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Synthesis and characterization of new organosoluble polyimides based on flexible diamine

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Abstract

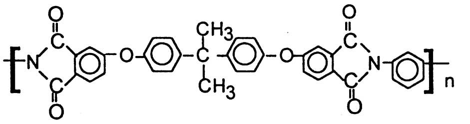
The new five benzene rings-containing diamine, α,α′-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**BDAPD**) was prepared by the aromatic nucleophilic substitution of α,α′-bis(4-hydroxy-3,5-dimethylphenyl)-1,4-diisopropylbenzene with 1-chloro-4-nitrobenzene, and subsequent hydrogenation of the intermediate dinitro. The diamine was reacted with various aromatic dianhydrides to prepare a series of new polyimides (IPs) via the poly(amic acid) precursors and thermal or chemical imidization. The polyimides were produced with inherent viscosities of 0.60–0.85 dl g^{-1} by chemical imidization. All the poly(amic acid)s films could be obtained by solution-cast from *N*,*N*-dimethylacetamide (DMAc) solutions and thermally converted into transparent, flexible, and tough polyimide films. The wide-angle X-ray diffraction diagrams revealed that all the polyimides showed amorphous character. All of the polyimides, except PI-1, showed excellent solubility in a variety of solvents such as *N*-methyl-2-pyrrolidinone, DMAc, *N*,*N*-dimethylformade, dimethyl sulfoxide, pyridine, cyclohexanone and tetrahydrofuran. Such polyimides had better solubility than those containing only one isopropylidene unit or a hexafluoroisopropylidene linkage in the repeating unit of polyimide backbone. These polyimides had glass transition temperatures (T_g) between 241 and 270°C, which were higher than the T_g value of **Ultem 1000** (215°C). The thermogravimetric analyses demonstrated that almost all of the polymers were stable up to 450°C, and the 10% weight loss temperatures were recorded in the range 466–488°C in air atmosphere. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: α,α′-Bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (BDAPD); Polyimides

1. Introduction

Aromatic polyimides (PIs) are well known as high-performance polymers, which possess excellent thermal stability, inert behavior against organic solvents, and good mechanical properties [1,2]. However, as their rigid structures cause high softening temperature and poor solubility in many organic solvents, it was often difficult to fabricate them. Therefore, many efforts have been concentrated on synthesizing soluble and tractable PIs without sacrificing their desired properties.

One of the successful approaches to increase solubility and moldability of polyimides is the introduction of flexible linkages into polymer backbone [3–9]. An important commercialized example, which contains flexible ether (–O–) and isopropylidene [$-C(CH_3)_2-$] groups, is **Ultem 1000** (developed by General Electric Co.).



It is known to exhibit reasonable thermal stability and good mechanical properties together with excellent moldability. Our previous works observed that the solubility of polyamides [10], polyimides [11] and polyamide-imides [12] was enhanced by incorporating the ether and isopropylidene units into the polymer backbone while retaining a satisfying thermal stability.

In this study the new diamine, α,α′-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**BDAPD**) containing flexible ether and isopropylidene units, and five benzene rings was synthesized and used to prepare a series of polyimides. Due to the presence of the flexible moieties on the polyimide backbone, there was a considerable decrease in the rigidity of polymer chain, which could be considered to be reduced the crystallinity and improved the solubility of polymer. Therefore, the diamine **BDAPD** would be a potential monomer for

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preparation of soluble and moldable polyimide. In the present article, we describe the synthesis and characterization of new polyimides derived from **BDAPD** by using various aromatic tetracarboxylic dianhydrides. The solubility, crystallinity, thermal and mechanical properties are also investigated herein.

