Novel Soluble Fluorinated Poly(ether imide)s with Different Pendant Groups: Synthesis, Thermal, Dielectric, and Optical Properties

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Received 5 January 2010; accepted 29 April 2010
DOI: 10.1002/pola.24111

ABSTRACT: Three types of new bis(ether dianhydride) monomers, [4,4′-(2-(3′-methylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4a)], [4,4′-(2-(3′-trifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4b)], and [4,4′-(2-(3′,5′-ditrifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4c)] were prepared via a multistep reaction sequence. Three series of soluble poly(ether imide)s (PEIs) were prepared from the obtained dianhydrides by a two-step chemical imidization method. Experimental results indicated that all the PEIs had glass transition temperature in the range of 200–230 °C and the temperature of 5% weight loss in the range of 520–590 °C under nitrogen. The PEIs showed excellent solubility in a variety of organic solvents due to introduction of the bulky pendant groups and were capable of forming tough films. The casting films of PEIs (80–91 μm in thickness) had tensile strengths in the range from 88 to 117 MPa, tensile modulus from 2.14 to 2.47 GPa, and elongation at break from 15 to 27%. The casting films showed UV-Vis absorption edges at 357–377 nm, low dielectric constants of 2.73–2.82, and water uptakes lower than 0.66 wt %. The spin-coated films of PEIs presented a minimum birefringence value as low as 0.0122 at 650 nm and low optical absorption at the optical communication wavelengths of 1310 and 1550 nm. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3281–3289, 2010

KEYWORDS: dielectric properties; fluoropolymers; optics; polyimides; synthesis

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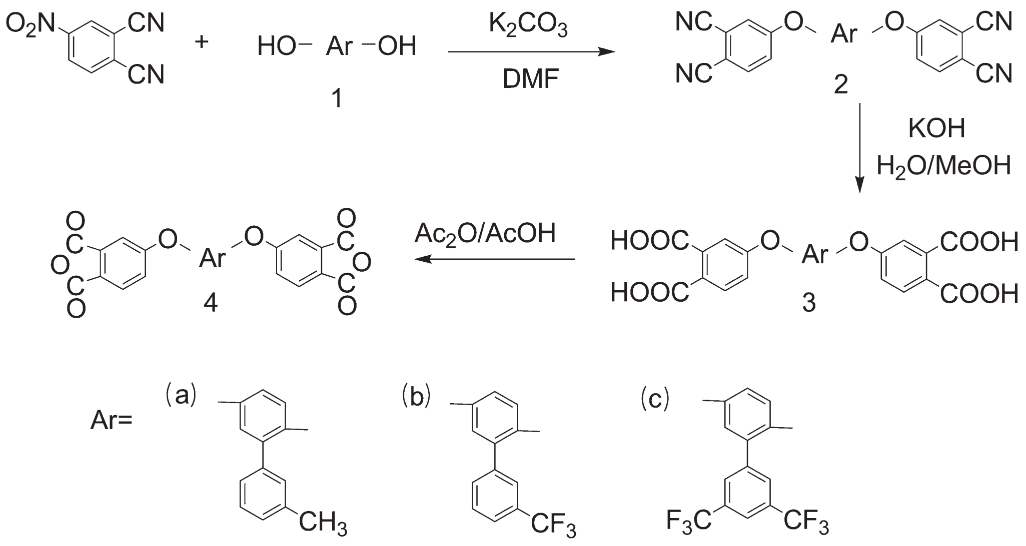
INTRODUCTION Aromatic polyimides (PI) are well known high performance materials because of their excellent thermal stability, mechanical, electric, and optical properties.[1–3] High optical transparency is one of the most attractive properties of polyimides materials for a variety of applications such as optical waveguides.[4,5] However, most of the conventional aromatic polyimide films show considerable coloration from light yellow to dark brown due to their highly conjugated aromatic structures, the formation of intermolecular charge-transfer complexes and electronic polarization interactions. In addition, the aromatic polyimides are difficult to be processed because of their poor solubility and high processing temperature, which are caused by their rigid polymer backbones and strong interchain interaction.[6,7]

