

# Preparation of Novel Copoly(bis[4-(3-aminophenoxy)phenyl]sulfone/3,3',4,4'-benzophenonetetracarboxyl/pyromellite)imide Derivatives

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**ABSTRACT:** Copolyimide derivatives were prepared from two carboxylic dianhydrides [3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and pyromellitic anhydride (PMDA)] and a single diamine (bis[4-(3-aminophenoxy)phenyl]sulfone [BAPS]) following one-step polymerization. Copolymers could be arranged in sequence through different molar ratios of dianhydride compounds. These polymers were characterized by viscosity, thermal and mechanical properties, solubility, etc. To understand the behavior

of the properties, according to the ratio of the dianhydride compound, a copolymer having various properties could be obtained. Further, it was proved that their properties could be determined from the compositions. The solubility of copolyimides with a large molecular weight was moderately improved. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 853–859, 2003

**Key words:** copolyimide; one-step polymerization; solubility

## INTRODUCTION

Polyimide derivatives have been one of the most important classes of high-performance polymers because of their outstanding properties and they have been used in various fields—film, vanish, engineering plastics, etc.—in recent years. However, their uses are limited because of their intractable properties.<sup>1–5</sup> Most polyimide derivatives are usually manufactured in classic two-step polymerization. A prepolymer as a soluble poly(amic acid) is obtained in the first step and then the prepolymer, formed into the desired shape, is thermally converted into a corresponding imide linkage by dehydrocyclization in the solid state. Thermal dehydrocyclization has been known to be a very complex physicochemical process.<sup>4</sup>

Recently, soluble polyimide derivatives with a large molecular weight were successfully synthesized in a single step.<sup>6–13</sup> Dehydrocyclization into the imide form proceeds in a homogeneous solution and a relatively mild condition is used, for instance, 100–200°C, which might prevent several possible side reactions that might occur during classic thermal treatment in the two-step method. As an approach to achieve the desired properties, copolymerizations are utilized. The main objective of this investigation was to relate the characteristics of copolyimide derivatives to com-

binations of two dianhydrides [3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and pyromellitic anhydride (PMDA)] and a single diamine (bis[4-(3-aminophenoxy)phenyl]sulfone [BAPS]) and to improve the solubility of the polyimide derivatives.

## EXPERIMENTAL

### Reagents

PMDA (Aldrich Co., Milwaukee, WI) and BTDA (Aldrich Co.) were recrystallized from 4-methyl-2-pentanone. BAPS (Wakayama Seika Kogyo Co., Wakayama, Japan) was purified by recrystallization in ethanol. *N*-methyl-2-pyrrolidinone (NMP) was dehydrated with CaH<sub>2</sub> and then distilled before being stored in 4 Å molecular sieves. Other laboratory-grade reagents were used without further purification.

### Measurements

Mechanical properties were obtained at room temperature with an Instron testing machine Model TTC. This test used film with a 200-μm thickness, 10-mm width, and 50-mm length. The viscosity of the polymer solution was measured with an Ubbelohde suspended viscometer in 0.5 dL/g NMP at 25°C. The IR spectrum was recorded in film using a Perkin-Elmer FTIR spectrometer Model PARAGON 500. The kinetics of imide formation could be evaluated according to the preceding article.<sup>6</sup> Gel permeation chromatography (GPC) was carried out using a Water Model 150 C

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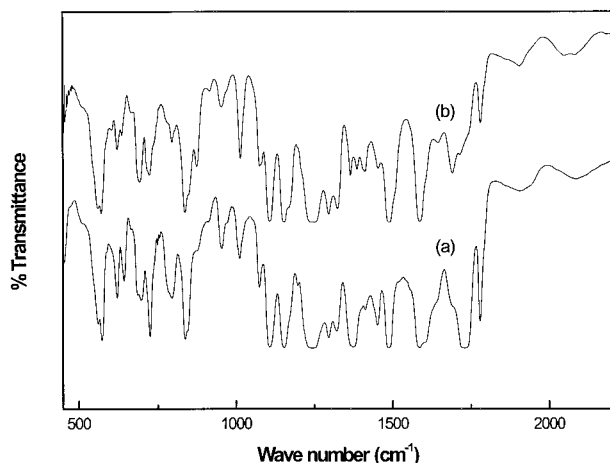


Figure 1 IR spectrum of (a) CPI-1 and (b) CPI-6.

equipped with microstyragel columns (porosity: 1.0–10.0 Å; solvent: DMF). Thermal properties were measured using a differential scanning calorimeter (DSC; DuPont 910) and thermogravimetric analysis (TGA; DuPont 951). To determine solubility, the polymer film was immersed in the solvent and allowed to shake at room temperature for 12 h.