2. Experimental

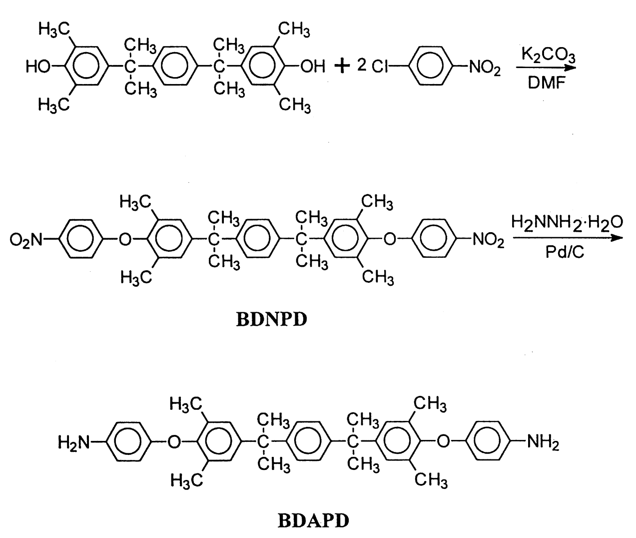
2.1. Materials

α,α′-Bis(4-hydroxy-3,5-dimethylphenyl)-1,4-diisopropylbenzene (from TCI), *p*-chloronitrobenzene (from Merck), anhydrous potassium carbonate (from Merck), hydrazine monohydrate (from Merck), and 10% palladium on activated carbon (Pd/C, from Merck) were used as received. Pyromellitic dianhydride (**DA1**, Scheme 2; from CHRISKEV), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**DA4**; from CHRISKEV), 4,4′-sulfonyldiphthalic anhydride (**DA5**; from New Japan Chemical Co.), and 4,4′-hexafluoro-isopropylidenebisphathalic anhydride (**DA6**; from CHRISKEV) were recrystallized from acetic anhydride before use. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**DA2**; from CHRISKEV), 4,4′-oxydiphthalic anhydride (**DA3**; from TCI) were used as received. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure before used. Acetic anhydride was purified by vacuum distillation.

2.2. Synthesis of monomers

2.2.1. α,α′-Bis[3,5-dimethyl-4-(4-nitrophenoxy)phenyl]-1,4-diisopropylbenzene (BDNPD)

BDNPD was synthesized by the reaction of α,α′-bis(4-hydroxy-3,5-dimethylphenyl)-1,4-diisopropylbenzene 8.05 g (20 mmol) and *p*-chloronitrobenzene 6.93 g (44 mmol) in the presence of potassium carbonate 6.08 g (44 mmol) and DMF 20 ml at 160°C for 8 h. The solution was then cooled and poured into methanol–water mixture. The crude product was recrystallized from glacial acetic acid to provide yellow crystal (m.p. 226–227°C) in 80% yield. The IR spectrum (KBr) exhibited absorptions at 1579 and 1334 cm^{-1} (NO_2), 1239 cm^{-1} (C–O–C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.71 (d, 4H), 7.24 (s, 4H), 6.97 (s, 4H), 6.84 (d, 4H), 2.04 (s, 12H), 1.68 (s, 12H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 164.1, 149.3, 148.9, 148.5, 142.9, 130.5, 128.4, 126.9, 126.8, 115.3, 41.7, 30.3, 15.6. Anal. calcd for $C_{40}H_{40}O_6N_2$: C, 74.51%; H, 6.25%; N, 4.34%; found: C, 74.59%; H, 6.32%; N, 4.37%.



Scheme 1.

2.2.2. α,α′-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (BDAPD)

The obtained dinitro compound **BDAPD** 5.0 g (7.76 mmol), 0.03 g of 10% Pd/C, and 25 ml ethanol were introduced into a three-necked flask to which 7 ml of hydrazine monohydrate was added dropwise at 85°C. After the addition was complete, the reaction was continued at reflux temperature for another 24 h. The mixture was then cooled and filtered. The crude product was recrystallized from 1,2-dichlorobenzene twice to provide **BDAPD** (m.p. 224–226°C) in 72% yield. The IR spectrum (KBr) exhibited absorptions at 3420 and 3342 (N–H), 1218 cm^{-1} (C–O–C). ^{1}H NMR (DMSO-d$_6$): δ (ppm) = 7.14 (s, 4H), 6.94 (s, 4H), 6.48 (d, 4H), 6.41 (d, 4H), 4.64 (s, 4H), 1.98 (s, 12H), 1.60 (s, 12H). ^{13}C NMR (DMSO-d$_6$): δ (ppm) = 150.6, 150.0, 148.7, 147.5, 144.2, 131.0. 128.1, 127.1, 115.9, 115.6, 41.5, 30.4, 16.0. Anal. calcd for $C_{40}H_{44}O_2N_2$: C, 82.15%; H, 7.58%; N, 4.79%; found: C, 81.73%; H, 7.34%; N, 4.61%.

2.3. Polymerization procedures

To a stirred solution of **BDAPD** (0.468 g, 0.8 mmol) in DMAc (4 ml), was gradually added pyromellitic dianhydride (**DA1**) (0.174 g, 0.8 mmol). The mixture was stirred at room temperature for 2 h under argon atmosphere to form the poly(amic acid) precursor. From this solution a poly(amic acid) film was cast onto a glass plate and heated (8 h at 80°C, 2 h at 150°C, 2 h at 200°C, 2 h at 250°C, and 2 h at 280°C) under vacuum to convert the poly(amic acid) into polyimide film. Alternatively, chemical imidization was also carried out by adding extra DMAc, and an equimolar mixture of acetic anhydride and pyridine into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then heating at 100°C for 3 h. It was subsequently poured into methanol and the brown solid precipitate was filtered off, washed with methanol and hot water, and then dried at 100°C for 24 h to afford polyimide **PI-1**. All other polyimides (**PI-2**–**PI-6**) were prepared using a similar procedure.