The development of soluble polyimides with high optical transparency has been to attract major interesting in the research of aromatic polymers. Fortunately, considerable efforts have got good progresses on the processing ability and solubility of polyimides on the basis of structure design and modification of aromatic dianhydride and diamine monomers. Introducing noncoplanar moiety into the backbone of the polyimides, contributed either by the dianhydrides or from the diamines, has been proven to be a successful approach to attain the solubility without sacrificing their excellent properties.[8–12] Moreover, it is an effective method to improve high optical transparency through introducing trifluoromethyl into polyimides. It has been demonstrated that the introduction of bulky trifluoromethyl group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lower dielectric constant, attributed to low polarizability of the C—F bond and the increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability, and low moisture absorption. In addition, the introduction of bulky trifluoromethyl moieties into the polymers could decrease the refractive index and the birefringence effectively.[13–17]

At present, most dissoluble aromatic polyimides containing fluorine were prepared by using different kinds of aromatic diamine containing fluorine rather than fluorinated aromatic dianhydrides, except for 6FDA, which is currently commercial available.[18–21] However, the widespread applications and commercialization for 6FDA are also hampered by the difficulty in handling of poisonous gaseous chemicals in the synthetic procedure. As part of our continuing efforts to gain colorless and soluble polyimides with high thermal stability and wide application potentials in optoelectronics, three novel bis(ether dianhydride)s, bis(ether dianhydride)

Additional Supporting Information may be found in the online version of this article. Correspondence to: Z. Jiang (E-mail: jiangzhenhua@jlu.edu.cn)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 3281–3289 (2010) © 2010 Wiley Periodicals, Inc.



SCHEME 1 Synthetic route of bis(ether anhydride) monomers.

[4,4′-(2-(3′-methylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4a)], [4,4′-(2-(3′-trifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4b)], and [4,4′-(2-(3′,5′-ditrifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (4c)] were designed and synthesized. Three series of soluble poly(ether imide)s (PEIs) (4aI–4aIII, 4bI–4bIII, and 4cI–4cIII) were prepared by polycondensation of the monomers with various aromatic diamines. This study deals with the synthesis and basic characterization of the PEIs on the basis of bis(ether anhydride)s derived from hydroquinone and its methylphenyl, trifluoromethylphenyl, and ditrifluoromethylphenyl pendant derivatives. The effect of methylphenyl, trifluoromethyl, and ditrifluoromethyl groups on solubility, thermal properties, mechanical properties, dielectric constant, and optical properties of the PEIs were investigated. It was characterized that the prepared PEIs exhibited good solubility, excellent thermal, and mechanical properties, low water uptake, low dielectric constant, high optical transparency, and low optical absorption in the optical communication wavelengths.

