

# Preparation and Characterization of Organosoluble Copolyimides Based on a Pair of Commercial Aromatic Dianhydride and One Aromatic Diamine, 1,4-Bis(4-aminophenoxy)-2-*tert*-butylbenzene, Series

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**ABSTRACT:** A series of copolyimides (co-PIs) with high molecular weights, excellent mechanical properties, heat-resistant properties, and good solubilities in organic solvents were synthesized from six kinds of commercial dianhydrides (**IIa-f**) and 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**I**). Monomers (**IIa-d**) for synthesizing insoluble PIs and monomers (**IIe,f**) for synthesizing soluble PIs were used to synthesize co-PIs with arbitrary solubilities. Nine kinds of soluble co-PIs (**IIIa-e** and **IVa-d**) were synthesized through chemical or thermal cyclodehydration. These co-PIs were found to be easily soluble as well as able to be processed by casting from their solutions such as NMP, DMAc, *m*-cresol, pyridine, THF, and CH<sub>2</sub>Cl<sub>2</sub>. The easily dissolved characteristics of this series of co-PIs stemmed from the *t*-butyl group and ether group within **I**. Besides, when the used dianhydride molecules contained the organosoluble groups, the solubilities in organic solvents could be greatly enhanced. The co-PIs could improve the processability of polymers, while increasing their flexible mechanical properties and maintaining their excellent heat-resistant properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 87–95, 2000

**Key words:** copolyimides; 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene; arbitrary solubilities

## INTRODUCTION

Aromatic polyimides (PIs) are well known as polymer materials of high performance for their excellent thermal stabilities and balanced mechanical and electric properties.<sup>1–5</sup> Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other applications of these polymers, in addition to be

used for adhesives, gas separation membranes, composite matrices, coatings, and foams are rapidly increasing. However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubilities in commercially available solvents; accordingly, studies to improve their solubilities or heat plasticities or both without decreasing their original excellent characteristics have been performed by numerous researches.

So far, many attempts have been made to improve the processabilities of aromatic polyimides.<sup>1–5</sup> The results reported include the incorporation of ether or other flexibilizing linkages into the main chain, which leads to lower glass tran-

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sition temperatures as well as significant improvements in solubilities and other process characteristics of the polymers without greatly sacrificing thermal stabilities. The introduction of a monosubstituted *para*-aromatic monomer into the polymer chain is expected to result in decrease in the order along the chain but enhancement in solubility.

The monomer *tert*-butylhydroquinone (*t*-BHQ), which contains the *tert*-butyl group, is frequently used in antioxidation, and some previous studies reported that it also was used in liquid-crystal material,<sup>6–9</sup> polyesters,<sup>10–13</sup> polyethers,<sup>14–17</sup> and polyphosphate esters.<sup>18,19</sup> On the other hand, the DuPont Company claimed in 1992 that the polyamides based on diamine 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**I**; BAP-*t*BB) had the potential to serve as gas separation membranes.<sup>20</sup> It was reported to incorporate the residue of BAP-*t*BB into PI backbones.<sup>21</sup> However, there has not been any report of the effects of the *t*-butyl group on the solubilities of PIs.

In the present article, we set out to investigate both the effect of the *t*-butyl side chain on the solubilities of aromatic PIs prepared from diamine BAP-*t*BB and the properties of their polyimides (co-PIs). Except for 6FDA and SDPA, the commercial dianhydrides form insoluble polyimides with diamine BAP-*t*BB.<sup>21</sup> We found that the co-PI based on diamine BAP-*t*BB had excellent solubilities in organic solvents. In this research, the anhydrides of both soluble and insoluble PIs copolymerized with BAP-*t*BB were used to investigate the solubilities of co-PIs, and the exploratory method for working out soluble polyimide formulas are provided. A comparative study on the properties of the homopolyimide (homo-PI) and co-PI, specifically, their solubilities, mechanical properties, and thermal stabilities, are also presented.

