

# Synthesis and Properties of Polyimides Containing Bisphenol Unit and Flexible Ether Linkages

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Received 8 October 2001; accepted 18 March 2002

**ABSTRACT:** A series of novel polyimides was prepared from various diamines (with bisphenol units) and various aromatic tetracarboxylic dianhydrides via a two-step (thermal imidization) method. The monomers and polymers were produced in high yields. The benzophenone series exhibited better solubility than the pyromellitic series and, especially, those with the alkyl (methyl)-substituted ring exhibited good solubility and could be readily dissolved in polar aprotic solvents such as dimethylformamide and *N,N'*-dimethylacetamide. The glass transition temperatures

of all polyimides were found to be 235–322 and 223–332°C, respectively, by DSC and dynamic mechanical analysis. Thermogravimetric analyses indicated that the polymers were fairly stable up to 482–617°C (10 wt % loss in N<sub>2</sub>) and 480–610°C (10 wt % loss in air). Wide-angle X-ray diffractograms revealed that most polyimides were predominantly amorphous. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 945–952, 2003

**Key words:** DSC; TGA; x-ray; amorphous

## INTRODUCTION

Polyimides are well known for their excellent thermal, electrical, and mechanical properties. They are important commercially available high-performance polymers. It has been reported that the incorporation of asymmetric,<sup>1,2</sup> non-coplanar,<sup>3–5</sup> and flexible linkages between aromatic rings, or bulky pendant group<sup>6–9</sup> in a polymer chain, will change its solubility and its thermal and mechanical properties. In this study, we report on the synthesis of a series of polyimides containing the bisphenol unit and aryl ether linkage to understand the relationship between the structure and properties of polyimides.

## EXPERIMENTAL

### Materials

All diol monomers of high purity were obtained from Honshu Chemical (Japan), including tetramethyl bisphenol-A (**I**<sub>1</sub>, mp 164–165°C), 3,3'-dimethyl bisphenol-A (**I**<sub>2</sub>, mp 138–139°C), 4,4'-cyclohexylidene bisphenol (**I**<sub>3</sub>, mp 186–188°C), 4,4'-ethylidene bisphenol (**I**<sub>4</sub>, mp 123–124°C), bis(4-hydroxy-3,5-dimethylphenyl)methane (**I**<sub>5</sub>, mp 175–176°C), 1,1'-biphenyl-4,4'-diol (**I**<sub>6</sub>, mp 281°C), 2,2'-bis(4-hydroxyphenyl)propane

