

## Synthesis and Properties of Polyimides Derived from 1,4-Bis(4-aminophenoxy)-2-*tert*-butylbenzene

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**ABSTRACT:** The novel diamine containing bulky *tert*-butyl substituent, 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (BATB) was used as monomer with various aromatic tetracarboxylic dianhydrides to synthesize polyimides *via* a conventional two-stage procedure that included ring-opening polyaddition in a polar solvent such as *N,N*-dimethylacetamide (DMAc) to give poly(amic acid)s, followed by cyclodehydration to polyimides. BATB(II) was prepared through the nucleophilic displacement of *tert*-butylhydroquinone with *p*-chloronitrobenzene in the presence of  $K_2CO_3$ , followed by catalytic reduction. Depending on the dianhydride used, the poly(amic acid)s obtained had inherent viscosities of 0.76—1.79 dL g<sup>-1</sup>. All poly(amic acid)s could be cast from the DMAc solutions and thermally converted to transparent, flexible, and tough polyimide films. The polyimide films had high tensile strength of 122—208 MPa, an elongation at breaks of 3—9%, and a tensile modulus of 1.92—2.68 GPa. Polyimides from 4,4'-sulfonyldiphthalic anhydride and 4,4'-hexafluoro-isopropylidenediphthalic anhydride had better solubility than the other polyimides. These polyimides had glass transition temperatures between 240—268°C and 10% mass loss temperatures were recorded at 479—522°C in nitrogen.

**KEY WORDS** 1,4-Bis(4-aminophenoxy)-2-*tert*-butylbenzene / Poly(amic acid) / Polyimides /

Polyimides have been investigated extensively and used widely over the past three decades because of high performance properties such as good thermal, mechanical, and electrical properties.<sup>1-3</sup> Unless carefully designed, however, polyimides are often insoluble and have high softening temperature, presenting serious processing difficulties. Therefore, the preparation of soluble or thermoplastic polyimides has been a major research interest.

Several approaches such as the incorporation of flexible bridging linkages<sup>4-8</sup> or *meta*-oriented or *ortho*-oriented phenylene rings<sup>9,10</sup> into polymer backbone, and introduction of bulky substituents<sup>11-15</sup> along polymer backbone has led to considerable success.

Aromatic ether linkages inserted in aromatic main chains provide them with significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperature and crystalline melting temperature as well as significant improvement in solubility and other process characteristics of the polymers without greatly sacrificing thermal stability.

The introduction of a monosubstituted monomer into the polymer chain is expected to decrease of order along the chain, enhanced solubility, and reduced crystallinity due to a random arrangement of substituents.<sup>16-22</sup> Some previous articles<sup>17-21</sup> that introducing a *tert*-butyl substituent monomer into polyester and poly(ether ether ketone) backbone lowers transition temperatures and improves solubility properties. However, there is little literature<sup>23</sup> on the characteristic of introducing *tert*-butyl group into polyimides.

The present article describes the successful synthesis of a new diamine containing aryl ether and *tert*-butyl aromatic ring, 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene, and use for the preparation of polyimides by the polymerization of the diamine with various aromatic tetracarboxylic dianhydrides. Chemical and thermal cy-

clodehydration were performed in this study. Percent imidization, solubility, thermal and mechanical properties, and X-ray diffraction patterns were investigated and are discussed.

### EXPERIMENTAL

#### Materials

Materials, *tert*-butylhydroquinone (from Janssen), *p*-chloronitrobenzene (from Merck), anhydrous potassium carbonate (from Janssen), hydrazine monohydrate (from Janssen), and 10% palladium on activated carbon (from Merck) were used as received. Reagent grade aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA, III<sub>a</sub>; from CHRISKEV), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, III<sub>b</sub>; from CHRISKEV), 4,4'-oxydiphthalic anhydride (ODPA, III<sub>c</sub>; from TCI), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, III<sub>d</sub>; from CHRISKEV), 4,4'-sulfonyldiphthalic anhydride (SDPA, III<sub>e</sub>; from New Japan Chemical Co.), and 4,4'-hexafluoro-isopropylidenediphthalic anhydride (6FDA, III<sub>f</sub>; from CHRISKEV) were recrystallized from acetic anhydride before use. *N,N*-Dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Acetic anhydride was purified by vacuum distillation.

