

# Synthesis and Characterization of New Soluble Polyimides from 3,3',4,4'-Benzhydrol Tetracarboxylic Dianhydride and Various Diamines

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New soluble polyimides were prepared from a series of diamines and a tetracarboxylic dianhydride with a benzhydrol unit, 3,3',4,4'-benzhydrol tetracarboxylic dianhydride (BHTDA), by one-step method polymerization. The diamines containing flexible units, bulky substituents, and/or noncoplanar conformation unit were prepared by the reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene, followed by catalytic reduction of the dinitro compounds. The polyimides obtained were soluble in various solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine,  $\gamma$ -butyrolactone, *m*-cresol, and even tetrahydrofuran except for polymer **PI**d. The polymers were amorphous and had number-average molecular weight ( $M_n$ ) in the range  $(3.0\text{--}10.2) \times 10^4$ . The glass transition temperatures ( $T_g$ ) of the polymers ranged from 268 to 341 °C. These polymers exhibited good thermal stability without significant weight loss up to 420 °C. The temperatures at 10% weight loss range from 457 to 524 °C in nitrogen and 449 to 519 °C in air, respectively. The polyimide films were found to be transparent, flexible, and tough. The films had a tensile strength range 72–105 MPa, an elongation range at break of 4–7%, and a Young's modulus range of 2.18–2.85 GPa.

## Introduction

Polyimides have been of great interest in engineering and microelectronics for a number of applications owing to their unique property combinations.<sup>1,2</sup> Although exceptional thermal stability is complemented by excellent mechanical and electrical performance, their insolubility in common organic solvents and their high glass transition and softening temperatures make these systems difficult to process and fabricate. Consequently, polyimide processing is generally carried out from poly(amic acid) solution, i.e., a processable precursor, and can be subsequently converted to intractable polyimide through thermal treatment. However, this manufacturing method has several inherent problems such as the hydrolytic characteristic of the poly(amic

acid); moreover, voids and stresses can be generated in the final product after thermal treatment.<sup>3,4</sup> Therefore, much effort has been concentrated on synthesizing soluble and tractable polyimides.

A variety of structural modifications to the polyimide backbone, such as bulky substituents,<sup>5–7</sup> noncoplanar biphenylene moieties,<sup>8–12</sup> and flexible<sup>13–17</sup> and kinked<sup>18,19</sup> units, can be employed to modify the polymer properties,

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either by lowering the interchain interactions or by reducing the stiffness of the polymer chain. Depending on the type and amount of structural modifications, the melting temperatures can be lowered and the solubilities improved, resulting in processable materials.

In recent years, a fluorinated dianhydride monomer, 4,4'-hexafluoroisopropylidenebisphthalic anhydride (6FDA), has been extensively investigated because the monomer produces highly soluble polyimides while maintaining their good thermal stability.<sup>2,20-23</sup> However, application of polyimide derived from 6FDA will be limited due to its high cost. Malinge et al.<sup>24</sup> reported that introducing benzhydrol units into the polyimide chain enhanced the solubility of polymer due to the strong interaction of the hydroxy group with polar solvents. Therefore, the benzhydrol-containing dianhydride, 3,3',4,4'-benzhydrol tetracarboxylic dianhydride (BHTDA), would be another promising monomer to synthesize soluble polyimides. In addition, the hydroxy group in the polymer chain would allow further modification of the polyimide, such as cross-linking reaction or incorporation of photosensitive functional groups.<sup>25-28</sup>

Our previous studies have synthesized a series of new diamine-containing flexible unit such as sulfone, ether, isopropylidene, and oxyethylene, as well as bulky *tert*-butyl substituents and noncoplanar 2,2'-dimethyl-4,4'-biphenylene units.<sup>29-34</sup> Most polyimides prepared from these diamines and various common dianhydrides were soluble and thermally stable. The present report relates the synthesis and characterization of new soluble polyimides derived from BHTDA and diamines such as 1,4-

bis(4-aminophenoxy)-2-*tert*-butylbenzene (BATB),<sup>29</sup> 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene (BADTB),<sup>30</sup> 3,3',5,5'-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane (TBAPP),<sup>31</sup> 2,2-bis[4-[2-(4-aminophenoxy)ethoxy]phenyl]propane (BAEPP),<sup>32</sup> 3,3',5,5'-tetramethyl bis[4-(4-aminophenoxy)phenyl]sulfone (TBAPS),<sup>33</sup> and 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl (DBAPB).<sup>34</sup>