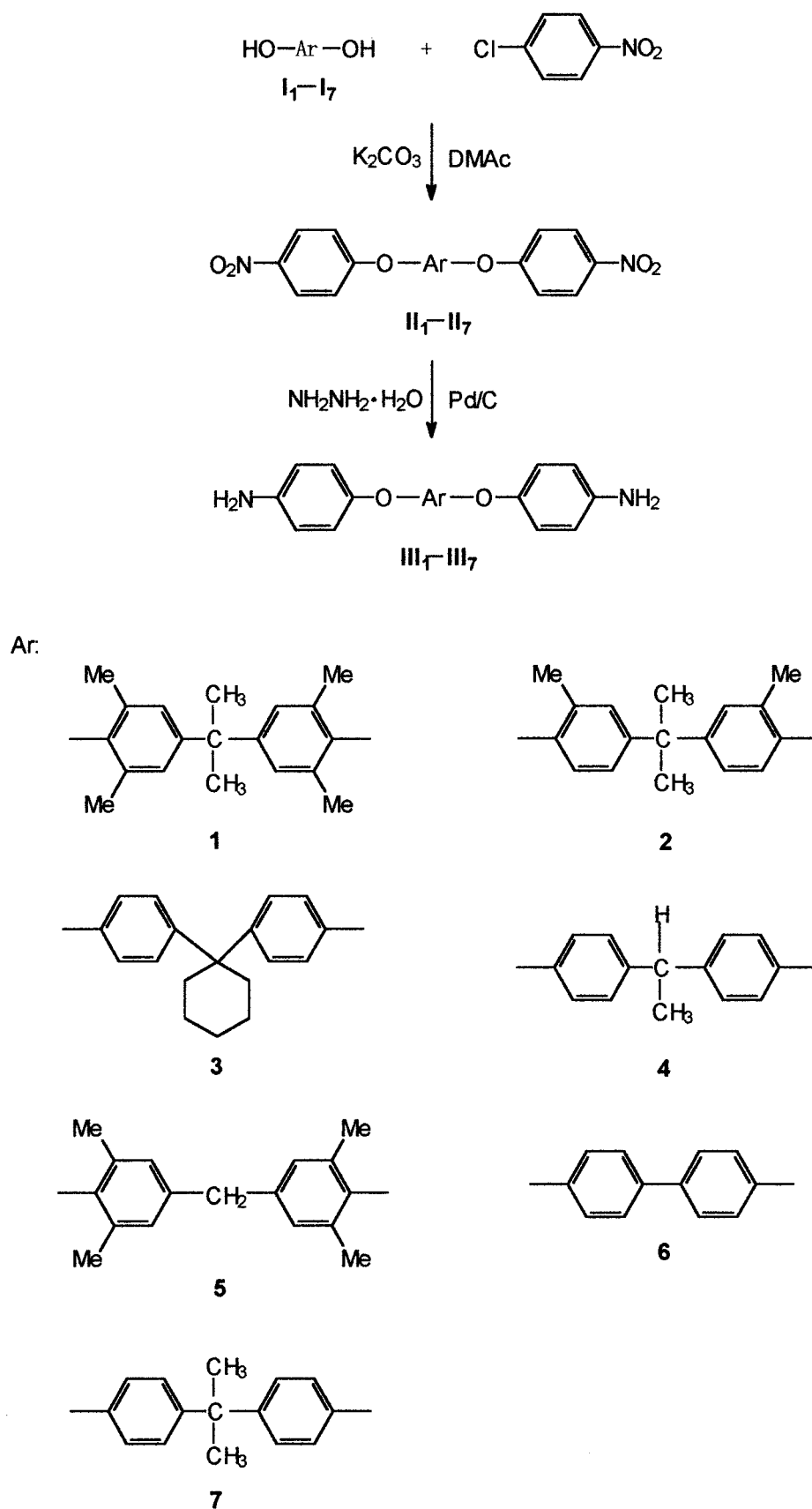
or bisphenol-A (**I**<sub>7</sub>, mp 150–151°C). Other monomers and solvents were obtained from various commercial sources, including pyromellitic dianhydride (PMDA, **IV**<sub>1</sub> Chriskev), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **IV**<sub>2</sub> Chriskev), *p*-chloronitrobenzene (Acros, Belgium), hydrazine monohydrate (SHOWA, Tokyo, Japan), anhydrous potassium carbonate (SHOWA), 10% palladium on activated charcoal (TCI, Tokyo, Japan), *N,N*-dimethylacetamide (DMAc, TEDIA), *N,N*-dimethylformamide (DMF, Fison, England), *N*-methyl-2-pyrrolidone (NMP, TEDIA). All the reaction solvents and chemicals were used as received and stored over calcium hydride or in a reduced pressure dry box.

### Measurements

Elemental analyses were carried out with a Heraeus CHN-Rapid elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-520 spectrometer with KBr pellets or 5- to 10- $\mu$ m film. Spectra in the optical range of 400–4000 cm<sup>-1</sup> were obtained by averaging 32 scans at a resolution of 4 cm<sup>-1</sup>. Electron impact (EI) source mass spectrometric analyses were performed on a VG 70-250S GC/MS spectrometer with a solid inlet. Differential scanning calorimeter (Perkin-Elmer DSC-7) measurements were used in this study. Samples of ~ 5–10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 20°C/min in the range of 30–480°C under N<sub>2</sub> atmosphere and the glass transition temperature (*T*<sub>g</sub>) values were taken as the change of the specific

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Contract grant sponsor: National Science Council of the Republic of China.