#### Monomer Synthesis

*1,4-Bis(4-nitrophenoxy)-2-tert-butylbenzene (BNTB, I)*. This compound was synthesized by reaction of *tert*-butylhydroquinone (41.5 g, 0.25 mol) and *p*-chloronitrobenzene (81.9 g, 0.52 mol) in the presence of potassium carbonate (79.4 g, 0.57 mol) and *N,N*-dimethylformamide (300 mL) at 160°C for 8 h. The mixture was cooled and poured into 600 mL of ethanol-water (1:1 by volume). The crude product was recrystallized from glacial acetic acid to provide brown needle (mp 154°C) in 85% yield. The IR spectrum (KBr) exhibited absorptions at 1509

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and  $1335\text{ cm}^{-1}$  ( $\text{NO}_2$ ), and  $1233\text{ cm}^{-1}$  ( $\text{C-O-C}$ ).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.33 (s, 9H), 6.91 (s, 2H), 7.03 (dd, 4H), 7.19 (s, 1H), 8.19 (dd, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 29.91, 34.91, 116.86, 117.21, 119.08, 120.13, 123.06, 125.87, 125.95, 142.59, 144.49, 150.58, 151.26, 163.09, 163.15. *Anal.* Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_6\text{N}_2$ : C, 64.70%; H, 4.90%; N, 6.86%. Found: C, 64.52%; H, 4.79%; N, 6.42%.

*1,4-Bis(4-aminophenoxy)-2-tert-butylbenzene (BATB, II)*. The obtained dinitro compound (57.1 g, 0.14 mol), 0.3 g of 10% Pd-C, and 400 mL ethanol were introduced into a three-necked flask to which 130 mL of hydrazine monohydrate was added dropwise over a period of 1 h at  $85^\circ\text{C}$ . After the addition was complete, the reaction was continued at reflux temperature for an additional 24 h. The mixture was then filtered to remove Pd-C. After cooling, the precipitated needle crystals were isolated by filtration and recrystallized from ethanol in 83% yield (mp  $134^\circ\text{C}$ ). The IR spectrum (KBr) exhibited absorptions at  $3364$  and  $3440\text{ cm}^{-1}$  ( $\text{N-H}$ ), and  $1203\text{ cm}^{-1}$  ( $\text{C-O-C}$ ).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.40 (s, 9H), 3.55 (s, 4H), 6.61–6.67 (m, 6H), 6.81 (dd, 4H), 7.05 (d, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 29.85, 34.74, 115.31, 116.23, 116.30, 116.91, 119.73, 120.12, 141.42, 141.72, 141.91, 149.50, 150.21, 151.85, 153.06. *Anal.* Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_2\text{N}_2$ : C, 75.86%; H, 6.89%; N, 8.04%. Found: C, 75.44%; H, 6.87%; N, 7.70%.

#### Polymerization

A typical example of polymerization is as follows. To a stirred solution of 0.87 g (2.5 mmol) of BATB in 13.5 mL of DMAc, was added gradually 0.545 g (2.5 mmol) of PMDA. The mixture was stirred at room temperature for 2 h under an argon atmosphere. The inherent viscosity of the poly(amic acid) in DMAc was  $1.79\text{ dL g}^{-1}$ , as measured at  $0.5\text{ g dL}^{-1}$  at  $30^\circ\text{C}$ . The poly(amic acid) solution thus obtained was spread on a glass plate and the solvent was removed at  $80^\circ\text{C}$ . Imidization was carried out by thermal cyclodehydration of the poly(amic acid) film by sequential heating at 110, 150, 180, 210, 250, and  $300^\circ\text{C}$  for 20 min each. The IR spectrum (KBr) exhibited absorptions at  $1729$  and  $1771\text{ cm}^{-1}$  ( $\text{C=O}$ ), and  $1366\text{ cm}^{-1}$  ( $\text{C-N}$ ).