## EXPERIMENTAL

### Materials

1,4-Bis(4-aminophenoxy)-2-*tert*-butylbenzene (**I**; BAP-*t*BB) (melting point, 129–130°C) was synthesized from *tert*-butylhydroquinone and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction with a 10% Pd-C catalyst and hydrazine hydrate in our previous studies.<sup>21–28</sup> Aromatic dianhydrides: pyromellitic dianhydride (**IIa**; from TCI) (PMDA), 3,3',4,4'-

biphenyltetracarboxylic dianhydride (**IIb**; from Chriskev) (BPDA), 4,4'-oxydiphthalic anhydride (**IIc**; from TCI) (ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**IId**; from TCI) (BTDA), 4,4'-sulfonyldiphthalic anhydride (**IIe**; from New Japan Chemical Co.) (SDPA), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (**IIf**; from Hoechst) (6FDA) were recrystallized from acetic anhydride before use. *N*-Methyl-2-pyrrolidone (NMP; from Fluka), *N,N*-dimethylacetamide (DMAc; from Fluka), pyridine (Py; from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

### Synthesis of Polyimides

#### Chemical Cyclodehydration

Diamine **I** (0.348 g, 1 mmol) was dissolved in 6.86 mL of dried DMAc in a 20-mL flask. After the diamine was dissolved completely, 0.147 g (0.5 mmol) BPDA **IIb** and 0.222 g (0.5 mmol) 6FDA **IIf** were added in one portion. The mixture was stirred at room temperature for 1 h. The inherent viscosity of the resulting poly(amic acid) (PAA) in DMAc was 1.52 dL g<sup>-1</sup>, measured at a concentration of 0.5 g dL<sup>-1</sup> at 30°C. Then a 1.5-mL mixture of acetic anhydride and pyridine (volume ratio 2 : 1) was added to the PAA solution. The mixture was stirred at 80–100°C for 1 h. The polymer solution was poured into methanol. The white fibrous precipitate (**IIIb**) was collected by filtration, washed thoroughly with methanol, and dried at 100°C ( $\eta_{inh} = 1.57$  dL g<sup>-1</sup>).

#### Thermal Cyclodehydration

In a method of synthesis similar to that of chemical cyclodehydration, PAA solution then was poured into a  $\phi = 9$ -cm glass culture dish, which was placed in a 80°C oven for 1 h to remove the solvent. The semidried PAA film was heated sequentially at 120°C for 30 min, 160°C for 15 min, 210°C for 15 min, and 250°C for 30 min. By soaking in water, a flexible PI film of **IIIb** was self-stripped from the glass surface ( $\eta_{inh} = 0.90$  dL g<sup>-1</sup>).

### Characterization

Elemental analyses were performed on a Perkin-Elmer Model 2400 C,H,N analyzer. The inherent viscosities were measured with a Cannon-Fenske viscometer at 30°C. Differential scanning calo-

rimeter (DSC) traces were measured on TA Instruments DSC 2010 at the rate of  $20\text{K min}^{-1}$  in flowing nitrogen ( $40\text{ cm}^3\text{ min}^{-1}$ ). Thermogravimetry analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100, and experiments were carried out on  $10 \pm 2$ -mg samples heated in flowing nitrogen ( $50\text{ cm}^3\text{ min}^{-1}$ ) at a heating rate of  $20^\circ\text{C min}^{-1}$ . A Lloyd instrument with a load cell of  $500\text{N}$  was used to study the stress-strain behavior of the polymer films. A gauge of 2 cm and a strain rate of  $5\text{ cm min}^{-1}$  were used for this study. Measurements were taken at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.5 mm thick), and an average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Polymer Synthesis

In order to investigate the effect of modification of the *t*-butyl group on the solubilities of PI, the synthesis of diamine (**I**) containing the *t*-butyl group with *t*-BHQ was carried out (Scheme 1). In this reaction, regardless of whether *p*-chloronitrobenzene or *p*-fluoronitrobenzene was used, high yields of dinitrocompounds were obtained. Besides, when reduced into **I**, **I** of high purity could be prepared, regardless of whether  $\text{H}_2\text{NNH}_2$  or  $\text{H}_2$  was used.

