

Synthesis and Properties of Poly(ether Imide)s Derived from 2,5-Bis(3,4-Dicarboxyphenoxy)biphenyl Dianhydride and Aromatic Ether–Diamines*

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ABSTRACT: A series of poly(ether imide)s (PEIs) with light colors and good mechanical properties were synthesized from 2,5-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride and various aromatic ether–diamines via a conventional two-step polymerization technique that included ring-opening polyaddition at room temperature to poly(amic acid)s (PAAs) followed by thermal imidization. The precursor PAAs had inherent viscosities ranging from 0.71 to 1.19 dL/g and were solution-cast and thermally cyclodehydrated to flexible and tough PEI films. All of the PEI films were essentially colorless, with ultraviolet–visible absorption cutoff wavelengths between 377 and 385

nm and yellowness index values ranging from 10.5 to 19.9. These PEIs showed high thermal stabilities with glass-transition temperatures of 206–262°C and decomposition temperatures (at 10% weight loss) higher than 478°C. They also showed low dielectric constants of 3.39–3.72 (at 1 MHz) and low water absorptions below 0.85 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3993–4002, 2009

Key words: dielectric properties; polyimides; structure–property relations; synthesis; thermal properties

INTRODUCTION

Aromatic polyimides have been widely used in microelectronics applications because of their excellent thermal and mechanical properties, good chemical resistance, and low dielectric constants.^{1–3} Despite their widespread use, most of them have high melting temperatures or softening temperatures and limited solubility in most organic solvents because of their rigid backbones and strong interpolymer interactions, which may restrict their applications in some fields. To overcome these drawbacks, structural modifications of the polymer backbone, such as the introduction of bulky groups,^{4–11} flexible aryl–ether linkages,^{12–15} and unsymmetrical structures,^{16–21} have been used to modify the polymer properties by the design and preparation of new diamines or dianhydrides.

The optical transparency of PI films is of special importance in some applications, such as flexible solar radiation protectors, orientation films in liquid crystal display devices, and optical half-wave plates for planar lightwave circuits. However, most conventional polyimide films generally show considerable coloration, from pale yellow to deep brown, because of charge-transfer (CT) complexing between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.^{22–24} A strategy for obtaining less colored or colorless polyimides is to use dianhydrides of lower electron-withdrawing abilities and diamines of lower electron-donating abilities as monomers to weaken both the intramolecular and intermolecular CT interactions.²⁴ Soluble and colorless polyimides can be obtained with alicyclic dianhydride or diamine monomers;^{25–29} however, the high-temperature stability is somewhat sacrificed because of the incorporation of less stable aliphatic segments. Thus, polyimides derived from aliphatic monomers are mostly used for applications that have less stringent thermal requirements. The incorporation of bulky pendent groups, such as *tert*-butyl groups, into either the diamine or dianhydride component reduces the interchain electronic interactions and, thereby, leads to soluble and colorless polyimides.^{30,31} In recent years, much effort has

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been spent on the synthesis of fluorinated aromatic polyimides, especially trifluoromethyl-containing polyimides.^{32–36} It has been demonstrated that the introduction of bulky trifluoromethyl groups into polyimide backbones results in enhanced solubility and optical transparency, together with a lowered dielectric constant. Meanwhile, the thermal properties of the polyimides can often be maintained because of the outstanding thermal and thermooxidative stabilities of the fluoro groups.

Poly(ether imide)s (PEIs) have attracted great attention as they may provide good processability because of the presence of flexible ether links. The development of nucleophilic displacement reactions and nitrodisplacement reactions, in particular, has led to the development of a large class of PEIs from bis(ether anhydride)s and various diamines.^{37–39} An important example is Ultem 1000 resin, developed and commercialized by General Electric Co.,⁴⁰ which exhibits a reasonable thermal stability and good mechanical properties, together with good moldability. As part of our continued efforts to develop soluble and colorless polyimides with high thermal stabilities and low dielectric constants, in this article, we report the synthesis and characterization of a series of PEIs from 2,5-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride (**I**) with various structurally different aromatic ether–diamines. The obtained PEIs should have diminished intramolecular and intermolecular CT interactions because of the decrease in electron-accepting properties of the dianhydride moieties caused by the electron-donating ether groups. In addition, the bulky pendent phenyl group in the bis(ether anhydride) component should have helped prevent the extended close chain packing and, consequently, the CT interactions. Thus, the resulting PEIs may have exhibited low coloration, high optical transparency in the visible region, good solubility in organic solvents, and low dielectric constants.

EXPERIMENTAL

Materials

Phenylhydroquinone (PHQ; TCI, Tokyo, Japan), 4-nitrophthalonitrile (TCI), and acetic anhydride (Ac₂O; Fluka, Buchs, Switzerland) were used as received. 4,4'-Oxydianiline (ODA or **IIa**; TCI), 1,4-bis(4-aminophenoxy)benzene (**IIb**; TCI), 1,3-bis(4-aminophenoxy)benzene (**IIc**; TCI), 4,4'-bis(4-aminophenoxy)biphenyl (**IIe**; Chriskev, Leawook, KS), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IIg**; Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IIh**; Chriskev) were used as received. 1,2-Bis(4-aminophenoxy)benzene (**IIId**; mp = 137–138°C),⁴¹ 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (**IIIf**; mp = 225–226°C),⁴² and 9,9-bis[4-

(4-aminophenoxy)phenyl]fluorene (**IIi**; mp = 177–178°C)⁴³ were synthesized by the chlorodisplacement reactions of *p*-chloronitrobenzene with catechol, 3,3',5,5'-tetramethyl-4,4'-biphenol, and 9,9-bis(4-hydroxyphenyl)fluorene, respectively, followed by the hydrazine Pd/C-catalyzed reduction of the dinitro intermediates. *N,N*-Dimethylacetamide (DMAc; Fluka) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of bis(ether anhydride) I

2,5-Bis(3,4-dicyanophenoxy)biphenyl (**I'**)

In a 250-mL flask, 7.0 g (37.5 mmol) of PHQ, 13.0 g (75 mmol) of 4-nitrophthalonitrile, and 10.4 g (37.6 mmol) of K₂CO₃ were dissolved/suspended in 110 mL of anhydrous *N,N*-dimethylformamide (DMF). The suspension was stirred at room temperature for about 24 h. Then, the reaction mixture was poured into 600 mL of water, and the precipitated pale orange solid was collected and washed thoroughly with methanol and water. The product was recrystallized by acetonitrile to give colorless crystals (13.0 g, 79% yield, mp = 229–230°C).