Chemical cyclodehydration was also carried out by adding a mixture of acetic anhydride and pyridine (volume ratio 2:1) to the above mentioned poly(amic acid) solution. The mixture was stirred at room temperature for 1 h, and then at  $100^\circ\text{C}$  for 3 h. The polymer solution was poured into methanol. The yellow precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at  $100^\circ\text{C}$  under vacuum. The IR spectrum (KBr) exhibited absorptions at  $1721$  and  $1770\text{ cm}^{-1}$  ( $\text{C=O}$ ), and  $1369\text{ cm}^{-1}$  ( $\text{C-N}$ ).

#### Measurements

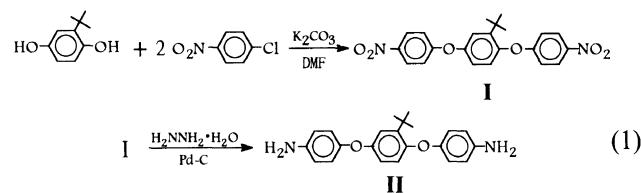
IR spectra were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  for the synthesized monomers and polymers in KBr disks with a JASCO IR-700 spectrometer. The inherent viscosities of all polyimides were measured at  $0.5\text{ g dL}^{-1}$  in concentrated sulfuric acid using an Ubbelohde viscometer. Elemental analysis was made with a Perkin-

Elmer 2400. Wide-angle X-ray diffraction patterns were obtained at room temperature with film specimens on an X-ray diffractometer with a Philips model PW 1710 using Ni-filtered  $\text{Cu-K}_\alpha$  radiation (40 kV, 30 mA). The scanning rate was  $3\text{ deg min}^{-1}$ . NMR spectra were recorded with a Bruker AM-300 WB FT-NMR spectrometer. Thermogravimetric data were obtained on a du Pont 2200 in flowing nitrogen ( $60\text{ cm}^3\text{ min}^{-1}$ ) at a heating rate of  $20^\circ\text{C min}^{-1}$ . Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-7 in flowing nitrogen ( $30\text{ cm}^3\text{ min}^{-1}$ ) at a heating rate of  $20^\circ\text{C min}^{-1}$ . A LLOYD instrument with a load cell of 500 N was used to study the stress-strain behavior of the samples. A gauge of 2 cm and strain rate of  $5\text{ cm min}^{-1}$  were used in this study. All measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 1 mm thick); the average of at least four individual determinations was used.

## RESULTS AND DISCUSSION

#### Monomer Synthesis

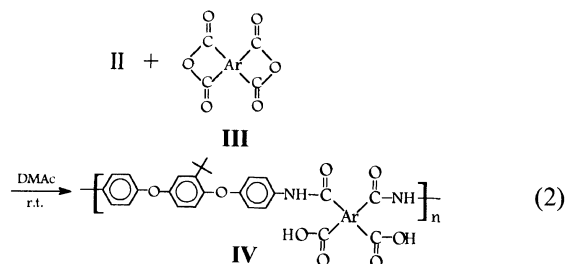
A new diamine, 1,4-bis(4-aminophenoxy)-2-tert-butylbenzene (II), was synthesized in two steps by the aromatic nucleophilic displacement reaction of *tert*-butylhydroquinone and *p*-chloronitrobenzene, giving the dinitro compound (I), followed by reduction with hydrazine monohydrate/Pd-C (eq 1). The structures of the