Scheme 1

TABLE I  
 Mass Spectra of Dinitro Monomers

Structure	M/E analyses
	527 $[M+1]^+$ ; 511 $[M-(CH_3)]^+$ 154 $[Ph-Ph]^+$ ; 77 $[Ph]^+$
	499 $[M+1]^+$ ; 483 $[M-(CH_3)]^+$ 289 $[ \text{C}_6\text{H}_4(\text{CH}_3)_2\text{O} ]^+$ 154 $[Ph-Ph]^+$ ; 77 $[Ph]^+$
	511 $[M+1]^+$ ; 154 $[Ph-Ph]^+$ 136 $[M-(\text{---O---C}_6\text{H}_4\text{---NO}_2)]^+$ 77 $[Ph]^+$
	457 $[M+1]^+$ ; 441 $[M-(CH_3)]^+$ 289 $[ \text{---O---C}_6\text{H}_4\text{---C(H)(CH}_3\text{)---C}_6\text{H}_4\text{---O---} ]^+$ 244 $[ \text{---C(H)(CH}_3\text{)---C}_6\text{H}_4\text{---O---} ]^+$ 154 $[Ph-Ph]^+$ ; 77 $[Ph]^+$
	498 $M^+$ 256 $[ \text{---CH}_2\text{---C(CH}_3\text{)}_2\text{---O---C}_6\text{H}_4\text{---NO}_2 ]^+$ 242 $[ \text{---C(CH}_3\text{)}_2\text{---C}_6\text{H}_4\text{---O---C}_6\text{H}_4\text{---NO}_2 ]^+$ 154 $[Ph-Ph]^+$ 136 $[ \text{---O---C}_6\text{H}_4\text{---NO}_2 ]^+$ 77 $[Ph]^+$
	428 $M^+$ 307 $[M-(\text{---C}_6\text{H}_4\text{---NO}_2)]^+$ 289 $[M-(\text{---O---C}_6\text{H}_4\text{---NO}_2)]^+$ 154 $[Ph-Ph]^+$ 137 $[ \text{---NO}_2\text{---C}_6\text{H}_4\text{---O---} ]^+$ 77 $[Ph]^+$
	471 $[M+1]^+$ ; 455 $[M-(CH_3)]^+$ 439 $[M-(CH_3)_2]^+$ 226 $[ \text{---O---C}_6\text{H}_4\text{---C(CH}_3\text{)}_2\text{---C}_6\text{H}_4\text{---O---} ]^+$ 154 $[Ph-Ph]^+$ 77 $[Ph]^+$

heat in the heat flow curves. Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer DMA-7 thermal analyzer system. A sample 15 mm in length (measuring system display of sample height, based on sample zero) and 5 mm in width was used. The modulus and  $\tan \delta$  were studied when the sample

was subjected to a temperature scan mode with an extension measuring system (by using the stainless steel extension kit) at a programmed heating rate of  $10^\circ\text{C}/\text{min}$  from 30 to  $300^\circ\text{C}$  at a frequency of 1 Hz. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 thermal analyzer by using a

TABLE II  
 Mass Spectra of Diamine Monomers

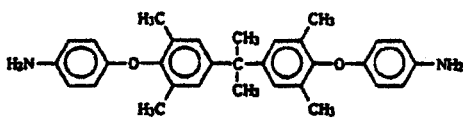
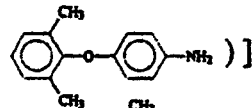
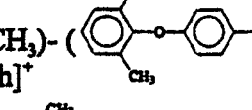
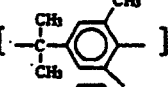
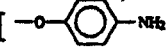
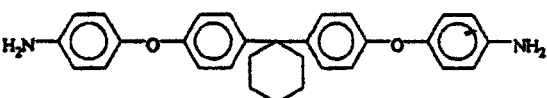
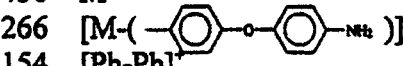

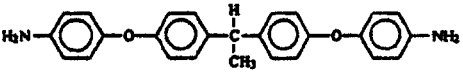
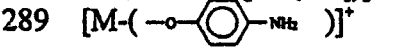
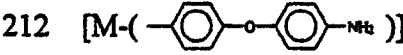
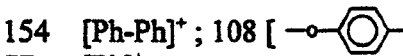
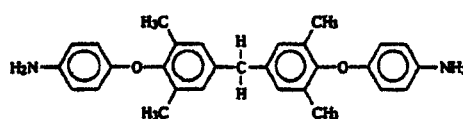
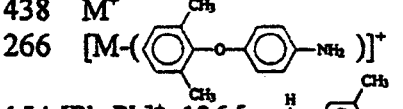
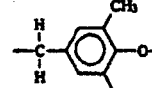
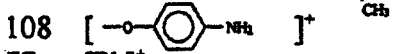
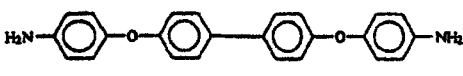
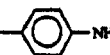
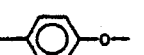
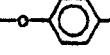
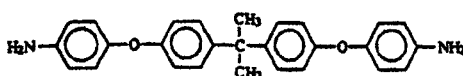
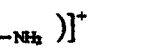
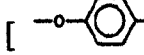
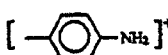
Structure	M/E analyses
<b>III<sub>1</sub></b> 	466 M <sup>+</sup> ; 451 [M-(CH <sub>3</sub> )] <sup>+</sup> 254 [M-(  )] <sup>+</sup> 238 [M-(CH <sub>3</sub> )-(  )] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> 133 [  ] <sup>+</sup> 108 [  ] <sup>+</sup> ; 77 [Ph] <sup>+</sup>
<b>III<sub>3</sub></b> 	450 M <sup>+</sup> 266 [M-(  )] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> 108 [  ] <sup>+</sup> 77 [Ph] <sup>+</sup>
<b>III<sub>4</sub></b> 	396 M <sup>+</sup> ; 381 [M-(CH <sub>3</sub> )] <sup>+</sup> 289 [M-(  )] <sup>+</sup> 212 [M-(  )] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> ; 108 [  ] <sup>+</sup> 77 [Ph] <sup>+</sup>
<b>III<sub>5</sub></b> 	438 M <sup>+</sup> 266 [M-(  )] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> ; 136 [  ] <sup>+</sup> 108 [  ] <sup>+</sup> 77 [Ph] <sup>+</sup>
<b>III<sub>6</sub></b> 	368 M <sup>+</sup> ; 276 [M-(  )] <sup>+</sup> 261 [  ] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> ; 108 [  ] <sup>+</sup> 77 [Ph] <sup>+</sup>
<b>III<sub>7</sub></b> 	395 M <sup>+</sup> ; 395 [M-(CH <sub>3</sub> )] <sup>+</sup> 380 [M-2(CH <sub>3</sub> )] <sup>+</sup> 226 [M-2(  )] <sup>+</sup> 154 [Ph-Ph] <sup>+</sup> ; 108 [  ] <sup>+</sup> 93 [  ] <sup>+</sup> ; 77 [Ph] <sup>+</sup>