¹H-NMR [500 MHz, dimethyl sulfoxide (DMSO)-*d*₆, δ, ppm; for the peak assignments, see Fig. 1]: 8.14 (d, *J* = 8.8 Hz, 1H, H_{b'}), 8.02 (d, *J* = 8.8 Hz, 1H, H_b), 7.92 (d, *J* = 2.4 Hz, 1H, H_{a'}), 7.77 (d, *J* = 2.4 Hz, 1H, H_a), 7.59 (dd, *J* = 8.7, 2.4 Hz, 1H, H_{c'}), 7.46 (d, *J* = 7.4 Hz, 2H, H_g), 7.38–7.28 (m, 7H, H_{c-f,h,i}). ¹³C-NMR (125 MHz, DMSO-*d*₆, δ, ppm; for the peak assignments, see Fig. 2): 161.09; 161.03 (C^{5,5'}); 151.50 (C⁷); 147.46 (C¹⁰); 136.23 (C¹³); 136.07, 135.83 (C^{3,3'}); 135.31 (C⁹); 128.76 (C¹⁵); 128.41 (C¹⁴); 128.09 (C¹⁶); 123.96, 123.21 (C^{4,4'}); 122.49, 121.73 (C^{6,6'}); 122.29 (C¹¹); 121.56 (C^{8,12}); 116.72, 116.53 (C^{1,1'}); 115.88, 115.77 (C^{18,18'}); 115.43, 115.30 (C^{17,17'}); 108.37, 107.95 (C^{2,2'}).

2,5-Bis(3,4-dicarboxyphenoxy)biphenyl (**I''**)

In a 500-mL flask, a suspension of bis(ether dinitrile) **I'** (12.66 g, 30 mmol) in an ethanol/water mixture (100 mL/100 mL) containing 27 g (0.48 mol) of dissolved KOH was boiled under reflux. Refluxing was continued for about 30 h until the evolution of ammonia had ceased. The resulting clear solution was filtered hot to remove any possible insoluble impurities. The filtrate was allowed to cool and was then acidified by concentrated HCl to a pH of 1–3. The white precipitated product was filtered off, washed with water until it was neutral, and dried *in vacuo* (100°C). The yield of bis(ether diacid) **I''** was 14.5 g (94%).

¹H-NMR (500 MHz, DMSO-*d*₆, δ, ppm; for the peak assignments, see Fig. 1): 7.93 (d, *J* = 8.6 Hz, 1H, H_{b'}), 7.81 (d, *J* = 8.7 Hz, 1H, H_b), 7.49 (d, *J* = 7.6

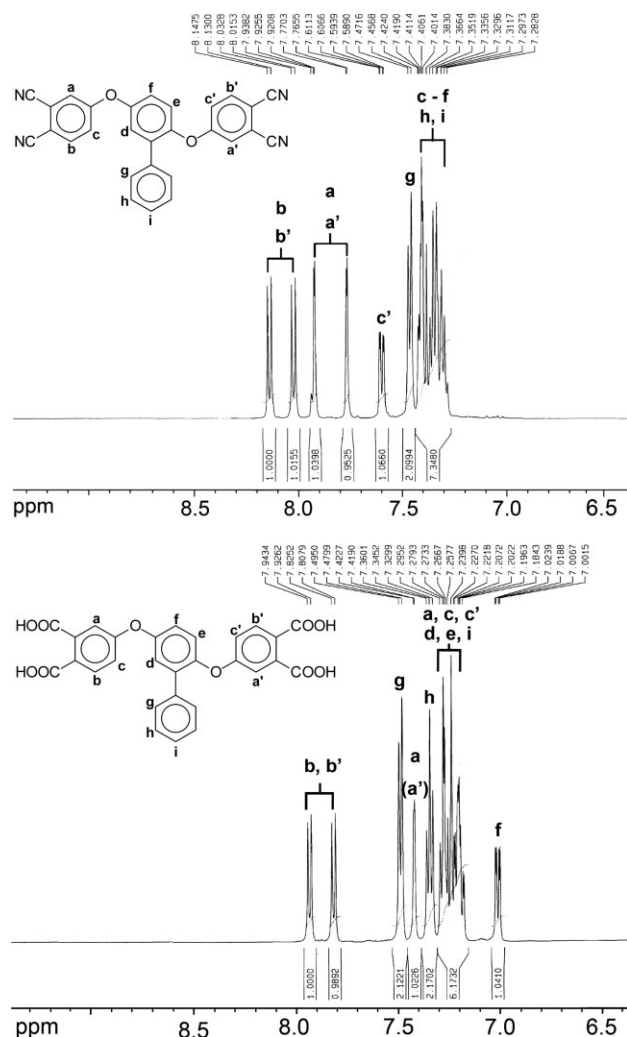


Figure 1 ^1H -NMR spectra of compounds **I'** and **I''** in $\text{DMSO-}d_6$.