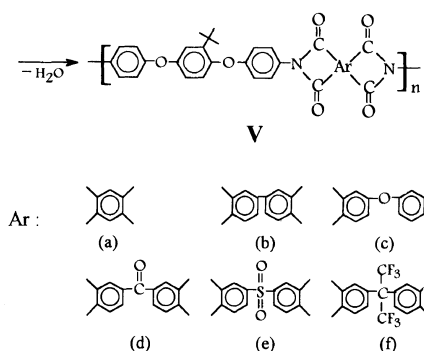


dinitro and diamine compounds were confirmed by elemental analysis, IR, and NMR spectra. As shown in the experimental section, elemental analysis data of the dinitro and diamine compounds agreed with calculated values of their structures. In the  $^1\text{H NMR}$  spectrum of BNTB (see Experimental), the absorption signals of benzene protons appear at 6.91 and 7.19 ppm. The non-first-order AA'BB' splitting patterns of the phenylene protons are very close and appear together at 7.03 and 8.19 ppm. When the dinitro compound BNTB is converted to diamine BATB, the signal at 3.55 ppm is peculiar to the amino group. The  $^{13}\text{C NMR}$  spectra of BNTB and BATB both exhibit 15 peaks. However, because the spectra were very complicated, no attempts were made to assign the signal of each carbon.

#### Preparation of Polyimides

Polyimides were prepared by the conventional two step procedure as shown in eq 2. In the preparation





of poly(amic acid)s from aromatic diamines and dianhydrides in a polar solvent, monomer addition plays an important role for successful polymerization. As described in the study of Yang *et al.*,<sup>24,25</sup> the multistep addition of PMDA to the solution of a diamine yielded poly(amic acid) with higher molar mass than by reverse addition or mixing both reactants. The poly(amic acid)s IV<sub>a-f</sub> were prepared by adding dianhydrides to the diamine solution as described previously.<sup>24,25</sup> The inherent viscosities of all the poly(amic acid)s together with those of the corresponding polyimides are summarized in Table I. The inherent viscosities of the poly(amic acid)s were 0.76–1.79 dL g<sup>-1</sup>.

Flexible and transparent polyimide films could be obtained by thermal cyclodehydration. Alternatively, chemical conversion of poly(amic acid)s with a mixture of acetic anhydride and pyridine is also effective in obtaining polyimides. The polyimides prepared by thermal procedure had inherent viscosities of 0.52–0.91 dL g<sup>-1</sup> in concentrated sulfuric acid.

The elemental analysis data of these polyimides listed in Table I were generally in good agreement with the respective structures for hydrogen and nitrogen, while carbon analysis data were below their theoretical values—a phenomenon common to high-temperature polyimides.

#### Thermal Cyclodehydration of Poly(amic acid)

The thermal conversion of poly(amic acid) to polyimide was monitored by infrared spectroscopy. The IR

films were prepared by casting 2–3 mass % poly(amic acid) solution in DMAc onto a glass substrate and heating at 80°C in a hot air oven for 2 h. The poly(amic acid) films were further dried and imidized by thermal treatment. Figure 1 shows the IR spectra of the representative poly(amic acid) IV<sub>f</sub> and corresponding polyimide V<sub>f</sub>. Characteristic C=O absorption bands appear at *ca.* 1777 and *ca.* 1719 cm<sup>-1</sup>. The degree of poly(amic acid) to polyimide conversion was analyzed by the band ratio method. The absorbance of the asymmetric carbonyl stretch at 1777 cm<sup>-1</sup> was compared with a reference aromatic stretch at 1500 cm<sup>-1</sup>. The percent imidization of poly(amic acid) was calculated as,<sup>26</sup>

$$\text{percent imidization} = \frac{[A(1)/A(2)]_t - [A(1)/A(2)]_{t=0}}{[A(1)/A(2)]_{t=\infty} - [A(1)/A(2)]_{t=0}}$$

where  $A(1)$  = absorbance of the imide peak at 1777 cm<sup>-1</sup>,  $A(2)$  = absorbance of the standard reference at 1500 cm<sup>-1</sup>, and  $t = \infty$  time beyond which no further change in the imide peak at 250°C occurred. The percent imidizations of poly(amic acid) IV<sub>a</sub> versus curing time at various temperatures are shown in Figure 2. Almost all the amic acids were cyclized to imide rings within 20 min at 250°C