TABLE III  
Yield and Elemental Analyses of Dinitro Monomers

Dinitro code	Yield <sup>a</sup> (%)	MP (°C)	Formula ( $M_w$ )		Elemental analyses (%)		
					C	H	N
II <sub>1</sub>	95	195–197	C <sub>31</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> (526)	Calcd.	70.72	5.70	5.32
				Found	69.95	4.93	5.84
II <sub>2</sub>	93	175–176	C <sub>29</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> (498)	Calcd.	69.87	5.22	5.26
				Found	69.42	5.13	5.30
II <sub>3</sub>	81	131–132	C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> (510)	Calcd.	70.59	5.09	5.49
				Found	69.98	5.21	4.89
II <sub>4</sub>	84	145–146	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>6</sub> (456)	Calcd.	68.42	4.39	6.14
				Found	67.83	4.47	5.49
II <sub>5</sub>	89	194–195	C <sub>29</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> (498)	Calcd.	69.88	5.22	5.62
				Found	69.03	5.28	4.93
II <sub>6</sub>	96	200–203	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub> (428)	Calcd.	67.29	3.74	6.54
				Found	66.60	3.80	5.91
II <sub>7</sub>	94	117–121	C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> (470)	Calcd.	68.94	4.68	5.96
				Found	68.84	4.70	5.88

<sup>a</sup> The yield of dinitro monomers were recrystallized from various solvents: II<sub>1</sub> (acetic anhydride), II<sub>2</sub> (acetic anhydride), II<sub>3</sub> (acetic anhydride/ethanol = 1/1), II<sub>4</sub> (acetic anhydride/ethanol = 1/2), II<sub>5</sub> (acetic anhydride/DMAc = 3/1), II<sub>6</sub> (acetic anhydride), II<sub>7</sub> (acetic anhydride).

heating rate of 20°C/min in N<sub>2</sub> at a purge pressure of 25 psi within the temperature range of 30–800°C. Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP. II). The wide-angle X-ray measurements were performed at room temperature with film specimens on an X-ray diffractometer (Rigaku Geiger Flex D-Max IIIa), by using Ni-filtered Cu K $\alpha$  radiation. The scanning rate was 4° min<sup>-1</sup>.

### Synthesis of monomers (II<sub>1</sub>–II<sub>7</sub> and III<sub>1</sub>–III<sub>7</sub>)

#### Synthesis of dinitro II<sub>1</sub> compound

A mixture of tetramethyl bisphenol-A (I<sub>1</sub>, 56.80 g, 0.2 mol), *p*-chloronitrobenzene 69.32 g (0.44 mol), potassium carbonate 60.82 g (0.44 mol), and 320 mL DMAc was refluxed at 160°C for 8 h under nitrogen. After completion of the reaction, the reaction mixture was

added to water to precipitate the product, which was collected by filtration, recrystallized from acetic anhydride, and then dried *in vacuo* (100°C). The yield of II<sub>1</sub> was 95% (light-yellow crystals, 100 g), mp 195–197°C; MS (EI) *m/z* 527 (M<sup>+</sup>, 100).

ANAL. calcd for C<sub>31</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>: C, 70.72; H, 5.70; N, 5.32. Found: C, 69.95; H, 4.93; N, 5.84.