### Polymerization

BAPS was dissolved in NMP and placed in a four-necked round flask equipped with a sealed stirrer,

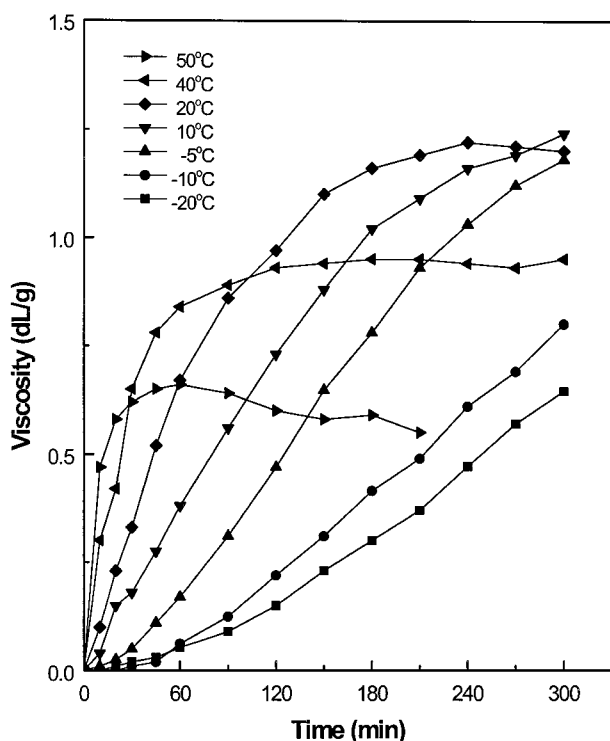


Figure 2 Effects of reaction time and reaction temperature. Reaction was carried out with 20 wt % solid content in NMP.

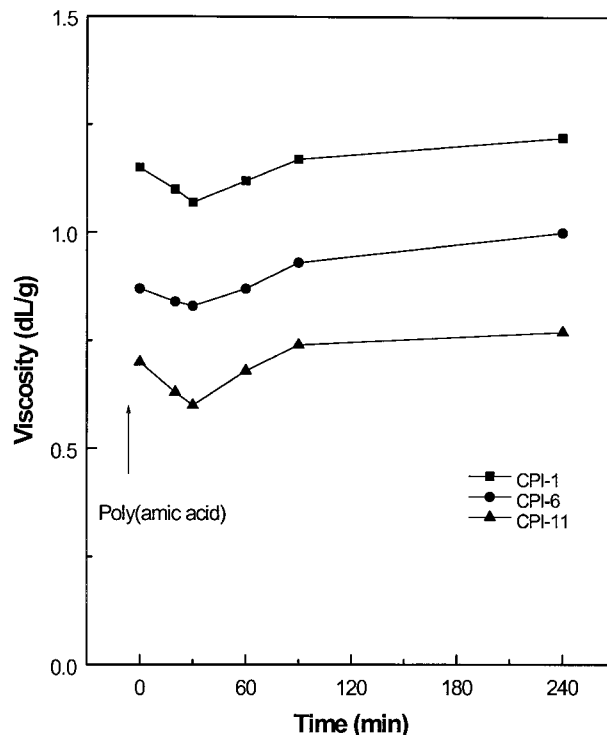


Figure 3 Viscosity change of CPIs during solution imidization at 180°C. Reaction for preparation of the prepolymer was carried out with a 20 wt % solid content in NMP at 20°C for 4 h under flowing nitrogen gas.

nitrogen gas inlet tube, reflux condenser that had a vessel for receiving water, and thermometer. Under nitrogen conditions, an equivalent amount of an anhydride compound composed of PMDA and BTDA was added to the flask, and the solid content was kept at 20 wt %. When the reaction was completed, the mixture was heated to 180°C until no more liberated water was in the nitrogen gas flow. On completion of dehydrocyclization, the polymer was separated in methanol, filtered off, and dried *in vacuo* at 70°C.