The most commonly used method for synthesizing polyimide is a two-stage process that involves ring-opening polyaddition in a polar solvent to produce poly(amic acid)s, followed by cyclodehydration to polyimides. Recently, several studies have found that the most effective way to prepare soluble polyimides with large molecular weights is by the one-step method.<sup>2,4,35-37</sup> The polyimide conducted by the one-step method remains in the solution during polymerization and can be processed afterward. Considering our final goal of soluble polyimides, we were exclusively interested in the one-step polymerization method. The solubility, crystallinity, mechanical, and thermal properties of the resulting polyimides is also investigated herein.

## Experimental Section

**Materials.** The diamines, 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (BATB, mp 134–135 °C),<sup>29</sup> 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene (BADTB, mp 242–243 °C),<sup>30</sup> 3,3',5,5'-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane (TBAPP, mp 164–165 °C),<sup>31</sup> 2,2-bis[4-[2-(4-aminophenoxy)ethoxy]phenyl]propane (BAEPP, mp 117–118 °C),<sup>32</sup> 3,3',5,5'-tetramethylbis[4-(4-aminophenoxy)phenyl]sulfone (TBAPS, mp 199–200 °C),<sup>33</sup> and 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl (DBAPB, mp 138–139 °C)<sup>34</sup> were synthesized according to the procedure described in the previous reports. Solvents such as *m*-cresol and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure.

**3,3',4,4'-Benzhydrol Tetracarboxylic Dianhydride (BHTDA).** To a solution of 8 g of benzophenonetetracarboxylic dianhydride (24.8 mmol) in 20% NaOH aqueous solutions (20 mL) was added a solution of 0.45 g (12 mmol) of sodium borohydride in 3 mL of water at 25 °C. The solution was stirred at 25 °C for 1.5 h and was made acidic by the addition of 6.5 N HCl. The solution was concentrated until the solution became "cloudy", at which evaporation was stopped, 200 mL of ethyl acetate added, and salt formation followed. The heterogeneous solution was treated with active carbon and then filtrated. After washing the filtrate with ethyl acetate several times, the organic layer was dried with MgSO<sub>4</sub>. The solution was concentrated under reduced pressure into a small volume to precipitate benzhydroltetracarboxylic acid. After filtration, the product was dried in vacuo at 50 °C, to give 6 g of benzhydroltetracarboxylic acid. It was then stirred at 25 °C with 800 mL of acetic anhydride. After about 4 or 5 days, acetic anhydride was removed under reduced pressure to obtain a crude BHTDA precipitate. The solid was isolated by filtration and lyophilized in dioxane, washed by pentane and dried in vacuo for 16 h at 50 °C, to give 3 g of white product; mp 180–181 °C. IR (KBr) 3514 (O–H), 1853 (asym C=O) and 1752 cm<sup>-1</sup> (sym C=O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 8.0–8.2 (m, 6H, ArH), 6.8 (s, 1H, OH), 6.3 (s, 1H, –CH–). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 163.26, 163.07, 153.28, 134.03, 132.02, 130.52, 125.87, 122.84, 72.69.

**Synthesis of Polyimides.** A typical polymerization procedure is as follows. Into a three-necked flask were placed

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0.348 g (1 mmol) of diamine BATB, 0.05 g of isoquinoline, and 7 mL of *m*-cresol. To the solution was added 0.324 g (1 mmol) of BHTDA under argon. The solution was heated with stirring at 50 °C for 3 h and at 150 °C for another 3 h period. Next, a short-path distillation unit and an additional funnel were equipped to the flask. The solvent was distilled at 210 °C, keeping the volume of the reaction mixture nearly constant by adding an appropriate volume of fresh *m*-cresol containing 0.5% of isoquinoline. The azeotropic removal of the water formed during the imidization was continued for 5 h under argon. The viscous clear polymer solution was poured into a large amount of methanol. The precipitate, **PIa**, was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100 °C under vacuum. The inherent viscosity of the polymer in DMAc was 1.03 dL g<sup>-1</sup>, measured at a concentration 0.5 g dL<sup>-1</sup> at 30 °C. The IR spectrum (KBr) exhibited absorptions at 3472 (O-H), 1768 (asym C=O), 1715 (sym C=O), and 1373 cm<sup>-1</sup> (C-N).