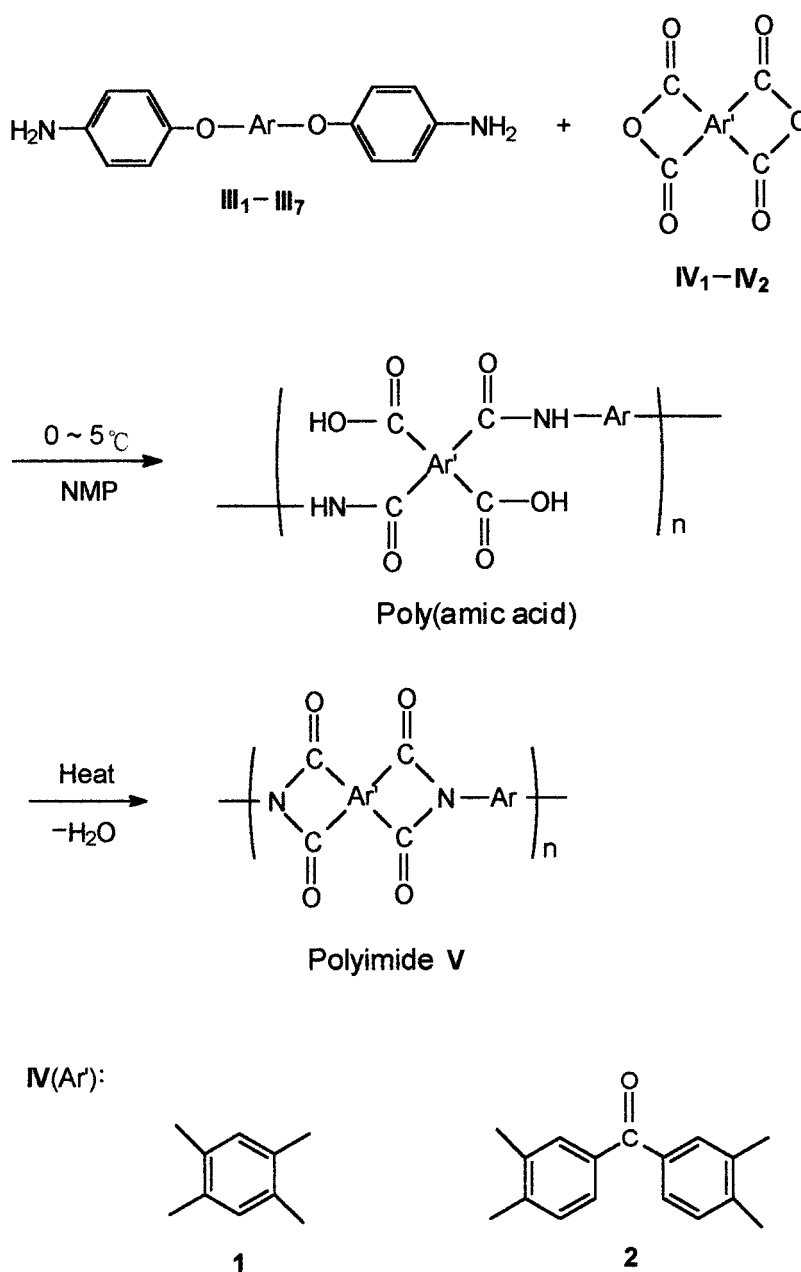
All other monomers (II<sub>2</sub>–II<sub>7</sub>) were prepared analogously.

#### Synthesis of diamine III<sub>1</sub> compound

To 52.60 g (0.1 mol) of the dinitro II<sub>1</sub> compound in 300 mL ethanol was added 0.25 g 10% palladium on carbon (Pd/C). Over a period of 1 h, 120 g of 80% hydrazine monohydrate was added to the above mixture at ~ 85°C and then maintained at that temperature for 12 h. After

TABLE IV  
Yield and Elemental Analyses of Diamine Monomers

Diamine code	Yield (%)	MP (°C)	Formula ( $M_w$ )		Elemental analyses (%)		
					C	H	N
III <sub>1</sub>	84	149–151	C <sub>31</sub> H <sub>34</sub> N <sub>2</sub> O <sub>2</sub> (466)	Calcd.	79.83	7.30	6.00
				Found	79.98	7.20	6.06
III <sub>2</sub>	75	96–97	C <sub>29</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub> (438)	Calcd.	79.45	6.85	6.39
				Found	79.48	6.89	6.43
III <sub>3</sub>	52	155–156	C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> (450)	Calcd.	80.01	6.67	6.22
				Found	79.93	6.67	6.23
III <sub>4</sub>	93	154–156	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> (396)	Calcd.	78.79	6.06	7.07
				Found	78.85	6.06	7.13
III <sub>5</sub>	77	177–178	C <sub>29</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> (438)	Calcd.	79.45	6.85	6.39
				Found	79.46	6.90	6.44
III <sub>6</sub>	87	153–154	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> (368)	Calcd.	78.26	5.43	7.61
				Found	78.70	5.57	7.53
III <sub>7</sub>	94	125–127	C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> (410)	Calcd.	79.00	6.34	6.83
				Found	79.04	6.41	6.85