Although the preparation of common PIs with diamine **I** has been reported in the literature, more detailed investigation of the effect of the *t*-butyl group on the solubility of PI in organic solvents has yet to be performed. We designed a simple method for synthesizing soluble PI that enabled us to detect PIs solubility. According to this method, equivalent weights of diamines and dianhydrides were first used to prepare the PAA solution of 10–12% in DMAc and then suitable solutions of acetic anhydride and pyridine were added. This solution was stirred at  $80\text{--}100^\circ\text{C}$  for 1 h. At this time, if the solution still remained in the transparent and homogeneous phase, then the PI formed would be soluble in organic solvents. If the solution showed gelation or produced precipitation, then the PI formed would be slightly soluble or insoluble in organic solvents.

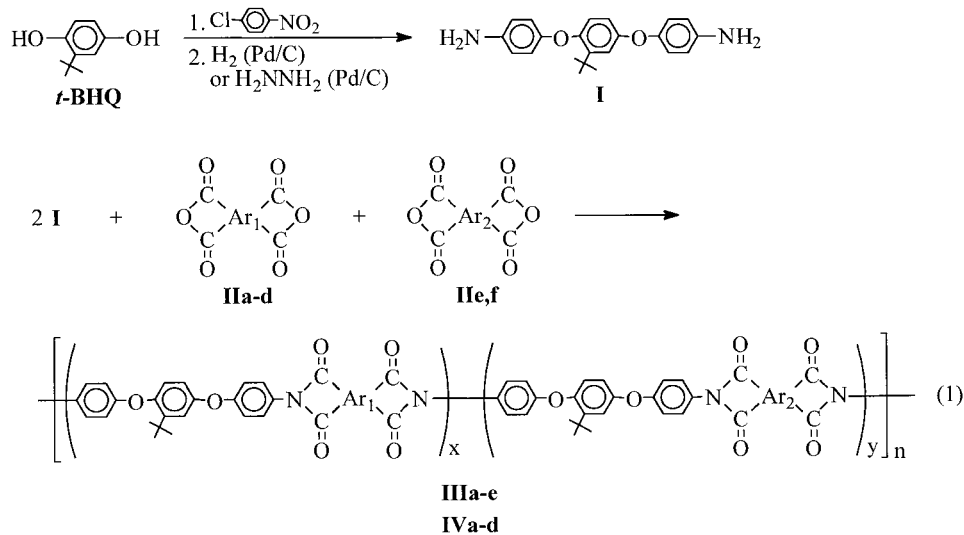
Homo-PIs **Va–f** were synthesized from diamine **I** with six kinds of commercial dianhydrides **Ila–f** through the conventional chemical process as shown in Scheme 1. Synthesis conditions and in-

herent viscosities of the PIs produced are shown in Table I. The diamine **I** forms insoluble precipitated PIs (**Va–d**), when **I** reacted with **Ila–d** (i.e., BPDA, ODPA, and BTDA). PIs **Va–d** were insoluble in DMAc, and their viscosities were measured in concentrated  $\text{H}_2\text{SO}_4$  were in the range of  $0.90\text{--}1.97\text{ dL g}^{-1}$ . When diamine **I** reacted with SDPA (**Ile**) or 6FDA (**IIf**), homogeneous transparent PI solutions were formed. After these polymer solutions were poured into methanol, the white filament-like products (**Ve,f**) were collected. PIs **Ve,f** were soluble in DMAc, and the inherent viscosities were 1.35 and  $0.78\text{ dL g}^{-1}$ , respectively.

The solubility of PIs depends upon the molecular structures of dianhydrides or diamines used. When both or either of these monomers tended to form easily soluble PI in organic solvents, the co-PIs synthesized were easily soluble in solvents. 6FDA recently has been known as a dianhydride monomer, which forms most easily the organic-solvent-soluble PI. While the solubility of the SDPA system containing sulfone depends on the characteristics of diamines used, most of SDPA-PIs are still insoluble or slightly soluble in organic solvents.

Three kinds of *para*-triphenylene-diether-diamine were made to react with SDPA to test the solubilities of PIs (Scheme 2). The results showed that both **VIIe** containing only ether groups and **VIe** containing ether and methyl groups formed precipitates during the imidization reaction, so that the PIs formed were soluble only in concentrated  $\text{H}_2\text{SO}_4$ . Only the reaction product **Ve** formed by reacting with diamine **I** containing a *tert*-butyl group could remain as a homogeneous and transparent solution during the reaction, and the PIs formed could dissolve in DMAc.