All other polymers were synthesized by an analogous procedure.

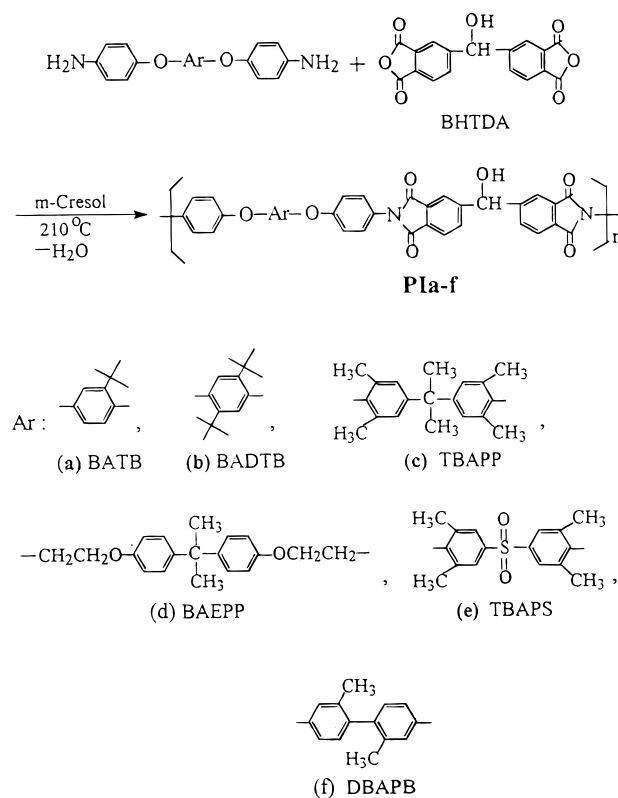
**Characterization.** Melting points were measured in capillaries on a Buchi apparatus (Model Buchi 535). IR spectra were recorded on a JASCO IR-700 spectrometer. The inherent viscosities of all polyimides were measured using an Ubbelohde viscometer. Elemental analysis was performed on a Perkin-Elmer 2400 instrument. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer Scintag-X1 using Ni filtered Cu K $\alpha$  radiation (40 kV, 30 mA). The scanning rate was 0.5° min<sup>-1</sup> over a range of 2 $\theta$  = 3–40°. Glass transition temperatures (*T*<sub>g</sub>'s) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling. Thermogravimetry (TG) was conducted with a Du Pont 2200 in flowing nitrogen (60 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>. Tensile properties were then determined from stress-strain curves obtained by an a Orientec tensilon with a load cell of 10 kgf. A gauge of 3 cm and a strain rate of 2 cm min<sup>-1</sup> were used for this study. Measurements were taken at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.05 mm thick).

## Results and Discussion

**Monomer Synthesis.** The diamines were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene in potassium carbonate, followed by hydrazine/Pd-C catalytic reduction of the intermediate dinitro compounds.<sup>29–34</sup> The dianhydride BHTDA was prepared by a two-stage route starting from the benzophenone-containing dianhydride 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The structure of the dianhydride BHTDA was confirmed by infrared and NMR spectroscopies. The satisfactory synthesis of high-molecular-weight polymers is also a good proof that pure diamines and dianhydride have been prepared.

**Synthesis of Polyimides.** All polyimides were prepared by one-step process outlined in Scheme 1. In a one-step synthesis, the polymerization and imidization is performed in high boiling solvents, without isolating the poly(amic acid). Different reaction systems are described in previous literature. Very commonly used solvents are phenolic solvents (phenol, *m*-cresol, or *p*-chlorophenol) in combination with a catalyst or accelerator, such as isoquinoline, tertiary amines, or *p*-hydroxybenzoic acid. In a series of experiments the best results were obtained with the system *m*-cresol with isoquinoline as a catalyst.<sup>35–37</sup> The first part of the reaction proceeded at 50 and 150 °C for 3 h, each. Then the temperature was raised slowly to 210 °C.