EXPERIMENTAL

Materials

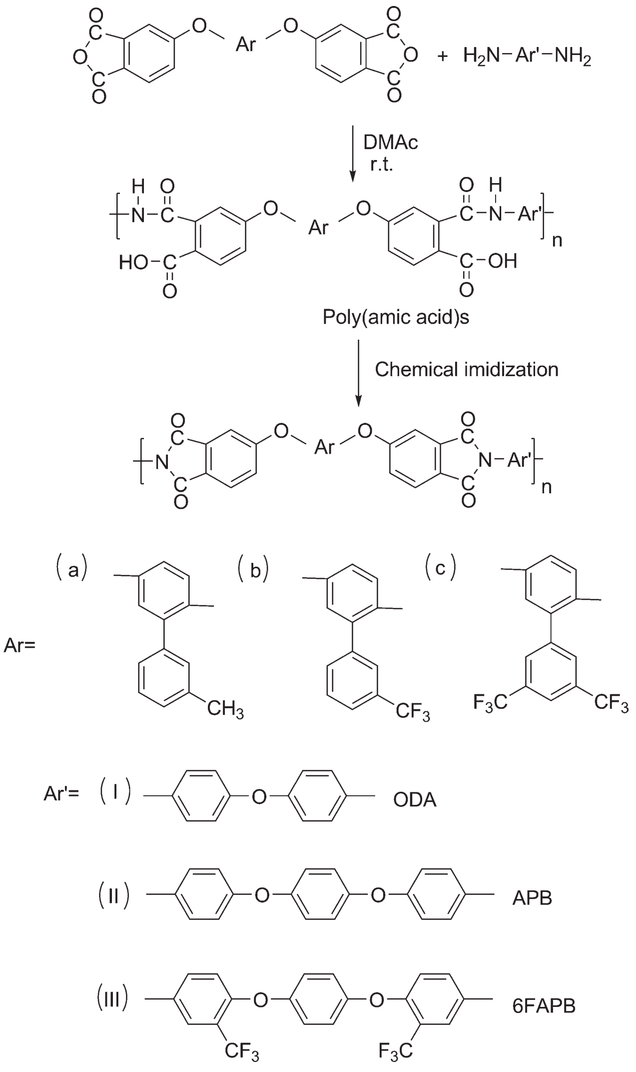
All the reagents were purchased from commercial sources and were used as received. The (3-methylphenyl)-1,4-hydroquinone, (3-fluoromethylphenyl)-1,4-hydroquinone, and (3,5-difluoromethylphenyl)-1,4-hydroquinone were synthesized according to the literature.[22] 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene (6FAPB) was synthesized in our laboratory according to the literature.[10] 4,4′-oxydianiline (ODA) (TCI) and 1,4-bis(4-aminophenoxy) benzene (APB) (TCI) were used without further purification.

Measurements

IR spectra (KBr) were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded on a Bruker 510 NMR spectrometer (500 MHz) with tetramethyl silane as a reference. Elemental analysis was performed on an Elemental Analyses MOD-1106. Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with tetrahydrofuran (DMF) as an eluent at a flow rate of 1 mL/min using polystyrene as a standard. Inherent viscosity was determined on an Ubblohde viscometer in thermostatic container with the polymer concentration of 0.5 g/dL in DMAc at 25 °C. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821^e instrument at a heating rate of 20 °C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C/min and polymers were contained within open aluminum pans on a PerkinElmer TGA-7. The birefringences of the polymer films at 650 nm were determined from coupling angles of TE (transverse electric) of TM (transverse magnetic) optical guided modes with a gadolinium gallium garnet (GGG) prism. UV-visible transparency was measured by a Shimadzu UV 2501-PC spectrophotometer. Wide-angle X-ray diffraction (WAXD) measurements were made at room temperature using a Rigaku/max-rA diffractometer equipped with a Cu Kα radiation source. The mechanical tests in tension were carried out using a Shimadzu AG-I at a constant crosshead speed of 10 mm/min. The ε at 1.0 MHz frequency was calculated from the equation as follows: $\varepsilon = 1.10n_{AV}^2$, where n_{AV} is average refractive index (i.e. $n_{AV} = (2n_{TE} + n_{TM})/3$). The equilibrium moisture absorption was determined by weighing the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

Monomer Synthesis

The monomers, 4a–4c were synthesized by the nitrodisplacement reaction of 4-nitrophthalodinitrile with 1a–1c in *N*,*N*-dimethylformamide (DMF) in presence of potassium carbonate as the base, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile)s and cyclodehydration of the resulting bis(ether diacid)s.[23] The synthetic procedure is shown in Scheme 1 and the elemental analysis, IR, and ^1H NMR data of the target bis(ether anhydride)s are given in Supporting Information.



SCHEME 2 Synthetic procedures of PEIs.

Polymer Synthesis

PEIs were synthesized by polycondensation of dianhydride monomers 4a, 4b, and 4c with diamine monomers ODA (I), APB (II), and 6FAPB (III). The resulting PEIs were abbreviated as 4aI–4aIII, 4bI–4bIII, and 4cI–4cIII, respectively (Scheme 2).