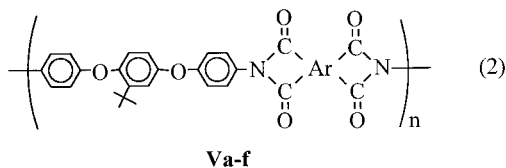
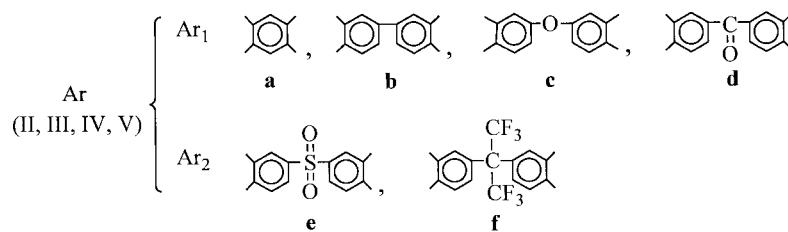
It was most convenient and economical to use the commercial dianhydride to prepare PI; among the PIs formed from **I** and from six kinds of commercial dianhydrides, two are organic-solvent soluble and four are insoluble or slightly soluble. In this research, we investigated the possibilities of preparing soluble PIs by carrying out the copolymerization of dianhydrides of both soluble and insoluble PIs with **I**. 6FDA and SDPA were first mixed individually with the rest of dianhydrides at varying mole ratios before reacting with **I** to prepare the co-PIs (**III**), as shown in Scheme 1. The inherent viscosities and the reaction conditions of the co-PIs produced are shown in Table I. The co-PIs formed from those mixed by 6FDA and equivalent moles of **Ila–d** were all soluble, the



Co-PI	IIIa	IIIa'	IIIb	IIIc	III d	IIIe
Ar <sub>1</sub> /Ar <sub>2</sub>	a/f	a/f	b/f	c/f	d/f	e/f
x/y	1/1	1/2	1/1	1/1	1/1	1/1

Co-PI	IVa	IVa'	IVb	IVc	IVd
Ar <sub>1</sub> /Ar <sub>2</sub>	a/e	a/e	b/e	c/e	d/e
x/y	1/1	1/2	1/1	1/1	1/1



**Scheme 1** Synthetic process.

chemical imidization reactions were carried out homogeneously, and the inherent viscosities were also very high. When SDPA was used to replace 6FDA, soluble co-PIs could be produced under the above-cited matching of diamines and dianhydrides. For this reason, **I** was used as the specific diamine, which could mix with various groups of dianhydrides to prepare PIs of any solubility; therefore, **I** could be said to be an important monomer for preparing easily soluble PIs.

The elemental analysis values of these co-PIs are shown in Table II. They agree roughly with the theoretical values.

#### Properties of Polymers

The qualitative solubilities of these PIs are shown in Table III. Except for H<sub>2</sub>SO<sub>4</sub>, the homo-PIs **Va,b**, synthesized from **I** and **IIa,b**, are insoluble in all the tested organic solvents. When the cho-

**Table I** Synthesis of Polyimides by Chemical Cyclodehydration Method

Co-Polyimides <sup>a</sup>			Polyimides <sup>a</sup>		
Code	$\eta_{inh}$ (dL g <sup>-1</sup> ) <sup>b</sup>	Remark <sup>c</sup>	Code	$\eta_{inh}$ (dL g <sup>-1</sup> ) <sup>b</sup>	Remark <sup>c</sup>
<b>IIIa</b>	1.20	G	<b>Va</b>	1.03 <sup>d</sup>	P
<b>III'a</b>	0.88	S	<b>Vb</b>	1.97 <sup>d</sup>	P
<b>IIIb</b>	1.57	S	<b>Vc</b>	0.90 <sup>d</sup>	P
<b>IIIc</b>	1.39	S	<b>Vd</b>	1.18 <sup>d</sup>	P
<b>III'd</b>	1.35	S	<b>Ve</b>	1.35	S
<b>IIIe</b>	0.99	S	<b>Vf</b>	0.78	S
<b>IVa</b>	1.00	G	<b>VIIe</b>	0.83 <sup>d</sup>	P
<b>IV'a</b>	0.80	S	<b>VIIe</b>	1.10 <sup>d</sup>	P
<b>IVb</b>	1.50	S			
<b>IVc</b>	1.16	S			
<b>IVd</b>	1.14	S			

<sup>a</sup> First, poly(amic acid) (PAA) was formed from 1 mmol of diamine and dianhydrides in 10% DMAc solution at room temperature for 1 h and then 1.4 mL of Ac<sub>2</sub>O and 0.7 mL of pyridine to PAA solution was added at 80°C for 1 h.