**Scheme 1**



**Table 1. Polyimides from Various Diamines with BHTDA**

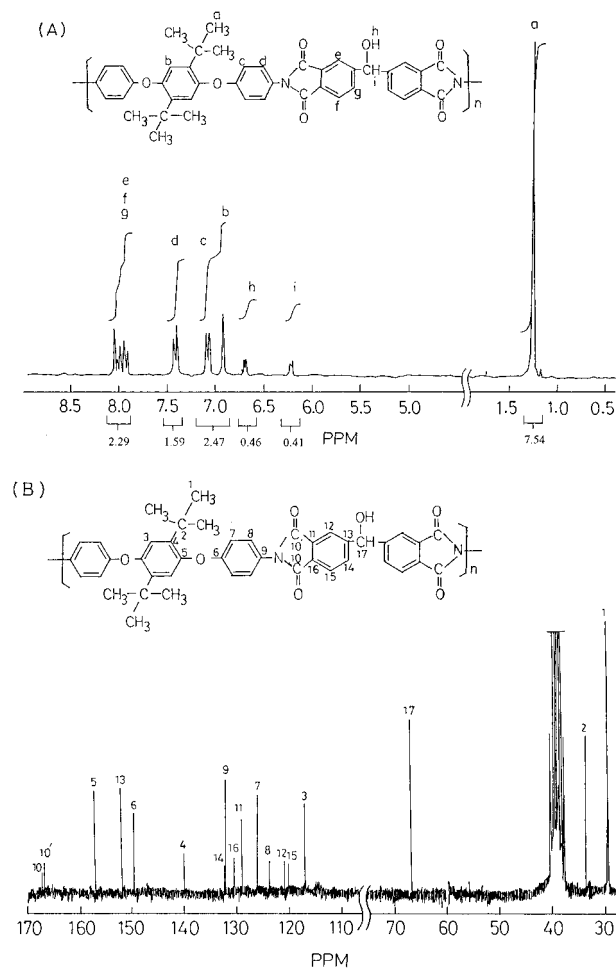
diamine	polymer code	$\eta_{inh}^a$ (dL g <sup>-1</sup> )	$\bar{M}_n \times 10^{-4b}$	$\bar{M}_w \times 10^{-4b}$	film quality
BATB	<b>PIa</b>	1.03	10.2	22.9	flexible
BADTB	<b>PIb</b>	0.78	4.8	7.7	flexible
TBAPP	<b>PIc</b>	0.71	3.0	4.1	flexible
BAEPP	<b>PId</b>	0.90	<i>c</i>		flexible
TBAPS	<b>PIe</b>	0.97	3.0	5.6	flexible
DBAPB	<b>PIf</b>	0.80	5.3	8.2	flexible

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

<sup>b</sup> GPC (10 mg mL<sup>-1</sup> THF solution), polystyrene standards. <sup>c</sup> Polymer is partially soluble in THF.

Water formed during the imidization was continuously removed with a stream of argon. The increasing viscosity of the reaction mixture indicated the progress of the polymerization and imidization. In all of the reactions, homogeneous solutions were obtained. According to Table 1, the polymerization of diamines with BHTDA gave moderate-to-high inherent viscosities of 0.71–1.03 dL g<sup>-1</sup>. The molecular weights of the soluble polyimides were measured by GPC (10 mg mL<sup>-1</sup> tetrahydrofuran solution as an eluent) after calibration with the standard polystyrenes, except for polymer **PId**, which was insoluble in tetrahydrofuran. The results, along with film quality, are also summarized in Table 1. These polymers had number-average molecular weight ( $\bar{M}_n$ ) in the range from  $3.0 \times 10^4$  to  $10.2 \times 10^4$ . All of the polyimide films could be obtained by casting from their DMAc solutions and also showed a transparent and flexible nature.

The polymers were identified by elemental analysis and IR and NMR spectra. The elemental analysis values of these polyimides that are listed in Table 2 correlated with their respective structures for hydrogen and nitrogen, while the carbon analyses were below



**Figure 1.** NMR spectra of polyimide **PIb**. Use DMSO- $d_6$  as solvent: (A)  $^1\text{H}$  NMR and (B)  $^{13}\text{C}$  NMR.