Scheme 2

the removal of Pd/C, the hot solution was added to water. The slurry was filtered and dried to give 55.7 g (84%) of crystals, mp 149–151°C; MS (EI)  $m/z$  466 ( $M^+$ , 100). ANAL. calcd for  $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2$ : C, 79.83; H, 7.30; N, 6.00. Found: C, 79.98; H, 7.20; N, 6.06.

All other monomers ( $\text{III}_2-\text{III}_7$ ) were prepared analogously and gave acceptable analytic results to confirm the identity and purity.

#### Polymer preparation and film casting ( $\text{V}_{11}-\text{V}_{71}$ and $\text{V}_{12}-\text{V}_{72}$ )

A three-necked flask equipped with an additional funnel and a high-purity  $\text{N}_2$  inlet was charged with a solution of diamine  $\text{III}_1$  in NMP; then dianhydride

(PMDA) was added all at once. The mole ratio and solid content of the diamine/dianhydride mixture were 1:1 and 15 wt %, respectively. The reaction mixture ( $\sim 20$  mL) was stirred at 0–5°C in a  $\text{N}_2$  atmosphere affording a viscous poly(amic acid) solution after 3 h. The solution was spread (with film-casting apparatus) on a heatproof glass plate and dried at 60°C for 12 h in a forced air oven. The film on the glass was then converted to the polyimide by heating in air at 100, 200, and 300°C for 1 h each, respectively. The film was cooled to room temperature and stripped from the plate by soaking in water.

All other polyimides ( $\text{V}_{21}-\text{V}_{71}$  and  $\text{V}_{22}-\text{V}_{72}$ ) were prepared analogously.

TABLE V  
Synthesis of Polyimides<sup>a</sup> from Various Diamines and Various Aromatic Tetracarboxylic Dianhydrides

Polymer <sup>b</sup>	Diamine	Dianhydride	Reaction time (h)	Film
V <sub>11</sub>	III <sub>1</sub>	IV <sub>1</sub>	3	Clear (Flexible)
V <sub>21</sub>	III <sub>2</sub>	IV <sub>1</sub>	6	Clear (Flexible)
V <sub>31</sub>	III <sub>3</sub>	IV <sub>1</sub>	4.5	Clear (Flexible)
V <sub>41</sub>	III <sub>4</sub>	IV <sub>1</sub>	5.5	Clear (Flexible)
V <sub>51</sub>	III <sub>5</sub>	IV <sub>1</sub>	6.5	Clear (Flexible)
V <sub>61</sub>	III <sub>6</sub>	IV <sub>1</sub>	4.5	Clear (Flexible)
V <sub>71</sub>	III <sub>7</sub>	IV <sub>1</sub>	3.5	Clear (Flexible)
V <sub>12</sub>	III <sub>1</sub>	IV <sub>2</sub>	3.5	Clear (Flexible)
V <sub>22</sub>	III <sub>2</sub>	IV <sub>2</sub>	7	Clear (Flexible)
V <sub>32</sub>	III <sub>3</sub>	IV <sub>2</sub>	5	Clear (Flexible)
V <sub>42</sub>	III <sub>4</sub>	IV <sub>2</sub>	4.5	Clear (Flexible)
V <sub>52</sub>	III <sub>5</sub>	IV <sub>2</sub>	4	Clear (Flexible)
V <sub>62</sub>	III <sub>6</sub>	IV <sub>2</sub>	3	Clear (Flexible)
V <sub>72</sub>	III <sub>7</sub>	IV <sub>2</sub>	3	Clear (Flexible)

<sup>a</sup> Reaction condition: Diamine/dianhydride = 1/1 (mole ratio), solid content = 15%.

<sup>b</sup> The first subscript number stands for diamine; the second subscript number stands for dianhydride.