### RESULTS AND DISCUSSION

Figure 1 shows a typical example the FTIR spectrum of samples CPI-1 and CPI-6. This spectrum displays a spectral profile characterized by the presence of specific bands to the imide, about 1780 and 1710  $\text{cm}^{-1}$ , which are assigned to the stretch vibration of the C=O linkage of cyclic imide, and about 1370  $\text{cm}^{-1}$ , which is due to the —C—N stretch vibration of the cyclic imide group, but the absorption peaks that identified poly(amic acid) with amide I, II, and III bands about 1650, 1520, and 1300  $\text{cm}^{-1}$  showed only weak traces.

Figures 2 and 3 show the fluctuation of the viscosity as a function of the reaction time and reaction temperature. In this polymerization, poly(amic acid) with a

TABLE I  
Properties of Copolyimide Derivatives

Polymer no.	Monomer (mol ratio)			Viscosity <sup>a</sup> (dL/g)	Elongation at break (%)	Tensile strength (kg/mm <sup>2</sup> )	T <sub>g</sub> <sup>e</sup> b (°C)
	BAPS	PMDA	BTDA				
CPI-1	1	1	0	1.22	7.7	7.2	425
CPI-2	1	0.9	0.1	1.22	7.7	7.2	426
CPI-3	1	0.8	0.2	1.17	7.2	6.9	425
CPI-4	1	0.7	0.3	1.10	8.0	6.7	420
CPI-5	1	0.6	0.4	1.07	8.2	6.5	416
CPI-6	1	0.5	0.5	0.95	8.2	6.5	412
CPI-7	1	0.4	0.6	0.94	9.7	5.7	405
CPI-8	1	0.3	0.7	0.90	13.2	6.0	400
CPI-9	1	0.2	0.8	0.84	13.2	5.2	385
CPI-10	1	0.1	0.9	0.80	13.4	4.8	372
CPI-11	1	0	1	0.76	15.0	4.7	370

Polymerization was carried out with 20 wt % of solid content in NMP at 180°C for 4 h.

<sup>a</sup> Measured at concentration of 0.5 dL/g copolyimide in NMP at 25°C.

<sup>b</sup> Obtained from DSC thermograms.

high molecular weight was prepared at a moderated temperature for 4 h, and, subsequently, the temperature of the reaction medium was rapidly elevated to 180°C for the dehydrocyclization. The influence of the reaction temperature was studied over a temperature range from -20 to 50°C. The value of the viscosity increased in proportion to the increasing temperature. The value, however, obviously was reduced at temperatures to 40°C. The reaction preparing poly(amic acid) was reversible between poly(amic acid) and the monomers.<sup>5,6,12,14</sup> As the forward reaction was exothermic, the reverse reaction occurred when the reaction temperature increased. Generally, the preparation

of polyimide using the common two-step method was performed in the temperature range 10–75°C.<sup>1,4,15</sup> In this reaction, the temperature was increased to about 40°C as soon as the compound of dianhydrides were added into the BAPS solution. After heating at 180°C, the value of the viscosity decreased, but it rapidly retrieved its initial value and slowly increased with time. A direct comparison of the molecular weight using the viscosity value was not possible because the molecular structure of amic acid changed into the imide ring; only the influence of temperature in the

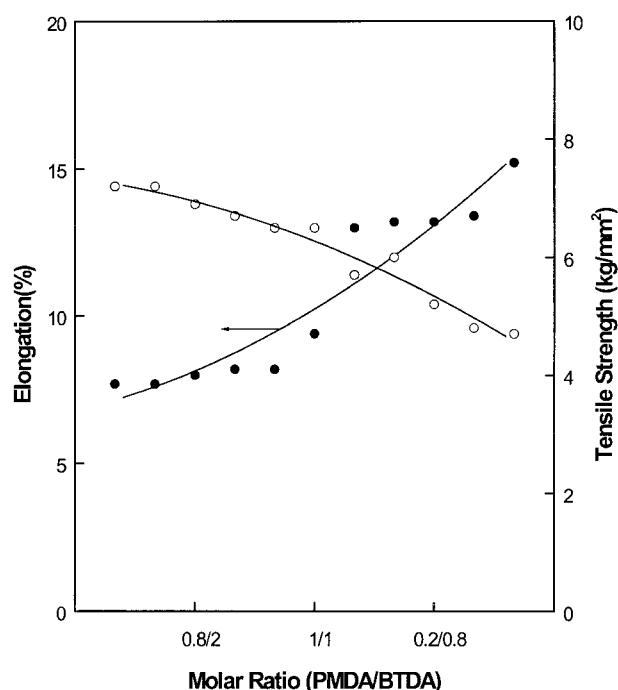


Figure 4 Mechanical properties of CPIs as a function of the molar ratio of dianhydrides.