In a typical experiment, PEI-4aI, which was derived from dianhydride 4a and ODA (I), was prepared as follows: dianhydride 4a (0.9848 g, 2 mmol) was dissolved in 10 mL of DMAc. To this diamine solution, ODA (0.4005 g, 2 mmol) and an additional 4 mL of DMAc were added. The mixture was stirred for 24 h at room temperature under nitrogen to yield a viscous poly(amic acid) (PAA) solution with 10 wt % solid content. Chemical imidization was carried out via the addition of 2 mL of an acetic anhydride/pyridine (5/4 v/v) mixture into the PAA solution (with mechanical stirring) at ambient temperature. The mixture was stirred at 60 °C for 4 h to yield a polyimide solution, which was poured into methanol to give a precipitate, 4aI was collected by filtration, washed thoroughly with methanol, and dried at 80 °C in vacuum. Other PEIs were synthesized in an analogous procedure.

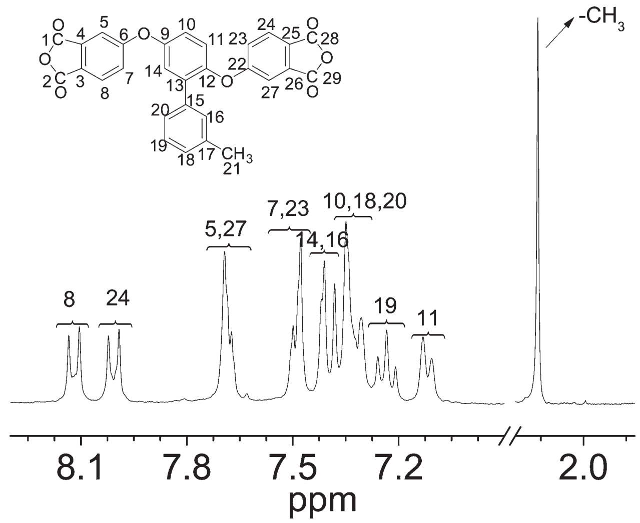


FIGURE 1 ^{1}H NMR spectrum of bis(ether anhydride) 4a in DMSO-d6.

Characterization of the Polymers

PEI-4cI: IR (KBr, cm^{-1}): 1780 and 1721 (asymmetric, symmetric imide C=O stretch), 1619–1480 (aromatic C=C stretch), 1382 (C—N stretch), 1100–1300 (C—O and C—F stretching). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.26 (2H), 8.06 (1H), 8.00 (1H), 7.90 (2H), 7.87 (1H), 7.69 (3H), 7.56 (2H), 7.47 (1H), 7.43 (1H), 7.37 (2H), 7.23 (4H), 7.19 (2H). The elemental analysis (Table S1), IR and ^{1}H NMR data of 4aI and 4bI are listed in Supporting Information.

RESULTS AND DISCUSSION

Monomer Synthesis

The bis(ether dinitrile)s 4a, 4b, and 4c were prepared by a three-step reaction sequence, shown in Scheme 1. First, the intermediate bis(ether dinitrile)s were obtained from the

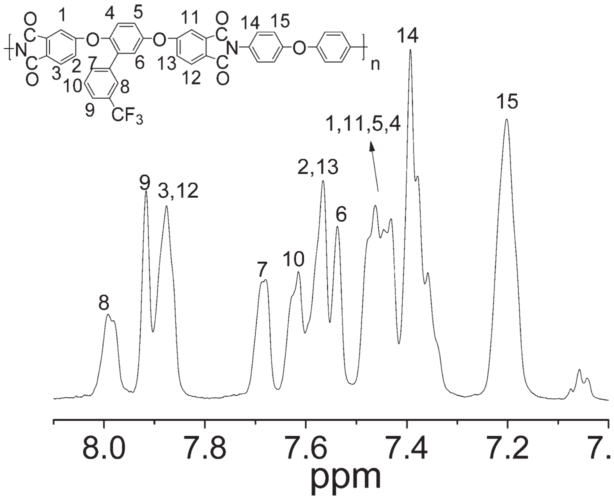


FIGURE 2 ^{1}H NMR spectrum of PEI-4bI in DMSO-d6.