## RESULTS AND DISCUSSION

### Monomer synthesis

Scheme 1 shows the synthetic routes to III<sub>1</sub>–III<sub>7</sub>. All dinitro monomers, except II<sub>3</sub> (steric hindrance), were obtained in high yields, which can be attributed to the fact that the dipotassium salts of I<sub>1</sub>–I<sub>7</sub> are good nucleophiles. For I<sub>1</sub>, I<sub>2</sub>, and I<sub>5</sub> monomers, the electron donating effect of dialkyl substituents at ortho positions to OH is greater than their steric hindrance.<sup>10</sup> In addition, the electron withdrawing NO<sub>2</sub> group in *p*-chloronitrobenzene also increases its reactivity. Similarly, all diamine monomers, except III<sub>3</sub>, were obtained in high yields. The structures of monomers were confirmed by mass spectrometry (Tables I and II) and elemental analysis (Table III and IV) and were in good agreement with the proposed structures. The typical infrared spectra of diamine and the corresponding dinitro compound exhibited several distinctive differences. The diamine showed two absorptions at 3332–3400 cm<sup>-1</sup> (NH stretching) and 1640 cm<sup>-1</sup> (NH bending), while lacking the absorption at 1590 cm<sup>-1</sup> (asymmetric) and 1350 cm<sup>-1</sup> (symmetric) for NO<sub>2</sub> stretching vibration.

### Preparation of polymers

A series of polyimides containing bisphenol units were synthesized by a conventional two-step method starting with diamines and aromatic tetracarboxylic dianhydrides through ring-opening polyaddition and subsequent thermal cyclo-dehydration imidization, as shown in Scheme 2. Poly(amic acid) formation is actually a very complex process which includes the competition between propagation and hydrolysis.<sup>11</sup> Ac-

ording to the Carother's equation, to obtain a high molecular weight poly(amic acid), the monomer purity and solvent dryness are extremely critical. Table V summarizes the obtained polyimides.

### Properties of polyimides

The solubilities of polyimides in various solvents were investigated and the results are summarized in Table VI. All polyimides were soluble in concentrated sulfuric acid at room temperature. In polar aprotic solvents, they exhibited somewhat limited solubility, whereas V<sub>11</sub> and V<sub>12</sub> (or V<sub>52</sub>) showed better solubility than other polyimides. Although the molecular structure of polyimides V<sub>11</sub> and V<sub>71</sub> (or V<sub>32</sub> and V<sub>62</sub>) were similar, their molecular volumes were different, and V<sub>71</sub> and V<sub>62</sub> packed denser than V<sub>11</sub>, which led to a decrease in solubility. The introduction of a cycloalkane group (V<sub>32</sub>) or alkyl-substituted ring (V<sub>11</sub>) into the polyimides resulted in a larger molecular volume, which also led to an increase in solubility and reduced crystallinity. Comparison of the wide-angle X-ray diffractograms of polyimides V<sub>11</sub> with V<sub>41</sub> and V<sub>71</sub> are shown in Figure 1. Polymer V<sub>11</sub> showed an amorphous pattern, whereas V<sub>41</sub> and V<sub>71</sub> showed some crystallinity. Moreover, polyimide V<sub>61</sub> revealed crystalline character and exhibited one peak around 20°, which may be due to the more efficient packing of polymer chains containing biphenylene structure.

The thermal properties of the polyimides were investigated by TGA, DSC, and DMA, as shown in Table VII. The 10 wt % degradation temperature ranged from 482 to 617°C in N<sub>2</sub> and from 480 to 610°C in air. The char yields at 700°C in N<sub>2</sub> atmosphere were 53–72%. The glass transition temperatures (*T<sub>g</sub>*) of the two families of polyimides were found to be 235–322 and 223–332°C, respectively, by DSC and DMA. The re-

TABLE VI  
Solubility of Polyimides<sup>a</sup>

Polymer	Solvent			
	NMP	DMF	DMAc	H <sub>2</sub> SO <sub>4</sub>
V <sub>11</sub>	±h	+h	+h	++
V <sub>21</sub>	—	±h	±h	++
V <sub>31</sub>	—	±h	—	++
V <sub>41</sub>	—	—	±h	++
V <sub>51</sub>	—	±h	±h	++
V <sub>61</sub>	—	—	—	++
V <sub>71</sub>	—	±h	±h	++
V <sub>12</sub>	±h	+h	+h	++
V <sub>22</sub>	±h	±h	+h	++
V <sub>32</sub>	—	±h	±h	++
V <sub>42</sub>	—	±h	±h	++
V <sub>52</sub>	±h	±h	+h	++
V <sub>62</sub>	—	—	—	++
V <sub>72</sub>	±h	±h	±h	++

<sup>a</sup> (++) Soluble at room temperature, (+h) soluble in hot solvent, (±h) swelled slightly soluble in hot solvent, (—) insoluble.