**Table 2. Elemental Analysis of Polyimides**

polymer	experiment formula (formula mass/g)		elem anal. (%)		
			C	H	N
<b>PIa</b>	( $\text{C}_{39}\text{H}_{28}\text{N}_2\text{O}_7$ ) $_n$	calcd	73.58	4.43	4.40
	(636.66) $_n$	found	71.56	4.60	4.45
<b>PIb</b>	( $\text{C}_{43}\text{H}_{36}\text{N}_2\text{O}_7$ ) $_n$	calcd	74.55	5.24	4.04
	(692.77) $_n$	found	72.75	5.38	4.00
<b>PIc</b>	( $\text{C}_{48}\text{H}_{38}\text{N}_2\text{O}_7$ ) $_n$	calcd	76.38	5.07	3.71
	(754.84) $_n$	found	74.42	5.10	3.65
<b>PId</b>	( $\text{C}_{48}\text{H}_{38}\text{N}_2\text{O}_9$ ) $_n$	calcd	73.21	4.87	3.56
	(786.84) $_n$	found	71.97	4.77	3.57
<b>PIe</b>	( $\text{C}_{45}\text{H}_{32}\text{N}_2\text{O}_9\text{S}$ ) $_n$	calcd	69.58	4.15	3.61
	(776.82) $_n$	found	66.85	4.53	3.53
<b>PIf</b>	( $\text{C}_{43}\text{H}_{28}\text{N}_2\text{O}_7$ ) $_n$	calcd	75.43	4.12	4.09
	(684.70) $_n$	found	73.40	4.33	3.97

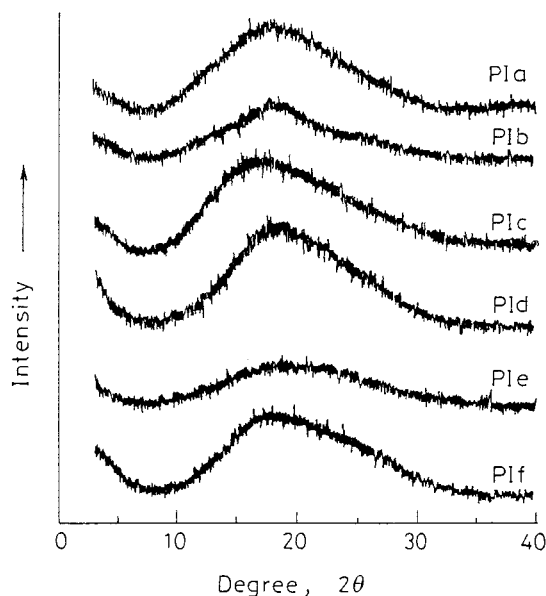
their theoretical values—a phenomenon common to high-temperature polyimides.<sup>29–31</sup>

IR spectroscopy supports the imide ring formation. These polyimides showed characteristic imide ring absorptions near 1770 (asym C=O str), 1720 (sym C=O str), and 1370  $\text{cm}^{-1}$  (C–N str). The hydroxyl (O–H) stretching is seen near 3470  $\text{cm}^{-1}$ . The representative  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polyimide **PIb** is shown in Figure 1. As Figure 1A reveals, the methyl protons resonate in the upfield region at 1.2 ppm. The resonance signal at 6.7 ppm is ascribed to the hydroxyl proton. The protons of the cyclic imide groups resonate in the region 7.9–8.0 ppm. The area of integration is in accordance with the assignment. The chemical shifts

**Table 3. Solubility of Polyimides**

solvents	solubility <sup>a</sup>					
	<b>PIa</b>	<b>PIb</b>	<b>PIc</b>	<b>PId</b>	<b>PIe</b>	<b>PIf</b>
<i>N</i> -methyl-2-pyrrolidone	+	+	+	+	+	+
<i>N,N</i> -dimethylacetamide	+	+	+	+	+	+
<i>N,N</i> -dimethylformamide	+	+	+	+	+	+
dimethyl sulfoxide	+	+	+	+	+	+
pyridine	+	+	+	+	+	+
$\gamma$ -butyrolactone	+	+	+	+	+	+
<i>m</i> -cresol	+	+	+	+	+	+
tetrahydrofuran	+	+	+	–	+	+
methylene chloride	+	–	+	–	–	–
chloroform	+	–	+	–	–	–
actone	–	–	–	–	–	–

<sup>a</sup> +, soluble at room temperature; + –, partial soluble; –, insoluble.