<sup>b</sup> Measured at a concentration of 0.5 g dL<sup>-1</sup> in DMAc at 30°C.

<sup>c</sup> Appearance of the polyimide solution during chemical cyclodehydration; S, solution through the reaction; P, precipitation during the reaction; G, gelation.

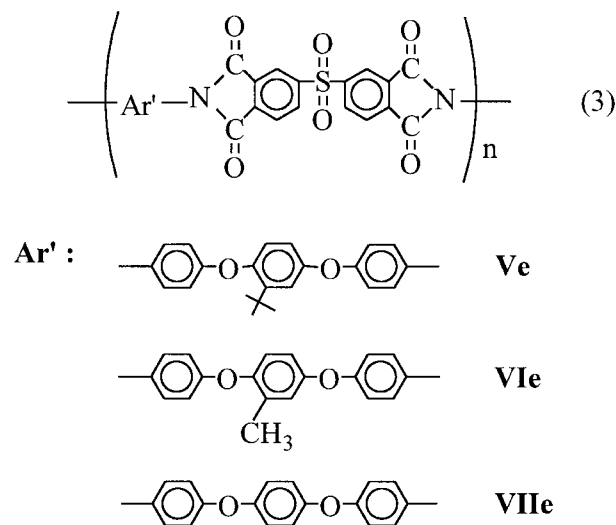
<sup>d</sup> Measured at a concentration of 0.5 g dL<sup>-1</sup> in H<sub>2</sub>SO<sub>4</sub> at 30°C.

sen dianhydrides were ODPA and BTDA, containing the ether and ketone groups, the PIs, though insoluble in DMAc, DMF, etc., were nevertheless soluble in NMP, Py, and *m*-cresol. However, when the dianhydrides adopted were SDPA and 6FDA, containing the sulfone and hexafluoroisopropyl groups, the PIs synthesized (**Ve** and **Vf**) could be dissolved in most solvents, even in THF and CH<sub>2</sub>Cl<sub>2</sub>.

When the PIs were formed from the dianhydrides (**IIa–d**) that caused low-solubility PIs, these dianhydrides were matched and mixed with dianhydrides (**IIe,f**) that led to easily soluble PI to form the co-PIs. These co-PIs could be modified into soluble or easily soluble polymers, such as **IIIa–e** and **IVa–d**, and their solubilities could be changed arbitrarily, depending on the change in the matching proportion. For example, when PMDA/6FDA was 1/1, **IIIa** could dissolve only in NMP or Py and partially soluble in DMAc or DMF; when the ratio was changed to 1/2, **III'a** became an easily soluble PI.

A comparison of the solubilities of PIs (**VIIe**, **VIIe**, and **Ve**) synthesized from three kinds of *para*-triphenylene-diether-diamine and dianhydride **IIe** revealed that the organic solvent solubilities of PIs of the DSDA system stemmed chiefly from the *t*-butyl group. When two ether groups were introduced into the aromatic diamines to form PI (**VIIe**) or when two ether groups and the side-chain methyl group were introduced to modify the polymer (**VIIe**), the results were poor solubility; however, when the side-chain *t*-butyl group was introduced, the result was good.