Hz, 2H, H_g), 7.42 (s, 1H, $H_{a'}$), 7.34 (t, $J = 7.5$ Hz, 2H, H_h), 7.29–7.18 (m, 6H, $H_{a,c,c',d,e,i}$). ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$, δ , ppm; for the peak assignments, see Fig. 2): 168.49, 168.47, 167.76, 167.69 ($\text{C}^{17,17',18,18'}$); 159.67, 159.21 ($\text{C}^{5,5'}$); 152.58 (C^7); 147.91 (C^{10}); 137.08, 136.96 ($\text{C}^{1,1'}$); 136.12 (C^{13}); 135.69 (C^9); 132.85, 132.66 ($\text{C}^{3,3'}$); 128.94 (C^{15}); 128.63 (C^{14}); 128.15 (C^{16}); 127.22, 126.38 ($\text{C}^{2,2'}$); 123.65, 122.30 ($\text{C}^{4,4'}$); 120.72, 119.36 ($\text{C}^{6,6'}$); 118.31 (C^{11}); 118.02 (C^{12}); 117.02 (C^8).

I

In a 200-mL flask, a mixture of 14.0 g (27 mmol) of bis(ether diacid) **I''** dissolved in 30 mL of Ac_2O and 50 mL of acetic acid was heated at a reflux temperature for 1 h. The resulting clear solution was filtered to remove any insoluble impurities. The product crystallized off when the filtrate was cooled, and it was filtered, washed with toluene, and dried at 150°C *in vacuo* (yield = 91%, mp = $231\text{--}232^\circ\text{C}$).

^1H -NMR (500 MHz, $\text{DMSO-}d_6$, δ , ppm; for the peak assignments, see Fig. 3): 7.82 (d, $J = 8.5$ Hz,

1H, H_b), 7.71 (d, $J = 8.5$ Hz, 1H, H_b), 7.53 (d, $J = 7.6$ Hz, 2H, H_g), 7.39 (t, $J = 7.6$ Hz, 2H, H_h), 7.33–7.22 (m, 6H, $H_{c,c',e,h,i}$), 7.07 (d, 1H, $J = 2.4$ Hz, H_d), 7.03 (dd, H, H_f , $J = 8.5, 2.4$ Hz). ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$, δ , ppm; for the peak assignments, see Fig. 3): 168.41, 168.39 ($\text{C}^{18,18'}$); 167.4, 167.3 ($\text{C}^{17,17'}$); 159.47, 159.05 ($\text{C}^{5,5'}$); 152.23 (C^7); 147.61 (C^{10}); 136.55, 136.47 ($\text{C}^{1,1'}$); 135.79 (C^{13}); 135.42 (C^9); 131.42, 131.29 ($\text{C}^{3,3'}$); 128.67 (C^{15}); 128.34 (C^{14}); 127.87 (C^{16}); 125.98, 125.19 ($\text{C}^{2,2'}$); 123.36, 122.13 ($\text{C}^{4,4'}$); 120.51 (C^{11}); 118.84 (C^{12}); 117.52 (C^8); 116.91, 115.69 ($\text{C}^{6,6'}$).

Synthesis of the PEIs

The general polymerization procedure is illustrated by the following example. Into a solution of diamine **IId** (0.234 g, 0.8 mmol) in dried DMAc (4.6 mL) in a 20-mL flask, an equimolar amount of bis(ether anhydride) **I** (0.383 g, 0.8 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to afford a viscous poly(amic acid) (PAA) solution with an inherent viscosity of 0.73 dL/g,

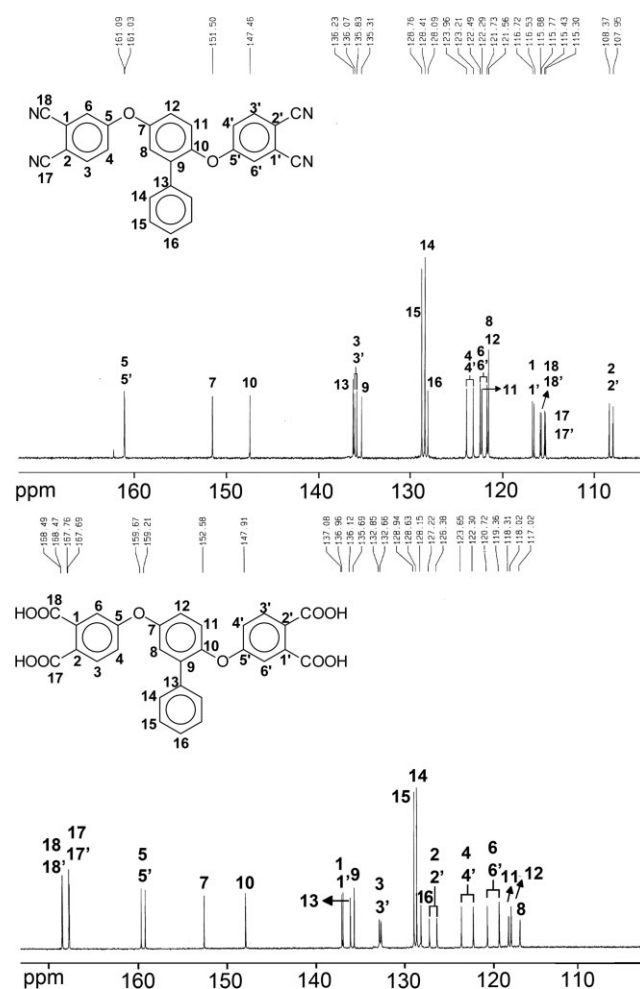


Figure 2 ^{13}C -NMR spectra of compounds **I'** and **I''** in $\text{DMSO-}d_6$.

