°C for 7 days, when the sample was partially soluble in the solvent, then was heated at 70°C for 24 h.

<sup>b</sup> Where S is soluble, SW is swell, and IS is insoluble in solvent.

one. Moreover, the anhydride groups belonging to prepolymer seriously destructured as they stayed in the reaction medium. Polymerization reaction was also influenced by the dimension of extending polymer. It was reported by several authors<sup>6</sup> that the viscosity decreased with increasing flexibility of prepared polymer. According to those reasons, the viscosity of polymer derived from BAPS was lower than that of others. From the results, the extent of copolymerization was affected by the form of prepolymer as well as the structural arrangements of polymer.

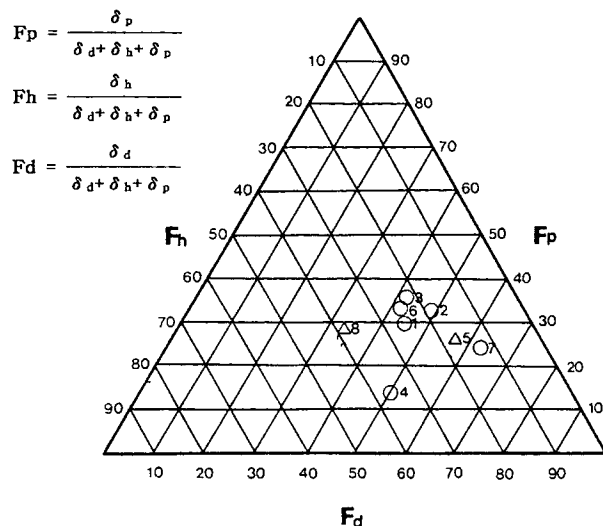
The results of the B-series copolyimides are summarized in Table VII. As given in the table, alternating copolymers even had a tendency to show a similar viscosity value as that of corresponding random ones. The distinctive feature of this process was not to leave unreacted anhydride groups but to exist only in amine-terminated prepolymers. The extent of this reaction might go on smoothly because the amine groups belonging to prepolymer was more stable than the anhydride ones. The viscosity of copolymers decreased as the proportion of BAPS increased in the backbone. It was clearly observed that

the extent of polymerization was influenced by the reactivity and structural effect of reagents.

The results of viscosity measurements of copolymers obtained from the C-series are shown in Table VIII. The extent of polymerization showed the similar tendency to the B-series, but the value of viscosity was practically lower than that of A- and B-series.

### Kinetics

Figure 4 shows the plot of percent imidization against times of various temperatures and that the polymer needed longer time to increase the extent of dehydrocyclization reaction at below 180°C, whereas above 250°C, it could completely convert into imide structures in 120 min. Two distinct stages of the dehydrocyclization reaction were exhibited; initially the reaction was rapid, but the rate decreased greatly as reaction continued. The contribution of the first stage increased with increasing the treating temperature and the degree of imidization was higher.



**Figure 13** Solubility region of H-3 PI in the Hansen space: (O) soluble and ( $\Delta$ ) swell in (1) DMAc, (2) NMP, (3) DMSO, (4) *m*-Cresol, (5) pyridine, (6) DMF, (7) nitrobenzene, and (8) formic acid.

Figure 5 represents the first-order kinetic plots of  $-\ln(1 - p)$  against time of each temperature for H-3 polymer among PIs prepared, and Figure 6 shows a second-order kinetic plots. The kinetics of the solid-phase imidization could be described by the first-order kinetics up to high conversion but deviated from the first-order kinetics at high conversion that was followed by the second-order kinetics. The conversion of PAA into corresponding PI in the initial stage was regarded as a first-order reaction, because it went on between two functional groups belonging to the same amic acid fragment.<sup>4</sup> Table IX represents the kinetic rate constants ( $k$ ) that were calculated for each temperature. The activation energy ( $E_a$ ) and frequency factor ( $A$ ) could be calculated from the Arrhenius plots generated from derived first- and second-order rate constants, and the activation parameters such as activation entropy ( $\Delta S^*$ ), activation enthalpy ( $\Delta H^*$ ), and Gibbs free energy ( $\Delta G^*$ ) were also measured from the absolute rate theory<sup>10,11</sup> and are summarized in Table X. The rate constants for the four kinds of polymers decreased in the following order: PMDA/BADB, PMDA/ODA, PMDA/BAPS, (PMDA/BTDA)/BAPS. The kinetics of the solid-phase imidization was not well established because it was significantly influenced by many factors,<sup>4,16,17</sup> such as the residual solvent, film thickness, molecular mobility, hydrogen-bonding formation, conformation of backbone, even degree of imidization, and so on. The kinetic results, however, showed that the rate of the cyclization reaction was influenced by