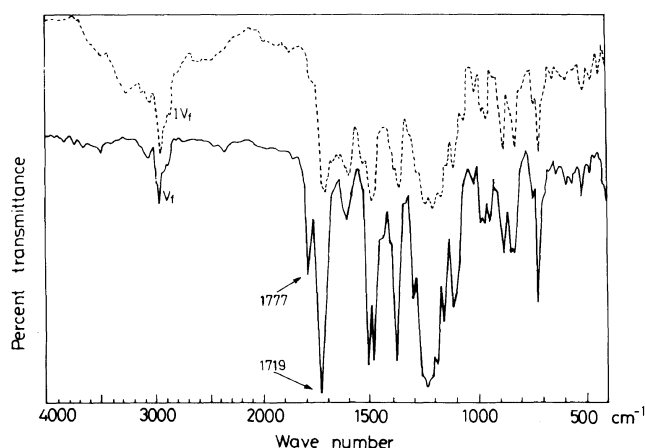


Figure 1. IR spectra of poly(amic acid) IV<sub>f</sub> and corresponding polyimide V<sub>f</sub>.

Table I. Preparation of BATB-based polyimides

Tetracarboxylic dianhydride	Poly(amic acid) <sup>a</sup>		Polyimide <sup>b</sup>					
	Code	$\eta_{\text{inh}}^c$ /dL g <sup>-1</sup>	Code	$\eta_{\text{inh}}^d$ /dL g <sup>-1</sup>	Elemental analysis			
					C%	H%	N%	
III <sub>a</sub>	IV <sub>a</sub>	1.79	V <sub>a</sub>	0.91	Found	71.15	4.16	5.14
					Caclcd	(72.45)	(4.15)	(5.28)
III <sub>b</sub>	IV <sub>b</sub>	1.30	V <sub>b</sub>	0.74	Found	74.59	4.31	4.59
					Caclcd	(75.25)	(4.29)	(4.62)
III <sub>c</sub>	IV <sub>c</sub>	0.76	V <sub>c</sub>	0.52	Found	72.73	4.20	4.46
					Caclcd	(73.31)	(4.18)	(4.50)
III <sub>d</sub>	IV <sub>d</sub>	1.40	V <sub>d</sub>	0.76	Found	73.22	4.14	4.38
					Caclcd	(73.82)	(4.10)	(4.42)
III <sub>e</sub>	IV <sub>e</sub>	1.19	V <sub>e</sub>	0.61	Found	66.93	4.13	4.11
					Caclcd	(68.06)	(3.88)	(4.18)
III <sub>f</sub>	IV <sub>f</sub>	1.78	V <sub>f</sub>	0.81	Found	65.04	3.76	3.83
					Caclcd	(65.08)	(3.44)	(3.70)

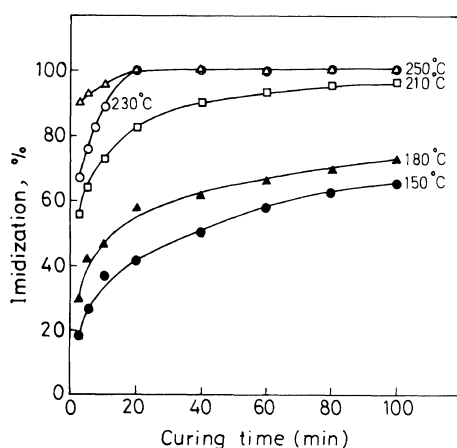
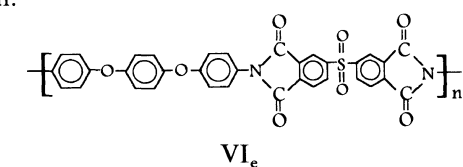
<sup>a</sup> Polymerization was carried out with equimolar quantities of BATB and aromatic dianhydrides to obtain 10 mass % poly(amic acid) solutions.