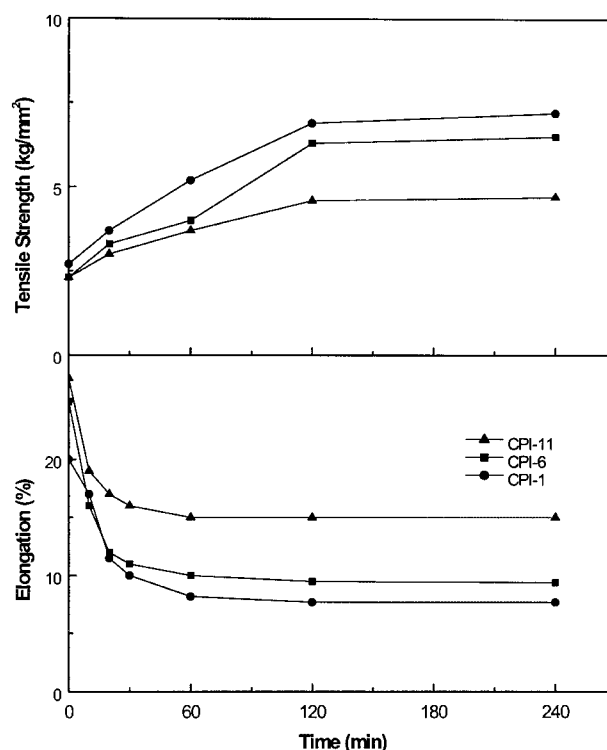
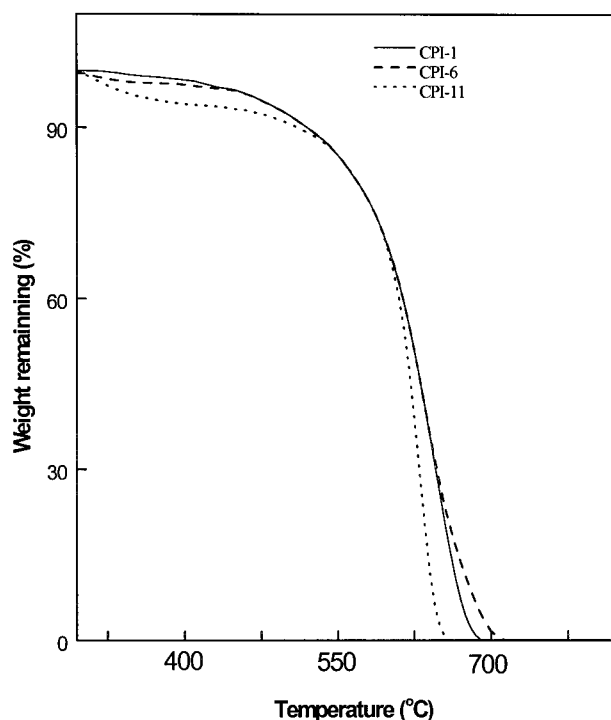


Figure 5 Evaluation of the mechanical properties versus the extent of solution imidization at 180°C.



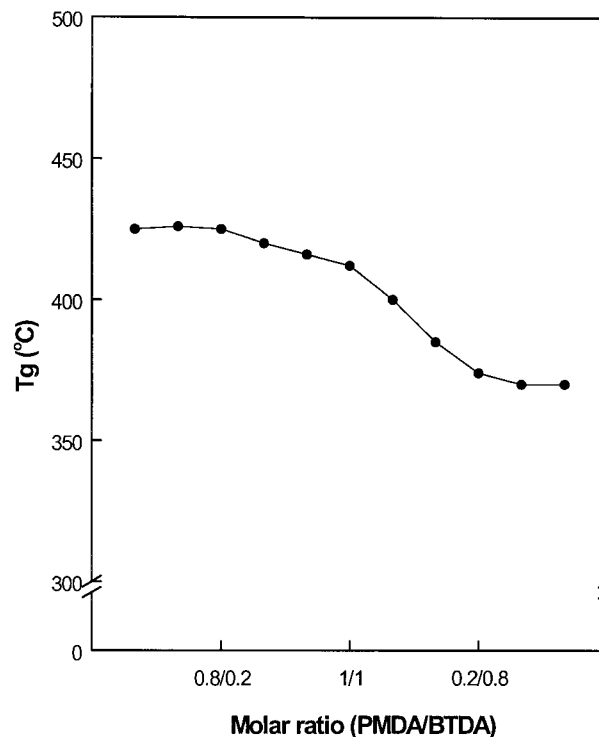
**Figure 6** TGA traces of CPIs: heating rate of 20°C/min in nitrogen atmosphere.