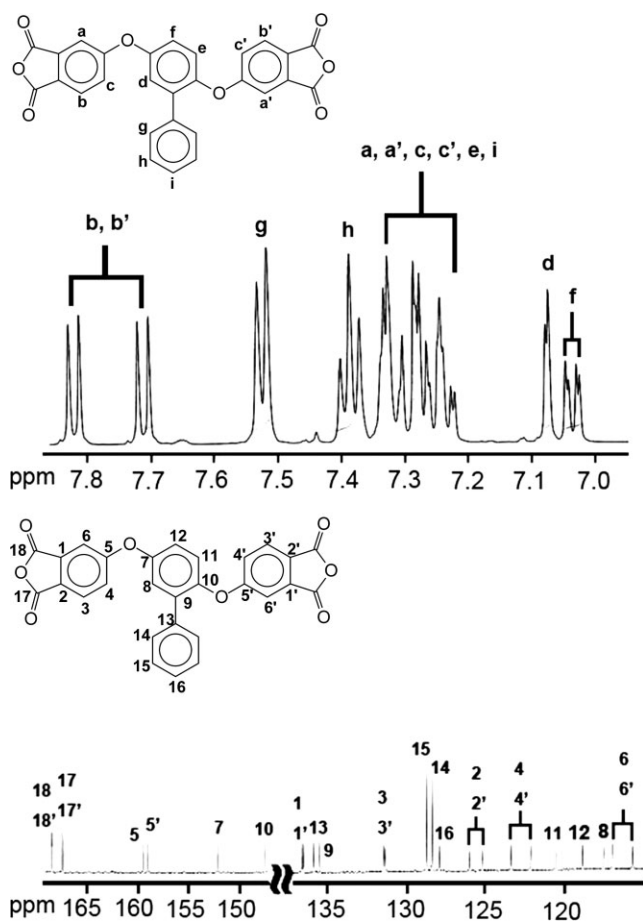


Figure 3 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of bis(ether anhydride) **I** in $\text{DMSO-}d_6$.

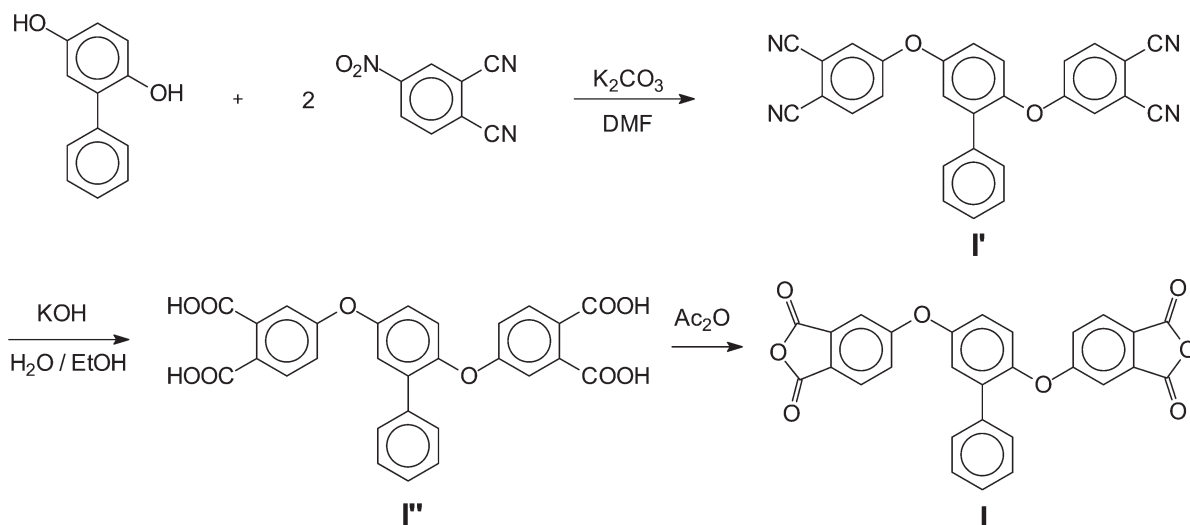
measured in DMAc at 0.5 g/dL concentration at 30°C. Then, the PAA solution was poured into a glass culture dish, which was placed in an 80°C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential heating

from 120 to 250°C at a heating rate of 3°C/min with holding at 250°C for 1 h. The cured PEI film (PEI **IVd**; see Scheme 2, shown later, for details) was stripped from the glass substrate by immersion in water followed by drying in an oven at 100°C.