<sup>b</sup> Obtained by thermal cyclization from the corresponding poly(amic acid)s. <sup>c</sup> Measured in DMAc at 0.5 g dL<sup>-1</sup> at 30°C. <sup>d</sup> Measured in concentrated sulfuric acid at 0.5 g dL<sup>-1</sup> at 30°C.

and 230°C. When a sample was heated at 180°C for 100 min, the imide peak grew to approximately 71% of its final size. The sample was then cured at 210°C for up to 100 min. The degree of imidization increased, indicating that the imidization reaction was not completed at 180°C.

#### Properties of Polyimides

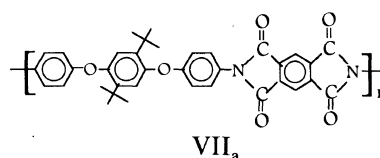
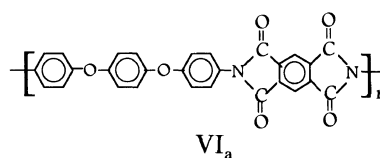
The solubility of these polyimides was studied qualitatively. The results are shown in Table II. Polyimides prepared by the chemical conversion method had better solubility compared with those by the thermal procedure. Polyimides V<sub>a-d</sub> were almost insoluble in organic solvents but dissolved in concentrated sulfuric acid. Polyimides V<sub>e</sub> and V<sub>f</sub> containing sulfone and hexafluoroisopropylidene linkage exhibit excellent solubility toward test solvents. For comparison, polyimide VI<sub>e</sub> was prepared by the condensation of 1,4-bis(4-aminophenoxy)benzene with SDPA through chemical cyclodehydration.



**Figure 2.** Variation in % imidization of poly(amic acid) IV<sub>a</sub> heated at various time intervals and various temperatures.

The results of the solubility test on different solvents are also listed in Table II. Comparing the results from *tert*-butyl substituted polyimide V<sub>e</sub> and analogous polyimide VI<sub>e</sub> shows that *tert*-butyl substituent incorporated into the polyimide indeed increased its solubility.

Crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams. The polyimide films obtained by thermal imidization were used as the samples. All polyimide films were amorphous. These results could be explained by the fact that the randomly distributed direction of the substituents reduces the symmetry within the polymer chain and leads to lower stereoregularity.<sup>16-21,27</sup> For comparison, the analogous polyimide VI<sub>a</sub> having a phenylene ring without substituent and polyimide VII<sub>a</sub> having symmetric di-*tert*-butyl substituents on phenylene ring were prepared by the polycondensation of 1,4-bis(4-aminophenoxy)benzene or 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene with PMDA.<sup>31</sup>



The X-ray diffraction diagrams of polyimides V<sub>a</sub>, VI<sub>a</sub>, and VII<sub>a</sub> were shown in Figure 3. It could be seen that the crystallinity of VI<sub>a</sub> is slightly greater than V<sub>a</sub>. This may be due to the absence of a bulky substituent that hinders packing of the polymer chain, therefore leading to greater stereoregularity and crystallinity. It was also observed that polyimide VII<sub>a</sub> has the highest degree of crystallinity among the other polyimides V<sub>a</sub> and VI<sub>a</sub> due to its symmetric substituents.<sup>31</sup>

The tensile properties of the polyimide films prepared by the thermal treatment are summarized in Table III. The polyimides V<sub>a</sub>—V<sub>f</sub> films had tensile strength of