the diamine structure as well as the dianhydride one.<sup>11,13</sup> The cyclization reaction occurred by the nucleophilic substitution of amide nitrogen atom ( $-\text{NHCO}-$ ) on the carbonyl carbon atoms of carboxylic acid in PAA. The cyclization rate probably accelerated with increasing electron density on the amide nitrogen atom and the electron affinity of carbonyl carbon atom of carboxylic acid belonging to PAA. The moderate orientation of the reactive functional groups was also required to adequate interaction between those groups, because the dehydrocyclization reaction was intramolecular. Because of this reason, the chain flexibility also played an important role in this reaction. The rigid compound probably reduced the rate of cyclization. The activation parameters were not easily explained, but they related to the dehydrocyclized rate. From the results, the rate of kinetics consisted of the fast initial part and the slowly final one, and the temperature strongly affected to the initial part. High-temperature treatment of PAAs was necessary to obtain high conversion PIs.

### Thermal Properties

Figure 7 shows the TGA thermograms. The relative thermal stability of polymers, the initial decomposition temperature  $T_i$ , 10% weight loss  $T_{10}$ , the maximum rate of weight loss  $T_{\text{max}}$ , and complete decomposition one  $T_f$ , for each step were observed from TGA thermograms. The temperature of maximum rate of weight loss was estimated from differential thermogravimetric trace. Those results are summarized in Table XI. All polymer samples degraded a similar pattern in TGA curves in air. The weight loss in the temperature range of 130–300°C might be due to the loss of either absorbed moisture or residual solvent or due to decomposition of the polymer chain with lower molecular weight. Alternating copolymers showed slightly better stability than the corresponding random or block ones. Those results probably related to the regular structure of the former that might lead to a better packing of the polymer chain. Those phenomenon have been explained by several authors.<sup>18–23</sup> In the thermal analysis of different compound systems, the thermal stability decreased with increasing the ratio of BAPS. The result was due to the introduction of polar linkages, such as  $-\text{O}-$  and  $-\text{SO}_2-$  and the unsymmetric structure. Those might lead to loose packing strength and to less stability.

Figure 8 shows the DSC thermograms. Alternating copolymers in all series showed some higher glass transition temperature ( $T_g$ ) than the corresponding

random and block one. Figure 9 shows the evaluation of the  $T_g$  versus the contents of BAPS, and Figure 10 represents the effect of the degree of imidization on the  $T_g$ .  $T_g$  gradually decreased with increasing BAPS, whereas it increased with extending dehydrocyclization. An overall decrease in  $T_g$  correlated with backbone flexibility or unsymmetric main chain.<sup>19</sup> The polymer with a higher degree of order in the backbone showed a tendency to increase  $T_g$ . The order in backbone related to the hydrogen bonding between the main chains and the flex and bulk characteristics of linkages.<sup>19</sup> The melting temperatures ( $T_m$ ) did not exist on the DSC curves.<sup>19</sup>

### Crystallinity

The crystalline was confirmed by X-ray diffraction. Figure 11 shows X-ray diffraction intensity curves. Both homo- and co-PI showed broad peaks. All polymers were probably amorphous.

### Mechanical Properties

The mechanical properties of several samples are listed in Table XII. In the test, the force buildup was measured as the specimen was being deformed at the constant rate. The effects of the composition and structure on mechanical properties were observed. It was shown that the tensile strength of alternating or partial block copolyimides was a little superior to that of random ones. Elongation was also the function of composition and structure. The elongation increased as the proportion of more flexible component, BAPS, as main chain increased.

### Molecular Weight Distribution

Figure 12 shows GPC of PI derivatives. In this diagram, molecular weight distribution of the polymers exhibited a similar polydispersity index of 2.5–3.0.

### Solubility

Table XIII shows the soluble characteristics of H-3 PI in various solvents, and Figure 13 represents the solubility chart of H-3 PI. By use of Hansen's solubility parameter,<sup>5</sup> composing of dispersion ( $\delta d$ ), polar ( $\delta p$ ), and hydrogen bonding ( $\delta h$ ) force, the solubility region was represented with weak polar and weak hydrogen force. Copolyimides derived from BAPS apparently dissolved well in some polar solvents. Alternating copolyimides in the all series showed a more soluble behavior than the corresponding random and block ones. The solubility of

PI derivatives increased with increasing the flexible and unsymmetric portion as demonstrated in BAPS PI derivatives. Those results were due to the separation of imide ring and the disturbance of the regular sequence introduced by meta-linkage. Those might induce the effect of diluting the high packing force; therefore, the solubility increased.<sup>3–5</sup> In this work, the PI derivatives containing BAPS had a good solubility in some aprotic solvents without much sacrifice in thermal stability. Thus, those soluble behaviors could be advantageous for processing and, moreover, extend the practical applications.