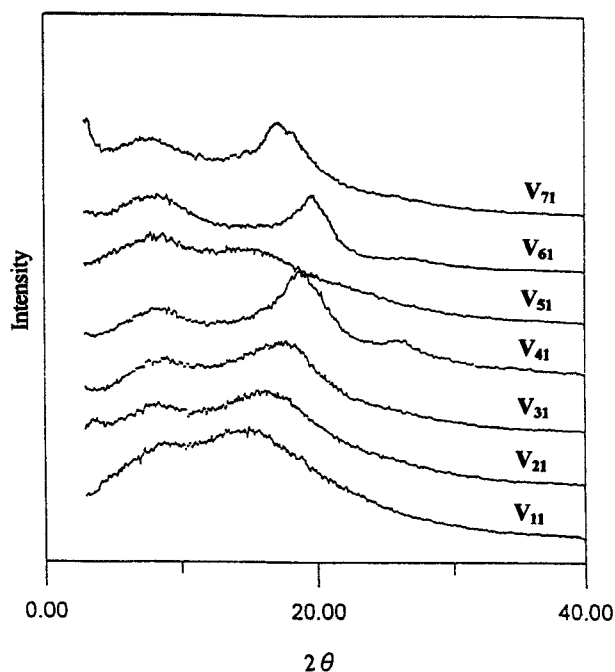


Figure 1 Wide-angle X-ray diffraction patterns of the PMDA (IV<sub>1</sub>) series polyimides.

sults of the thermal analysis indicated a high thermal stability of the synthesized polyimides. Moreover, the polymers of the V<sub>6</sub> series exhibited higher thermal properties than other polymers, which may be attributed to the rigid (biphenylene)<sup>12</sup> structure. Conversely, incorporation of a cycloalkane group or alkyl-substituted ring into the polymer main chain resulted in lower thermal stability. Figure 2 shows the isothermal TGA traces of polyimides at 500°C in N<sub>2</sub>. These curves reveal that the stiffer polyimides (V<sub>6</sub> series) had higher char yield than the others.

TABLE VII  
Thermal Properties of Polyimides

Polymer	$T_g$ (°C)		$T_d$ (°C) 10 wt% loss in		Char yield 700°C (%) N <sub>2</sub>
	DSC	DMA	N <sub>2</sub>	Air	
V <sub>11</sub>	294	290	493	490	59
V <sub>21</sub>	270	274	525	523	61
V <sub>31</sub>	308	296	538	534	65
V <sub>41</sub>	317	—	562	562	67
V <sub>51</sub>	312	332	536	519	68
V <sub>61</sub>	318	—	617	610	64
V <sub>71</sub>	298	295	570	564	72
V <sub>12</sub>	267	—	482	480	47
V <sub>22</sub>	249	239	528	525	63
V <sub>32</sub>	244	231	550	544	56
V <sub>42</sub>	254	—	559	554	58
V <sub>52</sub>	235	223	556	552	62
V <sub>62</sub>	322	—	583	563	65
V <sub>72</sub>	277	286	547	541	53

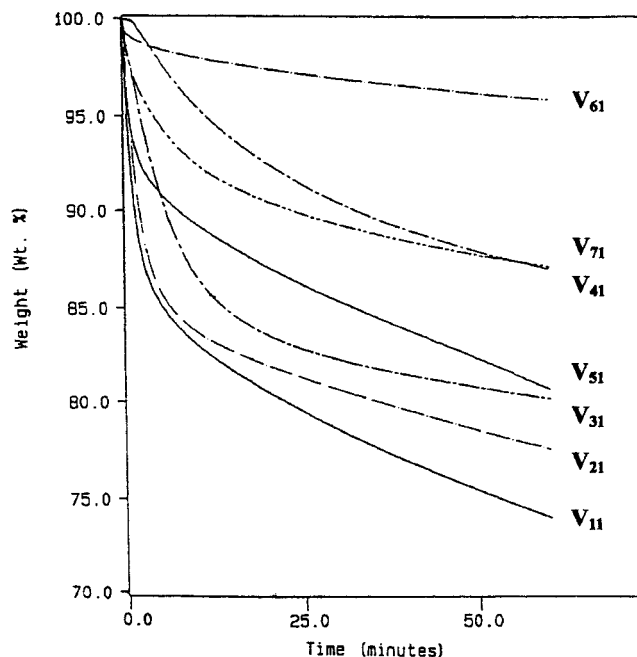


Figure 2 Isothermal weight loss of the PMDA (IV<sub>1</sub>) series at 500°C in N<sub>2</sub>.

## CONCLUSION

A series of polyimides were synthesized from bisphenols containing aryl ether linkage, cycloalkane, or ring alkyl substitution to study the relationship between the structure and the property. The two-step method was used to prepare polyimides. Solubility and thermal properties of polymers were greatly influenced by the alkyl-substituted ring and stiffness of the polymer main chain.

Financial support of this work by the National Science Council of the Republic of China is gratefully appreciated.

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