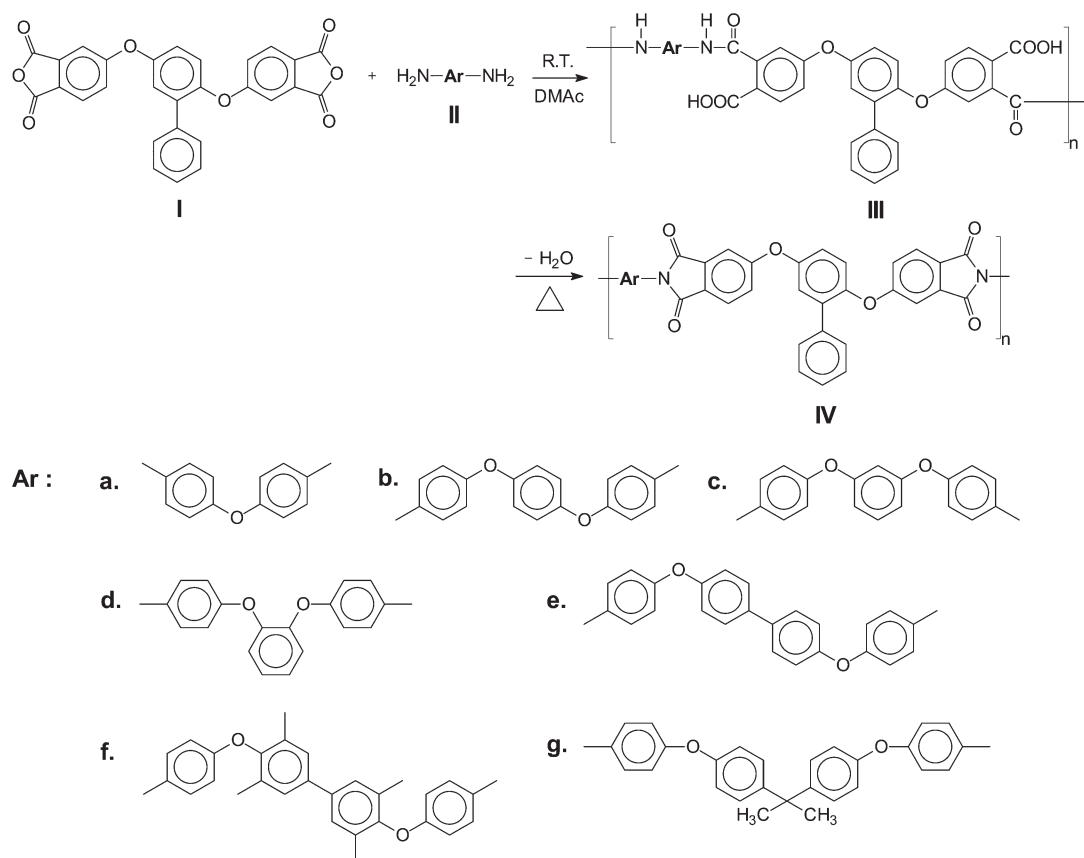
IR (film, cm^{-1}): 1776 (asymmetric C=O stretch); 1720 (symmetric imide C=O stretch); 1612–1502 (aromatic C=C stretch); 1379 (C–N stretch); 1242 (C–O); 1082, 746 (imide ring deformation). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm; for the peak assignments, see Fig. 5, shown later): 6.98–7.01 (appearing as a triplet because of the coincidental overlap, 4H, $\text{H}_{d,f,k}$), 7.15–7.35 (m, 16H), 7.43 (d, 1H, H_c or $\text{H}_{c'}$), 7.47 (d, 2H, H_g), 7.53 (s, 1H, H_a or $\text{H}_{a'}$), 7.77 (d, 1H, H_b or $\text{H}_{b'}$), 7.92 (d, 1H, $\text{H}_{b'}$ or H_b). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ , ppm; for the peak assignments, see Fig. 5, shown later): 166.68, 166.62 (imide carbonyl carbons); 163.36, 163.15 ($\text{C}^{5,5'}$); 157.11, 157.05 ($\text{C}^{22,22'}$); 152.66 (C^7); 148.19 (C^{10}); 147.28 (C^{23}); 136.88 (C^{13}); 135.73 (C^9); 134.40, 134.15 ($\text{C}^{1,1'}$); 128.83 (C^{15}); 128.48 (C^{14}); 128.19 (C^{15}); 127.77, 127.74 ($\text{C}^{20,20'}$); 126.17, 125.80 ($\text{C}^{3,3'}$); 125.70, 124.98 ($\text{C}^{2,2'}$); 125.54 ($\text{C}^{19,19'}$); 123.66 (C^{25}); 123.16, 121.98 ($\text{C}^{4,4'}$); 123.06 (C^{11}); 122.42 ($\text{C}^{8,12}$); 120.68 (C^{24}); 117.66, 117.64 ($\text{C}^{21,21'}$); 112.38, 111.17 ($\text{C}^{6,6'}$).

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR, Kyoto, Japan) spectrometer. Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer (Waltham, MA). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a Bruker AV-500 Fourier transform NMR spectrometer (Ettlingen, Germany). The inherent viscosities were determined at a 0.5-g/dL concentration with an Ubbelohde viscometer at 30°C. Thermogravimetric



Scheme 1 Synthesis of **I**.



Scheme 2 Synthesis of the PEIs (R.T. = room temperature).

analysis (TGA) was conducted with a TA Instruments TGA 2050 (New Castle, DE). Measurements were carried out on 9–11-mg film samples heated in flowing nitrogen or air (40 cm³/min) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen at a heating rate of 20°C/min. The mechanical properties of the films were measured with an Instron model 1130 tensile tester (Grove City, PA) with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–60 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth color-eye colorimeter (Ontario, Canada). The measurements were performed with films 30–60 μm thick with an observational angle of 10° and a Commission Internationale de l'Éclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer (Kyoto, Japan). The dielectric properties of the polymer films were tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric analyzer (Santa Clara, CA). Gold electrodes were vacuum-deposited on both surfaces

of the dried films. Experiments were performed at 25°C in a dry chamber. The equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25°C for 3 days.

RESULTS AND DISCUSSION

Synthesis of bis(ether anhydride) I and its derived PEIs

The bis(ether anhydride) monomer I was prepared by a three-step reaction sequence, as shown in Scheme 1. In the first step, the intermediate bis(ether dinitrile) I' was obtained from the nitrodisplacement of 4-nitrophthalonitrile with the phenoxide ion of PHQ in DMF. The purified compound I' was readily hydrolyzed to bis(ether diacid) I'' by ethanolic potassium hydroxide, and the generated compound I'' was subsequently cyclodehydrated to yield the target bis(ether anhydride) I. Although this bis(ether anhydride) has been mentioned in literature,^{44,45} its structural identification was not well done. Here, we confirm the molecular structures of bis(ether anhydride) I, together with its precursor compounds I' and I'' by ¹H-NMR and ¹³C-NMR spectroscopy. Figures 1 and 2 illustrate the ¹H-NMR and ¹³C-NMR