The solubilities listed in Table III are qualitative. Incidentally, the solubilities of PIs formed through chemical cyclodehydration were almost identical to those of PIs formed through thermal

**Scheme 2** Structures of **Ve**, **VIe**, and **VIIe**.



**Table II** Elemental Analysis of Polyimides

Polymer	Formula <sup>a</sup>	Elemental Analysis (%) <sup>b</sup>		
		C	H	N
<b>IIIa</b>	(C <sub>73</sub> H <sub>48</sub> O <sub>12</sub> N <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (1287.19) <sub>n</sub>	68.12 (67.10)	3.76 (4.13)	4.35 (4.58)
<b>III'a</b>	(C <sub>114</sub> H <sub>72</sub> O <sub>18</sub> N <sub>6</sub> F <sub>12</sub> ) <sub>n</sub> (2041.84) <sub>n</sub>	67.06 (65.98)	3.55 (3.81)	4.12 (4.26)
<b>IIIb</b>	(C <sub>79</sub> H <sub>52</sub> O <sub>12</sub> N <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (1363.29) <sub>n</sub>	69.60 (68.63)	3.84 (3.90)	4.11 (4.14)
<b>IIIc</b>	(C <sub>79</sub> H <sub>52</sub> O <sub>13</sub> N <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (1379.29) <sub>n</sub>	68.79 (67.86)	3.80 (3.78)	4.06 (4.04)
<b>IIId</b>	(C <sub>80</sub> H <sub>52</sub> O <sub>13</sub> N <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (1391.30) <sub>n</sub>	69.06 (68.20)	3.77 (3.75)	4.03 (4.03)
<b>IIIe</b>	(C <sub>79</sub> H <sub>52</sub> O <sub>14</sub> N <sub>4</sub> S <sub>1</sub> F <sub>6</sub> ) <sub>n</sub> (1427.35) <sub>n</sub>	66.48 (65.37)	3.67 (3.74)	3.93 (3.89)
<b>IV'a</b>	(C <sub>108</sub> H <sub>74</sub> O <sub>22</sub> N <sub>6</sub> S <sub>2</sub> ) <sub>n</sub> (1871.92) <sub>n</sub>	69.30 (66.98)	3.98 (4.22)	4.49 (4.74)
<b>IVb</b>	(C <sub>76</sub> H <sub>52</sub> O <sub>14</sub> N <sub>4</sub> S <sub>1</sub> ) <sub>n</sub> (1277.22) <sub>n</sub>	71.46 (69.83)	4.10 (4.13)	4.39 (4.34)
<b>IVc</b>	(C <sub>76</sub> H <sub>52</sub> O <sub>15</sub> N <sub>4</sub> S <sub>1</sub> ) <sub>n</sub> (1293.33) <sub>n</sub>	70.58 (69.36)	4.05 (4.14)	4.33 (4.32)
<b>IVd</b>	(C <sub>77</sub> H <sub>52</sub> O <sub>15</sub> N <sub>4</sub> S <sub>1</sub> ) <sub>n</sub> (1305.34) <sub>n</sub>	70.85 (69.37)	4.02 (4.10)	4.29 (4.32)

<sup>a</sup> Molecular weight in parentheses.<sup>b</sup> Calculated values, with found values in parentheses.

cyclodehydration, although the films obtained through thermal cyclodehydration were denser and the dissolving rates were slower than those obtained through chemical cyclodehydration (heating could be applied to promote the solubilization).

Flexible and transparent PIs films could be obtained through thermal cyclodehydration. Table IV summarizes the mechanical properties of the PIs. Co-PIs **IIIa–e** and **IVa–d** films have tensile strengths in the range of 102 to 122 MPa, elongations at break of 5% to 26%, and initial moduli of 2.1 to 2.9 GPa, respectively. It was found that the mechanical properties of a copolymer fused the properties of its corresponding homo-PI. The tensile strength and elongation of **IIIb** were between those of **Vb** and **Vf**. In homo-PI series (**V**), only **Vc** had a yield point; however, most co-PIs of the **III** and **IV** series had yielding points. Besides, the tensile strengths and initial moduli of these two series of PIs were in a similar range. In general, co-PI not only improved the solubility but the polymer films became tougher (had higher yield point).

The thermal properties of all the PIs obtained from thermal cyclodehydration were evaluated

through TG and DSC, and the results are summarized in Table V.