dehydrocyclization reaction was possible to investigate. The result might be related to the dissociation effect,<sup>5,12</sup> as the depolymerization and dehydrocyclization probably coexisted during dehydrocyclization at high temperature. If depolymerization was more dominant than was dehydrocyclization, the value of the viscosity might decrease; on the other hand, when the latter was the dominant factor, the value was probably maintained and/or slightly increased to its initial value. From the result, the molec-

**TABLE II**  
Thermal Behavior of Copolyimide Derivatives  
in TGA Thermograms

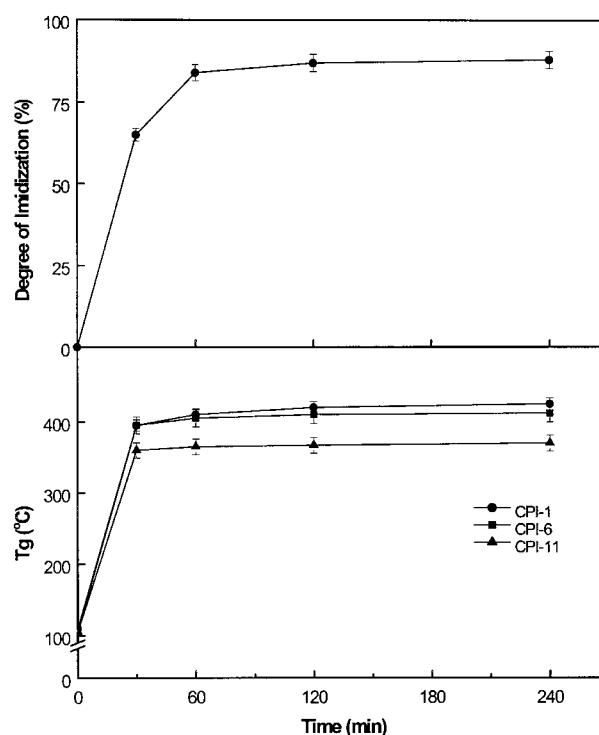
Polymer no.	$T_i$ (°C)	$T_{10}$ (°C)	$T_{60}$ (°C)	$T_{max}$ (°C)
CPI-1	410 ± 5	475 ± 5	690 ± 5	700
CPI-2	410 ± 5	475 ± 5	690 ± 5	700
CPI-3	405 ± 5	475 ± 5	680 ± 5	690
CPI-4	407 ± 5	465 ± 5	680 ± 5	675
CPI-5	407 ± 5	460 ± 5	670 ± 5	650
CPI-6	405 ± 5	460 ± 5	670 ± 5	650
CPI-7	400 ± 5	460 ± 5	660 ± 5	650
CPI-8	400 ± 5	450 ± 5	660 ± 5	640
CPI-9	395 ± 5	445 ± 5	650 ± 5	640
CPI-10	395 ± 5	440 ± 5	630 ± 5	630
CPI-11	395 ± 5	440 ± 5	630 ± 5	630

Measured at heating rate 10°C/min in N<sub>2</sub>.  $T_i$  is the initial decomposition temperature;  $T_{10}$ , the 10% weight loss temperature;  $T_{60}$ , the 60% weight residue temperature; and  $T_{max}$ , the temperature of maximum rate of weight loss.



**Figure 7** Evaluation of the  $T_g$ 's of CPIs versus the molar ratio of PMDA/BTDA.

ular weight during the dehydrocyclization reaction might be influenced by the rates of depolymerization and dehydrocyclization.