TABLE I
Inherent Viscosity (η_{inh}) and Elemental Analysis of the PEIs

Polymer code	Formula (formula weight)	Elemental analysis (%)			η_{inh} of PAA (dL/g) ^a	
		C	H	N		
IVa	(C ₄₀ H ₂₂ N ₂ O ₇) _n (642.62) _n	Calcd	74.46	3.45	4.36	0.75
		Found	73.70	3.46	4.22	
IVb	(C ₄₆ H ₂₆ N ₂ O ₈) _n (734.72) _n	Calcd	75.20	3.57	3.81	0.73
		Found	74.39	3.65	3.80	
IVc	(C ₄₆ H ₂₆ N ₂ O ₈) _n (734.72) _n	Calcd	75.20	3.57	3.81	0.71
		Found	74.53	3.54	3.74	
IVd	(C ₄₆ H ₂₆ N ₂ O ₈) _n (734.72) _n	Calcd	75.20	3.57	3.81	0.73
		Found	74.57	3.61	3.79	
IVe	(C ₅₂ H ₃₀ N ₂ O ₈) _n (810.82) _n	Calcd	77.03	3.73	3.45	1.19
		Found	76.00	3.46	3.17	
IVf	(C ₅₆ H ₃₈ N ₂ O ₈) _n (866.93) _n	Calcd	77.59	4.42	3.23	0.78
		Found	76.33	4.27	2.85	
IVg	(C ₅₅ H ₃₆ N ₂ O ₈) _n (852.90) _n	Calcd	77.45	4.25	3.28	0.86
		Found	76.56	4.09	2.87	
IVh	(C ₅₅ H ₃₀ N ₂ O ₈) _n (960.84) _n	Calcd	68.75	3.15	2.92	0.76
		Found	67.93	3.08	2.43	
IVi	(C ₆₅ H ₃₈ N ₂ O ₈) _n (975.03) _n	Calcd	80.07	3.93	2.87	0.71
		Found	79.08	3.82	2.57	

^a Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.

spectra of compounds I' and I'' in DMSO-*d*₆. An upfield shift of the protons on the outer benzene ring was observed after the cyano group was converted to the carboxyl group. In the ¹³C-NMR spectra, the most relevant change on passage from the tetranitrile to the tetracarboxylic acid was the disappearance of the resonance peaks for the cyano carbons at 115–116 ppm and the appearance of the carbonyl peaks at 167–169 ppm. Other important evidence of this change was the shifting of the resonance signals of the carbons adjacent to the cyano or carboxyl groups. The carbons C¹, C^{1'}, C², and C^{2'} of tetranitrile I' resonated at a higher field than other aromatic carbons because of the anisotropic shielding by the π electrons of the cyano group. After hydrolysis, the resonance peaks of these carbons shifted to a lower field because of the lack of an anisotropic field. The ¹H-NMR and ¹³C-NMR spectra of the target bis(ether anhydride) I are depicted in Figure 3. These spectra were in good agreement with the proposed structure of I.

A series of PEIs IVa–IVi were synthesized by a conventional two-step procedure in which PAAs were first prepared by the ring-opening polyaddition of bis(ether anhydride) I with various aromatic ether-diamines (IIIa–IIIi) in DMAc, followed by the thermal imidization of PAA (Scheme 2). As shown in Table I, the PAA inherent viscosity ranged from 0.71 to 1.19 dL/g. Tough and flexible PEI films were obtained by the casting of the PAA solution onto glass substrate followed by a thermal curing process at elevated temperatures.

The chemical structures of the polymers were confirmed by FTIR, NMR, and elemental analysis. All of

the PEIs showed characteristic imide absorption bands around 1780 and 1720 cm⁻¹ (imide carbonyl asymmetrical and symmetrical stretching), 1380 cm⁻¹ (C–N stretching), and 1050 and 750 cm⁻¹ (imide ring deformation), together with the C–O

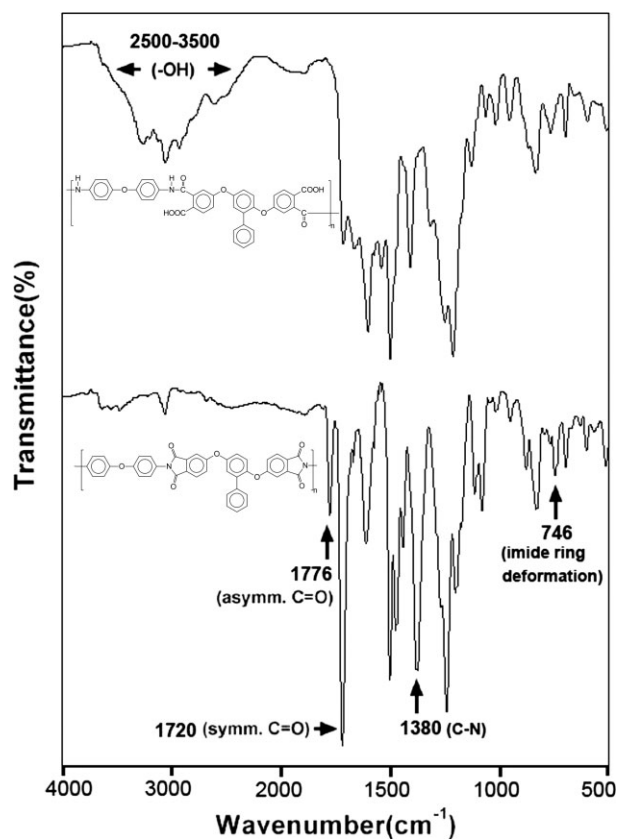


Figure 4 FTIR spectra of PAA IIIa and PEI IVa.