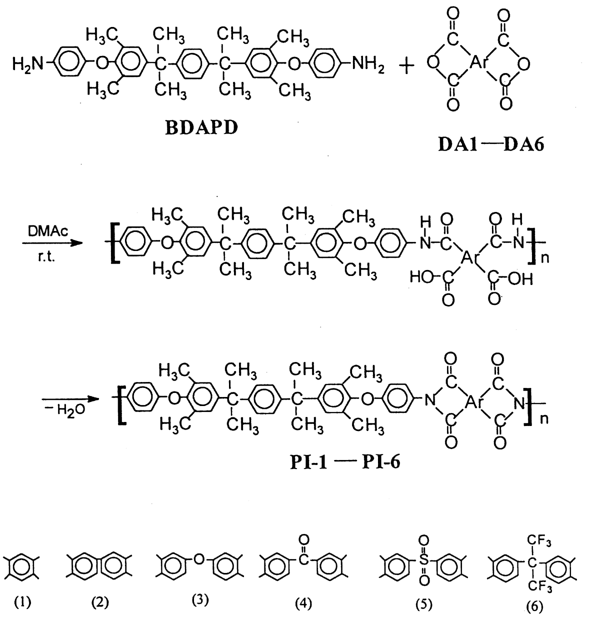
2.4. Instruments

Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). IR spectra were recorded in the range 4000–400 cm^{-1} on a JASCO IR-700 spectrometer. ^{13}C and ^{1}H NMR spectra were obtained using a Joel EX-400 operating at 100.40 MHz for carbon and 399.65 MHz for proton. The inherent viscosities of all polyimides were measured using Ubbelohde viscometer. Elemental analysis was made (Perkin–Elmer 2400 instrument). Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni filtered Cu-Kα radiation (30 kV, 20 mA). Thermogravimetric data were obtained on a DuPont 2100 in flowing nitrogen or air (60 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a DuPont 2000 differential scanning calorimeter at a heating rate of 20°C min^{-1}. Tensile properties were determined from stress–strain curves obtained with a Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.4 cm wide, 6 cm long, and ca. 0.15 mm thick).

3. Results and discussion

3.1. Monomer synthesis

The diamine **BDAPD** was synthesized in two steps by the aromatic nucleophilic substitution reaction of α,α′-bis(4-hydroxy-3,5-dimethyl-phenyl)-1,4-diisopropylbenzene and *p*-chloronitrobenzene in the presence of K_2CO_3, to obtain the dinitro compound (**BDNPD**), followed by reduction with hydrazine monohydrate/Pd–C (see Scheme 1). The structures of the dinitro and diamine compounds were confirmed by IR, NMR spectroscopy, and elemental analysis. In IR spectra, **BDAPD** revealed absorption bands appearing around 1579 and 1334 cm^{-1} due to symmetric and asymmetric stretching of nitro group. After reduction, the characteristics absorption of nitro groups disappeared and the characteristic bands of the amino groups at 3420 and 3342 (N–H stretching) and 1620 cm^{-1} (N–H bending) was observed. As shown in Section 2, the ^{13}C NMR spectra of **BDNPD** and **BDAPD** both exhibited 13 peaks each. When the dinitro compound **BDNPD** was converted into diamine **BDAPD**, the signal at 4.64 ppm in ^{1}H NMR spectra is peculiar to the amino group.



Scheme 2.

3.2. Preparation of polyimides

The polyimides were prepared by the conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid) and subsequently thermal or chemical cyclodehydration. The poly(amic acid) precursors were prepared by adding the dianhydride (**DA1–DA6**) to the diamine solution gradually. The molecular weights were high enough to cast flexible, tough, and transparent poly(amic acid) films. The films were thermally imidized at temperatures up to 280°C, producing polyimide films. These films were subjected to wide-angle X-ray and mechanical test. Alternatively, chemical cyclodehydration of poly(amic acid)s with dehydrating agents such as a mixture of acetic anhydride and pyridine was also effective in obtaining polyimides. The resulting polyimides had inherent viscosities of 0.60–0.85 dl g^{-1} (Table 1). The polymers, except polymers **PI-1**, exhibited number-average molecular weight ($\bar{M}$n)