DSC measurements were conducted with a heating rate of 20°C min<sup>-1</sup> in nitrogen. Quenching from an elevated temperature (~ 400°C) to room temperature in the air gave predominantly amorphous samples so that the glass transition temperatures ( $T_g$ s) of almost all the PIs could be easily observed in the second heating traces of DSC. The components of co-PIs **IIIa–e** and **IVa–d** combined two of the homo-PIs **Va–f**. It was found that the  $T_g$ s of most co-PIs were intermediate between the  $T_g$ s of their corresponding homo-PIs. For example, the  $T_g$  of **IIIa** was 295°C, and the  $T_g$ s of its corresponding homo-PIs **Va** and **Vf** were 303°C and 266°C, respectively. The  $T_g$ s of co-PIs (**III** and **IV**) were in the range of 262–295°C. Pyromellitimide-contained PIs **IIIa**, **IVa**, and **Va** showed the highest  $T_g$ . Homo-PI **Ve** and co-PI **IIIe** containing sulfonyl groups also had higher  $T_g$  than **Vc** and **IIIc** with oxy-linkage. This may be attributed to the intermolecular force of sulfonyl groups moiety.<sup>26</sup>

The thermal stability of the PIs was determined through TG analysis conducted at a heating rate of 20°C min<sup>-1</sup>. The temperatures of 10%

**Table III Solubility Behavior of Polyimides**

Polymer <sup>b</sup>	Solvent <sup>a</sup>										
	DMAc	NMP	DMF	DMSO	<i>m</i> -cresol	Py	THF	CH <sub>2</sub> Cl <sub>2</sub>	Acetone	Toluene	H <sub>2</sub> SO <sub>4</sub>
IIIa	±	+	±	-	-S	+	-	-	-	-	+
III'a	+	+	+	-	+	+	+	+	-	-	+
IIIb	+	+	+	+h	+	+	+	+	-	-	+
IIIc	+	+	+	+	+	+	+	+	-S	-	+
IIId	+	+	+	+	+	+	+	+	-	-	+
IIIe	+	+	+	+	+	+	+	+	-	-	+
III'f	+	+	+	+	+	+	-S	-S	-	-	+
IV'a	+	+	+	+	+	+	-S	±	-	-	+
IVb	+	+	+	+h	+	+	(-)± <sup>c</sup>	+	-	-	+
IVc	+	+	+	+	+	+	(-)±	+	-	-	+
IVd	+	+	+	+	+	+	(-)±	+	-	-	+
Va	-	-	-	-	-	-	-	-	-	-	+
Vb	-	-	-	-	(-)±	-	-	-	-	-	+
Vc	-	(-)±	-	-	(-)±	+	-	±	-	-	+
Vd	-	(-)±	-	-	(-)±	(-)±	-	-	-	-	+
Ve	+	+	+	+	+	+	+	+	-	-	+
Vf	+	+	+	+	+	+	+	+	-S	±	+
VIe	-	-	-	-	-	-	-	-	-	-	+
VIIe	-	-	-	-	-	-	-	-	-	-	+

Note. Measured at a concentration of 0.5 wt %; +, soluble at room temperature in 24 h; -, insoluble; ±, partially soluble; -S, swelling; +h, soluble on heating and then precipitated at room temperature.

<sup>a</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide.

<sup>b</sup> Polyimides obtained by both chemical and thermal methods.

<sup>c</sup> Parentheses represent the PI solubility behavior obtained by the thermal method.

weight loss ( $T_d$ ) both in nitrogen and in the atmosphere were determined from original thermograms and also are tabulated in Table V. The  $T_{ds}$

of these PIs stayed in the range of 511–545°C in nitrogen and 517–540°C in air. All PIs showed a similar pattern of decomposition with no signifi-

**Table IV Tensile Properties of Soluble Polyimide Films**

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
IIIa	111	105	15	2.2
IIIb	107	106	20	2.4
IIIc	107	103	26	2.1
IIId	129	113	12	2.9
IIIe	—	106	5	2.5
IVa	110	102	22	2.2
IVb	121	111	18	2.7
IVc	—	119	9	2.5
IVd	121	122	17	2.3
Va	—	124	22	2.4
Vb	—	116	39	2.6
Vc	112	104	15	2.4
Vd	—	106	6	2.6
Ve	—	114	7	2.6
Vf	—	103	8	2.1

Note. Polyimide films obtained by the thermal cyclodehydration method.