**Figure 2.** Wide-angle X-ray diffractograms of polyimides.

in Figure 1B were well assigned based on the literature data.<sup>25,30</sup> The results further provided clear evidence that the polyimides prepared herein correlated with proposed structures.

**Properties of Polyimides.** The solubility of these polyimides was tested qualitatively in various solvents. Table 3 summarized these results. All of the polyimides revealed good solubility in various solvents, particularly in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), DMAc, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO),  $\gamma$ -butyrolactone, and pyridine, as well as in phenolic solvents such as *m*-cresol. All polyimides, except that derived from BAEPP, were even soluble in less polar solvents such as THF. Only limited polymers were partially soluble in chlorinated solvents such as methylene chloride and chloroform.

Crystallinity of the polyimides was evaluated by wide-angle X-ray diffraction experiments. Figure 2 displays the diffraction patterns for the polyimides. All the polyimides showed amorphous diffraction patterns. The good solubility and highly amorphous nature of the polyimides could be attributed to the structural modification through the incorporation of the flexible units such as isopropylidene (**PIc** and **PId**), sulfone (**PIe**), oxyethylene (**PId**), and ether (**PIa–f**) and of methyl-substituted arylene ether (**PIc** and **PIe**) groups, and of bulky substituents such as *tert*-butyl group (**PIa** and

**Table 4. Thermal Properties of Polyimides**

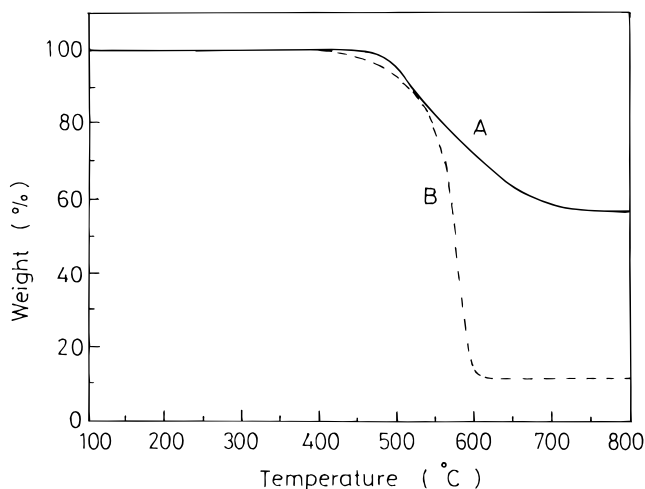
polymer code	$T_g^a$ (°C)	decomposition temp, $T_d^{10b}$ (°C)		char yield <sup>c</sup> (%)
		In N <sub>2</sub>	in air	
<b>PIa</b>	268	524	470	56
<b>PIb</b>	299	512	545	53
<b>PIc</b>	279	478	488	54
<b>PId</b>	320	457	449	31
<b>PIe</b>	341	457	451	63
<b>PIf</b>	309	521	519	57

<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 10% weight loss recorded on TG at a heating rate of 20 °C min<sup>-1</sup>. <sup>c</sup> Residual weight % at 800 °C in nitrogen.

**PIb**), as well as 2,2'-dimethylbiphenylene unit (**PIf**) into the polyimide structure. There was a considerable decrease in the rigidity and lowering of energy of internal rotation of polymer chain due to the presence of the flexible units, which in turn reduced the crystallinity and improved polymer solubility. Incorporating bulky *tert*-butyl substituent and noncoplanar conformation of 2,2'-dimethylbiphenylene in a para-linked polymer chain does not initially change the rodlike structure of the polymer backbone but might decrease the intermolecular forces between the polymer chains due to a looser packing of polymer chain as compared to the unsubstituted polyimides. Therefore, crystallization tendency is markedly lowered, and the solubilities are significantly enhanced. Numata et al.<sup>38</sup> reported that the rod-like polyimides without side groups seem to be able to pack more compactly and have higher packing density. However, in the case of rod-like polyimides with side groups on their molecular chain, their packing density becomes smaller on introduction of the side group. This result verified that dense packing should be hindered by a steric effect of substituents, which act as spacers for the polymer molecules.