TABLE 1 Inherent Viscosity, GPC Data, and Thermal Properties of the PEIs

Polymer	Inherent Viscosity	GPC Data		DSC	TGA		
	η_{inh}(dL/g)[a]	M_w[b] × 10^4	M_w/M_n[b]	T_g[c] (°C)	$T_{5\%}$[d] (°C)	$T_{10\%}$[d] (°C)	Char Yield[e] (%)
4aI	0.84	13.5	1.7	230	531	551	57
4aII	0.86	16.2	1.6	211	520	544	58
4aIII	0.82	13.5	1.9	208	536	574	61
4bI	0.65	7.1	1.4	216	590	604	62
4bII	0.71	7.8	1.4	203	575	597	60
4bIII	0.67	8.1	1.5	200	585	603	67
4cI	0.73	13.2	1.4	226	578	602	47
4cII	0.85	17.2	1.6	220	578	602	57
4cIII	0.75	9.3	1.5	218	576	598	50

[a] Determined with 0.5% solutions in a solvent (DMAc) at 25 °C.

[b] Relative to polystyrene standard, using DMF as the eluent.

[c] Baseline shift in the second heating DSC traces, with a heating rate of 20 °C/min in nitrogen.

[d] Temperature at 5 and 10% weight loss were recorded by TGA at a heating at 10 °C/min in nitrogen.

[e] Residual weight (%) when heated to 800 °C.

nucleophilic nitrodisplacement of 4-nitrophthalonitrile with the phenoxide ions of hydroquinones in DMF. The purified bis(ether diacid)s by ethanolic potassium hydroxide, and then the generated bis(ether diacid)s were cyclodehydrated to yield the final bis(ether dianhydride)s. The structures of the bis(ether anhydride)s products were confirmed by elemental analysis, IR, and NMR spectra.

The cyano group (—CN) of bis(ether dinitrile) 2a was evident from the peak at 2233 cm^{-1} in the IR spectra (Supporting Information, Figure S1). In the IR spectra of bis(ether diacid) 3a, the cyano stretching vibration was absent, but a broad O—H absorption appeared in the region between 2500 and 3500 cm^{-1} and carbonyl stretching absorption around 1700 cm^{-1}. The IR spectra of the bis(ether anhydride) 4a shows characteristic cyclic anhydride absorption at 1854 and 1773 cm^{-1}, suggesting the asymmetric and symmetric stretching vibrations of C=O. Figure 1 shows the ^1H NMR spectra of bis(ether anhydride) 4a, in which the proton ortho-positioned at C=O groups (H_8) appeared in the downfield of the spectra (8.14 ppm) owing to the strong electron-withdrawing effect of the C=O group, the methyl group appeared in 2.27 ppm (Fig. 1). In ^{13}C NMR spectra, the carbonyl carbon atoms (C_1, C_2, C_{28}, C_{29}) appeared in the downfield of the spectrum and the methyl carbon atom (C_{21}) appeared in the upfield. (Supporting Information, Figure S2)

Synthesis and Characterization of Polymers

The three types bis(ether anhydride)s 4a, 4b, and 4c were reacted with different diamine I–III with a conventional two-step procedure of ring-opening polyaddition at room temperature to form PAA and sequential chemical imidization by adding mixture of acetic anhydride and pyridine (volume ratio 5:4) into PAA solution at ambient temperature for 30 min followed by heating at 60 °C for 4 h to give poly(ether