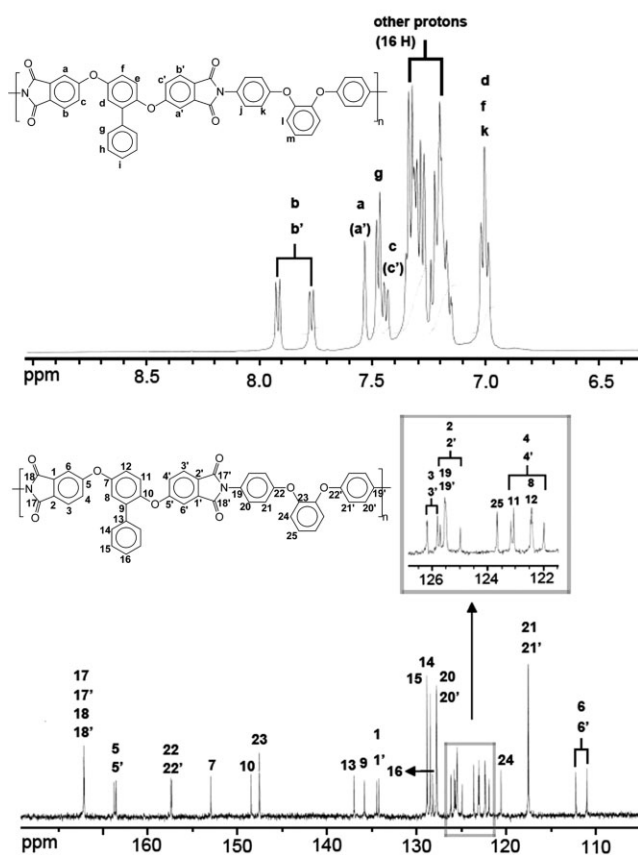


Figure 5 ^1H and ^{13}C -NMR spectra of PEI IVd in CDCl_3 .

stretching absorption around 1240 cm^{-1} (Fig. 4). The ^1H -NMR and ^{13}C -NMR spectra of the representative PEI IVd are reproduced in Figure 5. Assignments of each carbon and proton were assisted by the two-dimensional NMR spectra, and these spectra were in good agreement with the proposed molecular structures. In addition to the IR and NMR spectra, the elemental analysis results of PEIs also generally

TABLE III
Tensile Properties of the PEI Films

Polymer code	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
IVa	126	12	2.3
IVb	116	13	2.2
IVc	110	9	2.3
IVd	119	9	2.3
IVe	114	11	2.2
IVf	117	13	2.2
IVg	105	9	2.3
IVh	106	11	2.3
IVi	120	10	2.3

agreed with the calculated values for the proposed structures.

Properties of the PEIs

The solubilities of the PEIs synthesized in this study were determined for the film samples in excess solvents, and the results are listed in Table II. Almost all of the polymers were soluble in dipolar solvents, such as *N*-methyl-2-pyrrolidone (NMP), DMAc, DMF, and DMSO, at room temperature or upon heating. They also showed moderate solubilities in *m*-cresol and pyridine. The PEIs IVd, IVg, and IVh, derived from ortho-substituted phenylene ether-diamine and long-chain ether-diamines bearing flexible linkages, revealed higher solubilities; they were soluble in most of the tested solvents, including low-boiling dichloromethane and chloroform. In general, these PEIs displayed an increased solubility in comparison with conventional aromatic polyimides. This was attributable in part to the unsymmetrical, packing-disruptive structure of the bis(ether anhydride) component, which resulted in a high steric hindrance for close chain packing and, thus, reduced interchain interactions.

TABLE II
Solubility Properties of the PEIs^a

Polymer code	Solvent									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH_2Cl_2	CHCl_3
IVa	+h	+h	+h	+h	+h	+h	–	–	–	–
IVb	+h	+h	+h	+h	+h	+h	–	–	–	–
IVc	+h	+h	+h	+h	+h	+	–	–	–	–
IVd	+	+	+	+h	+	+	+	–	+	+
IVe	+	+	+h	+h	+h	+h	–	–	–	+
IVf	+	+	+h	+h	+h	+h	+	–	+	+
IVg	+	+	+	+h	+	+	+	–	+	+
IVh	+	+	+	+h	+	+	+	+	+	+
IVi	+h	+	–	+h	+	+	+	–	+	+

+ = soluble at room temperature; +h = soluble on heating at 80°C ; – = insoluble; Py = pyridine; THF = tetrahydrofuran.

^a The qualitative solubility was tested with 10 mg of sample in 1 mL of stirred solvent.

TABLE IV
Color Coordinates and λ_0 's of the Polymer Films

Polymer code	Film thickness (μm)	Color coordinate ^a			λ_0 (nm) ^b
		b^*	a^*	L^*	
Blank	—	1.0	-0.4	96.2	—
IVa	32	15.7	-3.2	93.0	381.5
IVb	44	15.5	-3.5	93.4	381.0
IVc	36	15.8	-2.2	91.8	382.0
IVd	44	19.9	-1.5	89.3	385.0
IVe	40	14.8	-3.2	92.9	380.0
IVf	40	16.9	-3.6	92.9	382.5
IVg	48	17.0	-2.5	91.6	383.5
IVh	42	10.5	-2.1	94.0	377.5
IVi	40	13.7	-3.0	93.7	378.0
PMDA/ODA (Kapton)	41	83.8	5.0	88.1	444.0

^a The color parameters were calculated according to a CIE LAB equation. L^* is the lightness, where 100 means white and 0 implies black. A positive a^* means a red color, and a negative a^* indicates a green color. A positive b^* means a yellow color, and a negative b^* implies a blue color.

^b Absorption edge from the UV-vis spectra of the polymer thin films.

All of the PEIs afforded good-quality films. The tensile properties of these films are summarized in Table III. These polymer films showed similar types of behavior with respect to the elastic deformation range at small strains. They showed tensile strengths of 105–126 MPa, elongations at break of 9–13%, and initial moduli around 2.2–2.3 GPa. All of these PEI films possessed good tensile properties, which indicated that they were strong materials.