**Table II.** Solubility of polyimides<sup>a</sup>

Polymer <sup>c</sup>	Solvent <sup>b</sup>						
	NMP	DMSO	DMAc	DMF	Py	<i>m</i> -Cresol	Concn. H <sub>2</sub> SO <sub>4</sub>
C-V <sub>a</sub>	—	—	—	—	—	—	++
T-V <sub>a</sub>	—	—	—	—	—	—	++
C-V <sub>b</sub>	+—	—	—	—	—	+—	++
T-V <sub>b</sub>	—	—	—	—	—	—	++
C-V <sub>c</sub>	+—	—	—	—	—	+	++
T-V <sub>c</sub>	—	—	—	—	—	—	++
C-V <sub>d</sub>	+	—	—	—	—	+	++
T-V <sub>d</sub>	—	—	—	—	—	—	++
C-V <sub>e</sub>	++	+	++	++	++	++	++
T-V <sub>e</sub>	++	+—	++	++	+	++	++
C-V <sub>f</sub>	++	++	++	++	++	++	++
T-V <sub>f</sub>	++	++	++	++	+	++	++
VI <sub>e</sub>	—	—	—	—	—	—	++

<sup>a</sup> Solubility: ++, soluble at room temperature; +, soluble on heating; +—, partial soluble on heating; —, insoluble. <sup>b</sup> Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMSO, dimethyl sulfoxide; DMF, *N,N*-dimethylformamide; Py, pyridine. <sup>c</sup> Polyimides obtained by the chemical cyclodehydration method are designated by C while those obtained by the thermal means, by T.

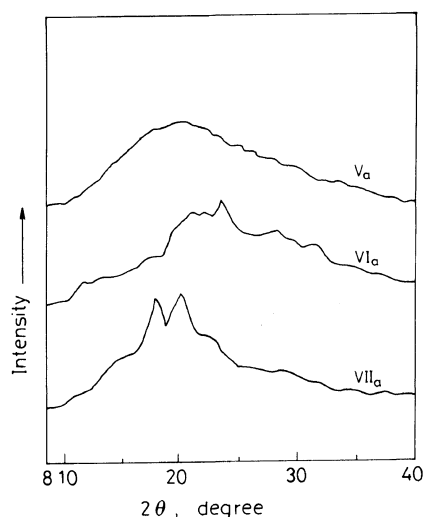


Figure 3. Wide-angle X-ray diffractograms of polyimides.

Table III. Mechanical properties of polyimides

Polymer	Tensile strength	Elongation at break	Initial modulus
	MPa	%	GPa
V <sub>a</sub>	168	6	2.18
V <sub>b</sub>	208	7	1.92
V <sub>c</sub>	122	5	1.93
V <sub>d</sub>	169	9	1.97
V <sub>e</sub>	196	6	2.35
V <sub>f</sub>	150	3	2.68
VI <sub>a</sub>	160	6	2.07
VII <sub>a</sub>	— <sup>a</sup>	—	—

<sup>a</sup> Could not be determined due to brittleness of casting film.

122–208 MPa, elongation at break of 3–9%, and initial modulus of 1.92–2.68 GPa. Most polymer films exhibited high tensile strength, high modulus and low elongation; thus they could be considered as hard and strong materials. The tensile properties of analogous polyimides VI<sub>a</sub> and VII<sub>a</sub> are also included in Table III. The mechanical properties of polyimide V<sub>a</sub> are similar to polyimide VI<sub>a</sub> and superior than brittle polyimide VII<sub>a</sub>.

The thermal behavior of the polyimides prepared by thermal cyclodehydration was evaluated by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. Table IV summarizes the thermal transition data of all the polyimides. All the polyimides showed similar patterns of decomposition with no mass loss below 450°C in an air or nitrogen atmosphere. The decomposition temperatures of 10% mass loss were in the range of 479–522°C in nitrogen and 480–528°C in air. The 10% mass loss temperature in air is similar to that in nitrogen, indicating that polyimides based on BATB showed thermooxidative stability in air. It was observed that polyimide V<sub>e</sub> containing a sulfone connecting groups, had the lowest decomposition temperature and aerobic char yield. The SDPA-based polyimide V<sub>e</sub> seemed to show lower thermal stability as reported in the literature.<sup>5,11,12,25</sup> The comparative TGA curves of polyimides V<sub>a</sub> and VI<sub>a</sub> are indicated in Figure 4. They showed similar behavior below 460°C. As expected, the