cant weight loss below 500°C in air or in nitrogen and with more than 40 wt % residue remaining when heated to 800°C in nitrogen. The range of  $T_d$ s of series **III** and **IV** co-PIs was similar to that of series **V** homo-PIs, meaning that the co-PIs maintain excellent thermal properties as homo-PIs do. Figure 1 shows the TGA curves of co-PI **IIIa**. As expected, the PI did not show significant weight loss below about 500°C in nitrogen and in air. The rate of initial weight loss was slower in nitrogen than in air. When the temperature exceeded 550°C, the rate in nitrogen slowed down; however, the rate in air remained fast. It also can be seen that the decomposition rate was lower in air than in nitrogen in the range of 500–600°C. This was different from the general aromatic PIs that decomposed more slowly in nitrogen.<sup>29</sup> This may be attributed to the effect of oxidative cross-linking between aliphatic segments of the polymer chain when the polymer is thermally degraded in air.

## CONCLUSIONS

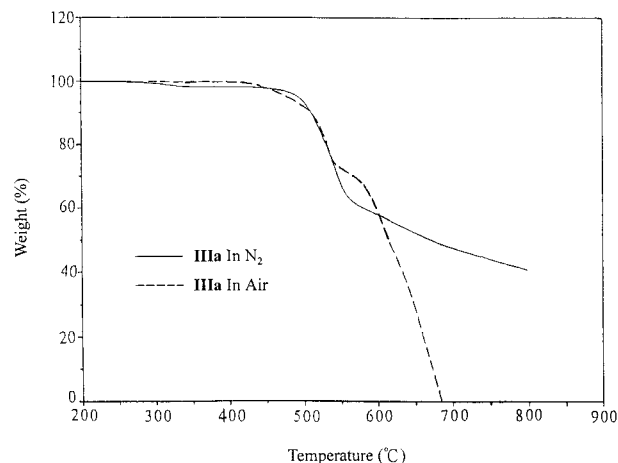
The introduction of the ether group and the side-chain *t*-butyl group into the aromatic polyimides

**Table V Thermal Properties of Polyimides**

Polymer	TGA			
	DSC <sup>a</sup> $T_g$ (°C)	$T_d$ (°C) <sup>b</sup>		Residual wt % at 800°C in N <sub>2</sub>
		In N <sub>2</sub>	In Air	
<b>IIIa</b>	295	533	526	50
<b>IIIb</b>	274	538	537	54
<b>IIIc</b>	262	538	540	50
<b>IIId</b>	268	536	535	53
<b>IIIe</b>	273	520	521	48
<b>IVa</b>	283	536	535	51
<b>IVb</b>	278	512	517	49
<b>IVc</b>	264	511	518	41
<b>IVd</b>	260	514	524	45
<b>Va</b>	303	540	527	46
<b>Vb</b>	268	545	538	52
<b>Vc</b>	245	538	535	45
<b>Vd</b>	255	538	530	53
<b>Ve</b>	278	512	519	41
<b>Vf</b>	266	540	534	54

<sup>a</sup> Baseline shift in the second heating DSC trace, with a heating rate of 20°C min<sup>-1</sup>.

<sup>b</sup> Decomposition temperatures at which 10% weight loss was recorded by TG at a heating rate 20°C min<sup>-1</sup>.



**Figure 1** TGA curves of copolyimide **IIIa** in nitrogen and in air with a heating rate of 20°C min<sup>-1</sup>.

could improve the organosolubilities. By using 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**I**) prepared from *t*-BHQ, the organosoluble co-PIs (**III** and **IV**) were obtained. The co-PIs prepared from **I** with commercial dianhydrides had excellent solubilities in organic solvents. Although the solubilities of homo-PIs synthesized from **I** with PMDA, BPDA, ODPDA, and BTDA were poor, the co-PIs based on these mixture dianhydrides of insoluble PI and soluble PI (used DSDA and 6FDA) could produce the arbitrarily soluble PIs. The solubilities of the PIs containing the *t*-butyl group were actually better than those of the PIs containing methyl side-chain groups or no side-chain groups. Not only were the co-PIs modified into soluble PIs, but they also became tougher and had yield points. The measurement results of the thermal properties of co-PIs showed that their  $T_g$  values and 10% weight loss temperatures would be close to those values of the two corresponding homo-PIs or between them.

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