### CONCLUSIONS

PI derivatives with different arrangement were synthesized by the most widespread two-step method. All PI derivatives showed good thermal and mechanical properties. In the DSC,  $T_g$  was shown in the temperature range of 250–346°C.  $T_m$  of all PI derivatives did not exist on the DSC curve, and the result proved the X-ray diffraction. In the TGA thermograms, a weight loss of 10 wt % was observed in the temperature of 470–645°C, whereas the major weight loss was 600–770°C. Thermal properties were influenced by the molecular structure and the chain arrangement. The stability decreased with increasing the ratio of BAPS, and alternating copolymer showed slightly better stability than the corresponding random or block one.

The reactivity of reagents, structure of polymer backbone and monomers, and feature of prepolymer could influence the extent of polymerization. The viscosity values of block and/or alternating sequences were lower than that of the corresponding random one. Those values decreased according to the proportion of more flexible component as the backbone increased.

PI derivatives from BAPS dissolved well in some polar solvents. Alternating PI represented a better solubility than the corresponding random and block ones.

The solid-phase thermal imidization was characterized by the two-step kinetic process, the initial first-order kinetics, and next second-order kinetics.

### REFERENCES

1. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier *Polymer*, **3**, 1373 (1965).

2. M. I. Bessonov, M. M. Koton, V. V. Kudryatsev, and L. A. Laius, *Polyimides: Thermally Stable Polymers*, Plenum, New York, 1987.
3. H. D. Burks and T. St. Clair, *J. Appl. Polym. Sci.*, **30**, 2401 (1985).
4. J. K. Lin, Y. Yuki, H. Kunisada, and S. Kondo, *J. Appl. Polym. Sci.*, **40**, 2123 (1990).
5. H. R. Lee and Y. D. Lee, *J. Appl. Polym. Sci.*, **40**, 2087 (1990).
6. C. P. Yang and S. H. Hsiao, *J. Appl. Polym. Sci.*, **31**, 979 (1986).
7. W. A. Feld, B. Ramalingam, and F. W. Harris, *J. Polym. Sci.*, **21**, 319 (1983).
8. A. Fukami, *J. Polym. Sci.*, **15**, 1535 (1977).
9. G. N. Babu and S. Samant, *Macromol.*, **183**, 1129 (1982).
10. Y. Oishi, M. A. Kakimoto, and Y. Imai, *Macromol.*, **24**, 3475 (1991).
11. Y. J. Kim, T. E. Glass, G. D. Lyle, and J. E. McGrath, *Macromol.*, **26**, 1344 (1993).
12. C. P. Yang and S. H. Hsiao, *J. Appl. Polym. Sci.*, **30**, 2883 (1985).
13. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., *Polyimides*, Blockie & Son, London, 1990.
14. S. V. Vinogradova, YA. S. Vygodskii, and V. V. Korshak, *Vysokomol. Soyed.*, **A12**, 1987 (1970).
15. M. I. Bessonov and V. A. Zubkov, *Polyamic Acids and Polyimides: Synthesis, Transformations, and Structure*, CRC Press Inc., Florida, 1993.
16. K. L. Mittal, *Polyimides: Synthesis, Characterization, and Applications*, Vol. 1-2, Plenum Press, New York, 1984.
17. B. Thomson, Y. Park, and C. P. Painter, *Macromol.*, **22**, 4159 (1989).
18. K. Varma, R. Kumar, and A. B. Bhattacharyya, *J. Appl. Polym. Sci.*, **40**, 531 (1990).
19. T. M. Adduci and E. T. Kuckoff, *J. Appl. Polym. Sci.*, **41**, 129 (1990).
20. S. K. Dolui, D. Pal, and S. Maiti, *J. Appl. Polym. Sci.*, **30**, 3867 (1985).
21. R. W. Lauver, *J. Polym. Sci.*, **17**, 2529 (1979).
22. V. L. Bell, L. Kilzer, E. M. Hett, and G. M. Stokes, *J. Appl. Polym. Sci.*, **26**, 3805 (1981).
23. V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci.*, **14**, 2275 (1976).

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