Table IV. Thermal properties of BATB-based polyimides

Polyimide	$T_g^a$ °C	Decomposition temp <sup>b</sup> °C		$R_{800}^c$ %
		In N <sub>2</sub>	In air	
	V <sub>a</sub>	268	512	515
V <sub>b</sub>	261	522	522	52
V <sub>c</sub>	240	521	517	46
V <sub>d</sub>	247	518	517	61
V <sub>e</sub>	246	479	480	43
V <sub>f</sub>	248	522	528	53

<sup>a</sup> Glass transition temperature ( $T_g$ ) measured on DSC at a heating rate of 20°C min<sup>-1</sup>. <sup>b</sup> Temperature at which 10% mass loss was recorded on TG at a heating rate of 20°C min<sup>-1</sup>. <sup>c</sup> Residual mass % at 800°C in nitrogen.

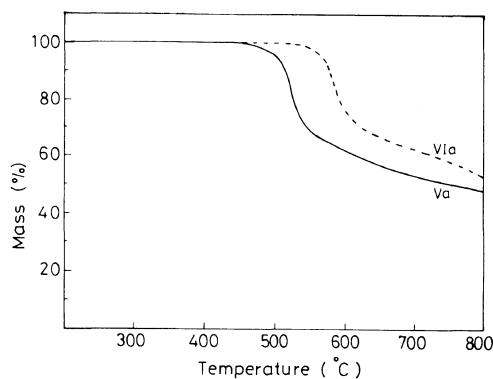


Figure 4. TGA curves of polyimides V<sub>a</sub> and VI<sub>a</sub> with heating rate of 20°C min<sup>-1</sup> in nitrogen.

*tert*-butyl substituted polyimide (V<sub>a</sub>) began to decompose at lower temperatures than unsubstituted polyimide (VI<sub>a</sub>) but it is worth noting that the polyimides V<sub>a</sub> left a similar char residue compared with polyimide VI<sub>a</sub>. This implies that there is possibility of crosslinking between the polymer chains during the degradation process.<sup>28,29</sup> TG analysis also shows that VII<sub>a</sub> has greater mass loss and less char yield than V<sub>a</sub> and VI<sub>a</sub>.<sup>31</sup> The polyimides had  $T_g$ s in the 240–268°C range. This order was comparable to the decreasing order of stiffness and polarity of the polymer backbones. Polyimides V<sub>e</sub> and V<sub>f</sub> had higher  $T_g$ s than oxy-bridge containing polyimide V<sub>c</sub>. This may be attributed to the intermolecular force of sulfonyl groups and the steric hindrance of hexafluoroisopropylidene bridging moieties.<sup>30</sup> Glass transition temperatures of VI<sub>a</sub> and VI<sub>b</sub> were measured to be 286 and 298°C, respectively. The order of  $T_g$ s among V<sub>a</sub>, VI<sub>a</sub>, and VI<sub>b</sub> is VI<sub>b</sub> > VI<sub>a</sub> > V<sub>a</sub>, corresponding to the order of crystallinity VI<sub>b</sub> > VI<sub>a</sub> > V<sub>a</sub>. In general, the  $T_g$  increased with crystallinity.

## CONCLUSIONS

A novel diamine, 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene, containing bulky *tert*-butyl substituent was successfully prepared in high purity and high yield in this study. Poly(amic acid)s were obtained in moderate to high molar mass. All poly(amic acid)s could be thermally converted to transparent, tough, and flexible polyimide films with excellent tensile properties. Polyimides derived from SDPA and 6FDA had good solu-

bility in a few polar organic solvents. The use of bulky monosubstituted diamine into the polymer chain results in decrease in crystallinity and the glass transition temperature.

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