Table 1
Inherent viscosities and average molecular weights of polyimides

Polymer code	η_{inh} (dl g^{-1})[a]	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w \times 10^{-4}$ [b]	PDI[b]
PI-1	–[c]	–[d]	–[d]	–[d]
PI-2	0.71	4.9	11.5	2.3
PI-3	0.60	4.1	8.3	2.0
PI-4	0.65	3.1	7.9	2.5
PI-5	0.70	2.9	5.5	1.9
PI-6	0.85	9.3	14.8	1.6
Ref 1	0.90[e]	–[d]	–[d]	–[d]
Ref 2	0.69[f]	–[d]	–[d]	–[d]
Ref 3	0.68[f]	–[d]	–[d]	–[d]

[a] Inherent viscosity measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C.

[b] Measured by GPC in THF, polystyrene was used as standard.

[c] Polymer is not soluble in DMAc.

[d] Polymer is not soluble in THF.

[e] Inherent viscosity measured in NMP at a concentration of 0.5 g dl^{-1} at 30°C.

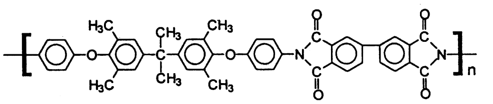
[f] Inherent viscosity measured in conc. H_2SO_4 at a concentration of 0.5 g dl^{-1} at 30°C.

and weight-average molecular weight ($\bar{M}$w) in the range of 29,000–93,000 and 55,000–148,000, respectively. These polyimides obtained by chemically imidization were subjected to thermal and solubility test.

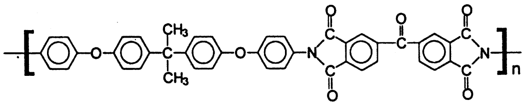
3.3. Polymer characterization

The solubilities of the polyimides in several organic solvents at 3.0% (w/v) are summarized in Table 2. Most of the polyimides obtained by chemical imidization, except **PI-1**, were soluble in the test solvents including NMP, DMAc, dimethyl sulfoxide (DMSO), pyridine, tetrahydrofuran and cyclohexanone. The good solubility was possibly governed by the structural modification through the incorporation of the flexible isopropylidene and arylene ether groups into the polyimide structure. For comparison, polyimides **Ref 1** [11] and **Ref 2** [13] containing only one isopropylidene unit in the repeating unit were prepared. In addition, polymer **Ref 3** [13] containing hexafluoroisopropylidene unit was also synthesized as a reference.

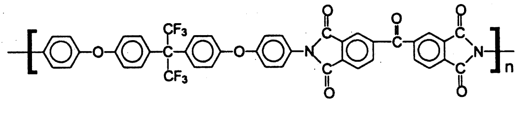
Ref 1:



Ref 2:



Ref 3:



It had been observed that polyimides **Ref 1** and **Ref 2** showed less solubility than their analogous polymers (**PI-2** and **PI-4**, respectively). This result demonstrated that the presence of more isopropylidene unit in the repeat unit led to an enhanced solubility. It was noted that polyimide **Ref 3** containing hexafluoroisopropylidene unit in the polymer backbone showed less solubility than polymer **PI-4** derived from **BDAPD**. It implied that the **BDAPD**-based polymers showed better solubility than those containing hexafluoroisopropylidene unit which was incorporated in the polymer backbone to prepare soluble polyimides [13]. The solubility of the polyimides obtained by thermal imidization method is also listed in Table 2. It was observed that the polyimides obtained by chemical imidization showed better solubility compared with those obtained by thermal imidization. The polyimides obtained by chemical imidization were further thermally treated. It was observed that after thermal treatment, the solubility of the polyimides prepared by chemical imidization showed less solubility than that of the polyimides before thermal treatment. The solubility of the polyimides obtained by chemical imidization after thermal treatment was similar to those obtained by thermal imidization. The poor solubility of the thermally treated polymer was possibly due to the presence of partial intermolecular crosslinking during the solid state thermal imidization stage [14,15].

The crystallinity of the polyimides was examined by wide-angle X-ray diffraction diagrams. The polyimide films obtained by thermal cyclodehydration were employed as samples. All the polyimides exhibited amorphous patterns. These results could be explained by the presence of the flexible isopropylidene and ether groups which reduced the rigidity of the polymer chain. In addition, methyl groups on the phenylene also inhibited close packing of the polymer chains [11].