The color intensities of the polymers were elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. The results shown in Table IV indicate that all the PEIs exhibited a low b^* value (a yellowness index) of 10.5–19.9. In addition, thin films were measured for optical transparency with UV-vis spectroscopy. Figure 6 depicts the UV-vis spectra of two representative PEI films, IVa and IVb. The cutoff wavelengths

(λ_0 's; absorption edge) from the UV-vis spectra of all PEIs are listed in Table IV. For comparison, the color coordinates and λ_0 values of a standard polyimide film (Kapton) from pyromellitic dianhydride (PMDA) and ODA (IIa) are also included in Table IV. All of the PEI films exhibited λ_0 's shorter than 400 nm and were entirely transparent and essentially colorless. The low color of these PEIs could be explained by the decreased intermolecular electronic interactions. The asymmetry and the bulky pendent phenyl group in the bis(ether anhydride) component were effective in decreasing CT complexing between the polymer chains through a steric hindrance effect.

DSC and TGA were used to evaluate the thermal properties of the PEIs. The thermal properties of all of the polymers are summarized in Table V. DSC experiments were carried out at a heating rate of 20°C/min in nitrogen. Rapid cooling from 400°C to

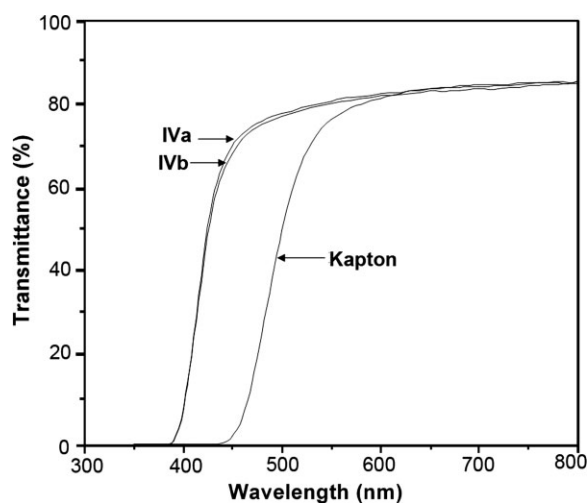


Figure 6 UV-vis spectra of the IVa, IVb, and Kapton films.

TABLE V
Thermal Properties of the PEIs

Polymer	T_g (°C) ^a	T_{10} (°C) ^b		Char yield (%) ^c
		In N ₂	In air	
IVa	237	498	496	53
IVb	222	504	497	52
IVc	206	502	502	51
IVd	207	500	480	51
IVe	233	511	507	58
IVf	262	478	480	64
IVg	215	505	504	50
IVh	220	518	507	58
IVi	262	519	512	59

^a Baseline shift in the second-heating DSC traces with a heating rate of 20°C/min.

^b Recorded by TG at a heating rate of 20°C/min.

^c Residual weight (%) when the sample was heated to 800°C in nitrogen.

TABLE VI
Water Absorption and Dielectric Constants of the PEIs

Polymer	Film thickness (μm)	Water absorption (%)	Dielectric constant			
			1 kHz	10 kHz	1 MHz	40 MHz
IVa	25	0.50	3.86	3.82	3.72	3.71
IVb	32	0.58	3.63	3.61	3.55	3.57
IVc	34	0.67	3.84	3.81	3.70	3.71
IVd	63	0.85	3.72	3.63	3.55	3.61
IVe	42	0.58	3.72	3.63	3.56	3.60
IVf	28	0.40	3.60	3.58	3.54	3.56
IVg	34	0.41	3.72	3.68	3.62	3.65
IVh	19	0.38	3.44	3.44	3.39	3.37
IVi	28	0.40	3.58	3.52	3.48	3.51
PMDA/ODA	28	0.52	3.89	3.85	3.67	3.69

room temperature produced predominantly amorphous samples, so the glass-transition temperatures (T_g 's) of all the polymers were easily read in the subsequent heating traces. The IV series PEIs revealed T_g values in the range 206–262°C. Compared to conventional aromatic polyimides, these PEIs showed decreased T_g values because of the flexible ether linkages and the less symmetrical repeating unit. In comparison, polymers IVc and IVd displayed lower T_g values than the other PEIs because of their more flexible backbones, which arose from the meta- and ortho-substituted phenylenedioxy segments. PEI IVi had a high T_g of 262°C because of the presence of the rigid fluorene unit. PEI IVf also showed a high T_g value similar to that of IVi, which could be explained by the increase in chain stiffness caused by the tetramethyl substitution ortho to the ether linkages in the diamine moiety.

The thermal stability was measured by TGA in both air and nitrogen atmospheres. The decomposition temperatures at 10% weight loss (T_{10} 's) in nitrogen and air atmospheres determined from the original TGA thermograms are given in Table V. The T_{10} values of these PEIs stayed in the range 478–519°C in nitrogen and 480–512°C in air. They left 50–64% char yield at 800°C in nitrogen. It is quite reasonable that the methyl-substituted PEI IVf began to decompose at lower temperatures compared to the corresponding methyl-free IVe and the other PEIs.

The dielectric constants and water absorption values of the PEIs are listed in Table VI. The measurements of the dielectric constants were performed between gold layers: the polyimide film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the polymer film. The PEI films showed dielectric constants in the range 3.39–3.72 (at 1 MHz), which was slightly lower than or comparable to the PMDA/ODA polyimide. The PEI films showed low water absorptions of 0.38–0.85%. The low water absorptions ensured that these PEIs had stable dielectric performances.

CONCLUSIONS

A series of PEIs were synthesized from I and various aromatic ether-diamines. These PEIs afforded virtually colorless and tough films. They also exhibited moderately high T_g 's and good thermal stabilities, together with low dielectric constants. Thus, these PEIs demonstrated a good combination of properties and may be of interest for microelectronic and optoelectronic applications.

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