**Figure 8** Relation between the  $T_g$ 's of CPIs and the treating time at 180°C in a solution state.

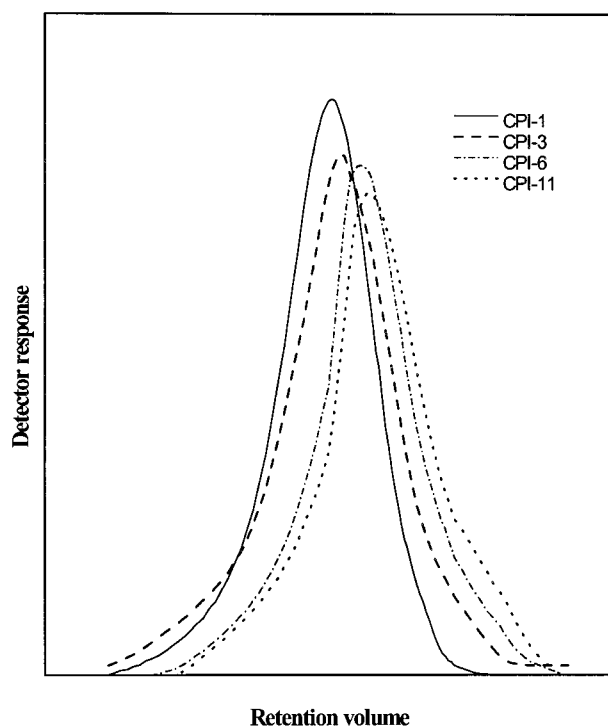


Figure 9 GPC of CPIs.

The properties of copolymers from three-component systems are shown in Table I. The polymer from BAPS–PMDA had the highest properties among those polymers. The values of the viscosity decreased as the proportion of BTDA increased in the backbone. The result might be related to the chemical structure of dianhydride. Poly(amic acid) was yielded by the nucleophilic substitution at the carbonyl carbon atom of anhydride. The extent of the nucleophilic substitution reaction was strongly dependent on the electron affinity of carbonyl carbon atoms of the anhydride portion, and the strong electron-withdrawing anhydride moieties might be active toward nucleophilic attack. From the published data, the electron affinity of PMDA is higher than that of BTDA.

The effects of the composition and structure on the mechanical properties were observed and the result is

shown in Figure 4. The copolymer synthesized revealed good mechanical properties. It was shown that the tensile strength slightly increased in proportion to the increasing fraction of PMDA. On the other hand, the elongation decreased with an increase of the PMDA portion. These properties might be attributed to the rigid structure of PMDA because of a reduction in the flexible linkage in the backbone structure. Figure 5 shows the relationships between the mechanical properties and the reaction time during dehydrocyclization at 180°C. The elongation rapidly decreased at the first stage—the value gradually decreased in proportion to the treated time to the limiting value; on the other hand, the tensile strength slowly increased with the reaction time up to the limiting value. Those results were also related to the change of the chemical structure from amic acid to the corresponding imide form.

Figure 6 shows the TGA thermograms. The initial decomposition temperature  $T_i$  was taken as the onset temperature when the fastest weight loss process begins. The temperature of the maximum rate of weight loss  $T_{\max}$  was obtained from the differential thermogravimetric trace. These results are listed Table II. The copolymers degraded to a similar pattern in the TGA thermograms. The  $T_i$ 's in the range 390–410°C,  $T_{\max}$ 's in the range 630–670°C, and the weight residues at 650°C in nitrogen over 60% qualify these copolymers as thermally stable. The weight relationship between the molar ratios of PMDA/BTDA was observed from TGA.  $T_i$  decreased with an increasing ratio of BTDA in the backbone. This was due to the flexible linkage in BTDA.

Figure 7 shows the relationship of  $T_g$  and the molar ratio of PMDA/BTDA. As the fraction of BTDA decreased, the  $T_g$  increased, but it was somewhat changed. The  $T_g$  of polyimide yielded from PMDA/BAPS was about 425°C, while that of BTDA/BAPS was 370°C. Even if the small moieties of BTDA, having a more flexible linkage, were incorporated into the chain structure, the bending and rotation motions of the main chains increased and a decrease of  $T_g$  occurred. These results had a similar tendency to those

TABLE III  
Activation Parameters for Copolyimide Derivatives at 453 K

Polymer No.	$E_a$ (kJ mol <sup>-1</sup> )	In A (min <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J mol <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
CPI-1	29.22	2.4	21.69	-233.5	127.5
CPI-3	30.50	2.7	22.97	-231.4	127.8
CPI-5	33.52	3.3	25.99	-228.1	129.3
CPI-6	34.46	3.4	26.93	-231.3	131.7
CPI-7	43.23	5.4	35.70	-215.2	133.2
CPI-9	49.00	6.0	41.46	-203.6	133.5
CPI-11	54.08	7.1	46.55	-201.4	137.8

$E_a$  is the activation energy; In A, the Arrhenius frequency factor;  $\Delta H^*$ , the activation enthalpy;  $\Delta S^*$ , the activation entropy; and  $\Delta G^*$ , the activation Gibbs free energy.