In addition, tetramethyl substituents on the phenylene units would lower the solubility parameter of the polymers and also inhibit close packing of the polymer chains.

The thermal properties of the polyimides were evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG). The results are tabulated in Table 4. Glass transition temperatures ( $T_g$ 's) of polyimides were found in the range 268–341 °C. No melting endotherm peak was observed from DSC curves. Thus DSC measurements also revealed the amorphous nature of the polyimides. As can be expected, the sulfone-containing polyimide **PIe** exhibited the highest  $T_g$  due to its higher intermolecular force. Polymer **PId** having the most flexible backbone structure gave relatively higher  $T_g$  value. This may be attributed to its higher molecular weight. On the other hand, the introducing a flexible and linear oxyethylene group into the polymer backbone favors regular packing of the polymer chain. This results in higher crystallinity and higher  $T_g$  value.<sup>39,40</sup> Notably, polymer **PIb** having two *tert*-butyl substituents gives higher  $T_g$  than **PIa**, which has only one *tert*-butyl substituent. This is due to polymer **PIb** containing symmetric di-*tert*-butyl substituents appear

**Figure 3.** TG curves for polyimide **PIf** at a heating rate of 10 °C min<sup>-1</sup> in (A) nitrogen and (B) air.**Table 5. Mechanical Properties of Polyimides Films**

polymer code	tensile strength (MPa)	elongation at break (%)	Young's modulus (GPa)
<b>PIa</b>	105	6	2.18
<b>PIb</b>	91	5	2.59
<b>PIc</b>	72	5	2.28
<b>PId</b>	97	4	2.70
<b>PIe</b>	75	5	2.34
<b>PIf</b>	99	7	2.85

to pack efficiently (perhaps better than expected) while polymer containing unsymmetric mono-*tert*-butyl substituent pack quite loosely.<sup>29,30</sup> Therefore, **PIb** has smaller free volume and higher  $T_g$  than **PIa**. Our previous study revealed similar result.<sup>29</sup>

As we reported previously,<sup>29–34</sup> polyimides derived from BTDA with these diamines used herein had  $T_g$  ranging from 247–295 °C. It was interesting to note that although the BTDA-based polyimides exhibited higher crystallinity than BHTDA-based polyimides, the former had lower  $T_g$  values. This result may be attributed to the higher interchain interaction due to the polar hydroxyl group in BHTDA-based polymer, which results in a higher  $T_g$ .<sup>24</sup> Thermogravimetry (TG) analysis was conducted in nitrogen and air atmosphere. Representative TG curves of polyimide **PIf** are shown in Figure 3. The polymers almost exhibited a one-step pattern of decomposition with no significant weight loss below 420 °C in nitrogen and air. The temperatures at 10% weight loss ( $T_d^{10}$ ), examined by TG analysis, showed values ranging from 457–524 °C in nitrogen and 449–545 °C in air, respectively. The oxyethylene- and sulfone-containing polymers seem to have lower thermal stabilities. Polyimide derived from DBAPP containing a biphenylene unit had the best thermal stability in nitrogen and air atmosphere. Almost all polymers had char yields above 53%, while oxyethylene-containing polyimide **PId** had the lowest one of 31% at 800 °C in nitrogen.

The flexible cast films were subjected to a tensile test. Table 5 summarize the results. The films had tensile strength, elongation at break, and Young's modulus in the ranges 72–105 MPa, 4–7%, and 2.18–2.85 GPa, respectively.

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### Conclusions

This work has synthesized several new polyimides having moderate-to-high molecular weights from a series of diamines with the dianhydride BHTDA containing hydroxyl moiety. Incorporating of the flexible units such as isopropylidene, sulfone, oxyethylene, ether, and methyl-substituted arylene ether groups and bulky substituents such as a *tert*-butyl group, as well as a 2,2'-dimethylbiphenylene unit into the polyimide structure decreases the rigidity of polymer chain. The

polyimides are soluble in various solvents and exhibited amorphous natures. In addition, the polymers are thermally stable, and strong flexible films could be cast from solution. These properties can make these polyimides attractive for practical applications such as processable high-performance engineering plastics.

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