The tensile properties of the polyimide films prepared by thermal treatment are summarized in Table 3. The films had tensile strength of 77–95 MPa, elongation at break of 7–10%, and initial modulus of 2.0–2.4 GPa. The films showed strong and tough natures.

The thermal properties of the polyimides are tabulated in Table 4. Glass transition temperatures (T_g) of polyimides, determined by means of differential scanning calorimeter, were found to be in the range of 241–270°C. No melting endotherm peak was observed from DSC traces. This also verified the amorphous nature of the polyimides. As expected, PI-1 derived from pyromellitic dianhydride (**DA1**) exhibited the highest T_g value. Upon comparison with the T_g value of the commercial available polyimide, **Ultem 1000** ($T_g = 215°C$), all of the **BDAPD**-based polyimides exhibited higher T_g values than **Ultem 1000**. The temperatures at 10% weight loss ($T_{d_{10}}$), examined by thermogravimetric analysis (TGA), showed values reaching to 455–477 and 466–488°C in nitrogen and air atmosphere, respectively. It is interesting to find that most of the polymers showed higher $T_{d_{10}}$ in air than in nitrogen. The higher $T_{d_{10}}$ value in air may reflect the oxidation of CH_3 group in polymer chain, which forms carbonyl (C=O) and hydroxyl (O–H) groups and then causes weight gain [16–18].

4. Conclusions

The new diamine **BDAPD** was successfully prepared in high purity and high yields in this study, and moderate to high molecular weights of polyimides were obtained. All the poly(amic acid)s could be thermally converted into transparent, tough, and flexible polyimide films with good mechanical properties. These new polyimides are amorphous and exhibited excellent solubility except **PI-1**. It demonstrated that these polyimides had better solubility than those containing only one isopropylidene unit or a hexafluoroisopropylidene linkage in the repeating unit of polyimide backbone. The T_g values of the **BDAPD**-based polyimides were higher than that of **Ultem 1000** ($T_g = 215°C$). These polyimides could be considered as new processable high-performance polymeric materials.

Table 2
Solubility of polyimides (polyimides obtained by the chemical imidization method; the concentration of solubility test was measured at 3.0% (w/v); the symbols have the following meanings: (++), soluble at room temperature; (+), soluble on heating at 70°C; (+−), partially soluble at 70°C; (−), insoluble at 70°C)

Polymer code	Solvent[a]						
	NMP	DMAc	DMF	DMSO	Py	THF	Cyclohexaone
PI-1	−	−	−	−	−	−	−
	(−)[b]	(−)	(−)	(−)	(−)	(−)	(−)
PI-2	++	++	+−	+	++	++	++
	(++)	(+)	(−)	(+−)	(+)	(+−)	(+−)
PI-3	++	++	++	+−	++	++	++
	(++)	(++)	(++)	(−)	(+)	(+)	(+)
PI-4	++	++	++	+	++	++	++
	(++)	(++)	(+)	(+−)	(+)	(+)	(+)
PI-5	++	++	++	++	++	++	++
	(++)	(++)	(++)	(++)	(+)	(+)	(+)
PI-6	++	++	++	++	++	++	++
Ref 1	+	+−	+−	−	+−	+−	+−
	(−)	(−)	(−)	(−)	(−)	(−)	(−)
Ref 2	+−	+−	+−	−	+−	−	−
	(−)	(−)	(−)	(−)	(−)	(−)	(−)
Ref 3	+−	+−	+−	−	+−	−	−
	(−)	(−)	(−)	(−)	(−)	(−)	(−)

[a] Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF: tetrahydrofuran.

[b] Data in parentheses are the solubility of polyimides obtained by the thermal imidization method.

Table 3
Mechanical properties of polyimides

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
PI-1	88	10	2.1
PI-2	77	9	2.1
PI-3	95	10	2.0
PI-4	86	7	2.4
PI-5	90	8	2.1
PI-6	86	10	2.1

Table 4
Thermal properties of polyimides

Polymer code	T_g[a] (°C)	$T_{d_{10}}$[b]		Char yield[c] (%)
		In nitrogen (°C)	In air (°C)	
PI-1	270	474	479	36
PI-2	253	470	485	35
PI-3	241	461	475	38
PI-4	241	472	481	42
PI-5	250	455	466	31
PI-6	247	477	488	34

[a] From the second heating trace of DSC measurements conducted at a heating rate of 20°C min^{-1}.

[b] Temperature at 10% weight loss ($T_{d_{10}}$) determined by TGA in nitrogen at a heating rate of 20°C min^{-1}.

[c] Char yield at 800°C in nitrogen.

Acknowledgements

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