TABLE IV  
Soluble Behavior of Copolyimide Derivatives

Solvents	Polymer No.						
	CPI-1	CPI-3	CPI-5	CPI-6	CPI-7	CPI-9	CPI-11
Acetic acid	IS	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS	IS
Chloroform	IS	IS	IS	IS	IS	IS	IS
<i>m</i> -Cresol	S	S	S	S	S	S	S
DMAc	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S
1,4-Dioxane	IS	IS	IS	IS	IS	IS	IS
Formamide	IS	IS	IS	IS	IS	IS	IS
Formic acid	IS	IS	SW	SW	SW	SW	SW
NMP	S	S	S	S	S	S	S
Nitrobenzene	S	S	S	S	S	S	S
1-Propanol	IS	IS	IS	IS	IS	IS	IS
Pyridine	SW	SW	SW	SW	PS	PS	PS
Tetrahydrofuran	IS	IS	IS	IS	IS	IS	IS

Continuously shaken at 25°C for 12 h. S, soluble; PS, partially soluble; SW, swell; IS, insoluble in solvent.

of the TGA. Figure 8 represents the change of  $T_g$  as a function of the treating time at 180°C. The  $T_g$  of CPIs rapidly increased at first, but after that time, the values gradually increased up to the limiting values. The result might be related to the content of the imide ring in the main chain and explained by the density of the imide rings in the polymer.<sup>16–18</sup> The melting temperature was not observed in the DSC traces. All the copolymers were probably amorphous.

Figure 9 shows the GPC of the copolymers. The molecular weight distribution of the polymers revealed a similar polydispersity index of 2.5–2.7.

The kinetics of dehydrocyclization was calculated from the degree of imidization.<sup>4,6,16</sup> The conversion of poly(amic acid) into corresponding polyimide was regarded as first-order kinetics, because it occurred between amide linkages and carboxylic acid groups belonging to the same amic acid fragment. The first-order rate constant ( $k$ ), Arrhenius frequency factor ( $A$ ), and the activation energy parameters were obtained in the same method as in previous articles<sup>4,6</sup> and are summarized in Table III. The activation entropy provided an indication of the nature of the transition state. A positive value of the entropy means that the entropy of the product was greater than was the value of the reactants. In a bimolecular reaction, the product was formed by association of two functional groups, and there was a loss of translational and rotational freedom, so that the value of entropy was usually negative. The cyclization reaction was propagated by the nucleophilic substitution of the nitrogen atom of amide on the carbonyl carbon atom of carboxylic acid in amic acid. The imidization rate might be governed by the electron density on the nitrogen atoms and the electron affinity of the carbonyl carbon atoms. The moderate orientation of those groups was also required for an adequate interreaction between ni-

trogen atoms and carbonyl carbon atoms, because it was an intramolecular reaction. Therefore, the dehydrocyclization in the solution state could be defined as a chemical process.<sup>4,19</sup> The activation parameters were not easily explained, but they might relate to the chain flexibility, because it probably played an important role in the intramolecular cyclization.

The solubility of copolyimide derivatives is shown in Table IV. They were well soluble in aprotic polar solvents, such as NMP, DMAc, and DMSO, at a concentration high enough (20–30%) to fabricate film. The soluble behavior depends on the BTDA moiety. The solubility of the polymers increased with an increasing flexible BTDA portion. Those results might induce the effect of diluting the packing force.

## CONCLUSIONS

Copolyimide derivatives having different chemical structures were synthesized from BAPS and two dianhydride monomers. All the polymers had good thermal and mechanical properties and outstanding chemical stability. Those properties might be related to the chemical structure of the main chains. The copolymer having various molar ratios of dianhydride compounds improved the solubility and that behavior could be also controlled by the molar ratio. They were well soluble in aprotic polar solvents and had a molecular weight sufficiently large for application in various areas.

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