TABLE 2 Solubility of the PEIs in Organic Solvents

Polymer	Solvents[a]								
	NMP	DMAc	DMF	DMSO	THF	Py	$CHCl_3$	Actone	Ethanol
4aI	++	++	+	++	+	++	++	−	−
4aII	++	++	+	++	+	++	++	−	−
4aIII	++	++	++	++	++	++	++	+	−
4bI	++	++	+	++	+	++	++	−	−
4bII	++	++	++	++	+	++	++	−	−
4bIII	++	++	++	++	++	++	++	+	−
4cI	++	++	++	++	+	++	++	+	−
4cII	++	++	++	++	++	++	++	+	
4cIII	++	++	++	++	++	++	++	++	−

Qualitative solubility was determined with as 10 mg of polymer in 1 mL of solvent. ++: soluble at room temperature; +: soluble on heating at 100 °C.

[a] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

TABLE 3 Mechanical Properties of the PEIs

Polymers	Film Thickness (μm)	Tensile Strength (MPa)	Elongation at Break (%)	Youngs' Modulus (GPa)
4aI	91	113	20	2.40
4aII	85	93	25	2.21
4aIII	80	89	27	2.19
4bI	90	117	18	2.47
4bII	85	92	22	2.18
4bIII	87	90	22	2.16
4cI	87	107	15	2.34
4cII	85	88	27	2.15
4cIII	89	92	20	2.14

imide)s 4aI–4aIII, 4bI–4bIII, and 4cI–4cIII as displayed in Scheme 2.

The structures of the PEIs were characterized by FTIR and ^{1}H NMR spectra. The FTIR spectrum of PEI-4aI exhibited characteristic imide carbonyl asymmetrical and symmetrical stretches at 1788 and 1727 cm^{-1} and the peak of amide carbonyl at 1650 cm^{-1} disappeared, indicating the complete imidization during polycondensation. In ^{1}H NMR spectrum of soluble PEI-4bI, all protons resonated in the region of 7.1–8.0 ppm (Fig. 2). The signal of H$_8$ in the ortho-positioned at —CF$_3$ group appeared at the farthest downfield region of the spectrum because of the strong electron–withdrawing effect of the —CF$_3$ group. The resonance of H$_{15}$ shifted to a higher field because of the electron-donating effect of aromatic ether. The above results demonstrated that the bis(ether anhydride) held a good polymerization activity to form PEIs. Meanwhile, complete chemical imidization could be achieved at lower temperatures than those for thermal imidization, which should be profitable to get soluble polyimide. It is characterized that the molecular weights (M_w) of the resulting PEIs were in the range of 71,000–162,000 with the M_w/M_n values of 1.4–1.9 and the intrinsic viscosities of the PEIs were in the range of 0.65–0.86 g/dL (Table 1).

Solubility of the Polyimides

The solubility of synthesized PEIs was tested in a variety of organic solvents at 1.0% (w/v) and the results are summarized in Table 2. All the PEIs showed excellent solubility in aprotic polar solvents such as DMSO, DMAc, DMF, and NMP and were also soluble in less polar solvents such as pyridine and THF at room temperature. Some of them were even soluble in acetone. The improved solubility is attributed to the introduction of bulky pendant methylphenyl, trifluoromethylphenyl, and ditrifluoromethylphenyl groups which could inhibit close packing and reduce the interchain interactions (Supporting Information, Fig. S3).

The fluorinated PEIs 4aIII, 4bIII, and 4cIII exhibited better solubility than the PEIs derived from unfluorinated aromatic diamines. PEI-4cIII even exhibited excellent solubility in acetone. The good solubility of PEI-4cIII was attributed to the high fluorine content in the polymer backbone, in which four CF$_3$ groups were attached to each polymer unit. It should be noted that the good solubility of the PEIs in low boiling point solvents is beneficial to prepare the polymer films at relative low processing temperatures, which is desirable feature for advanced microelectronics manufacturing applications.

Thermal Properties of the Polyimides

The thermal behavior data of all the PEIs are also listed in Table 1. Generally, the decreasing order of T_g correlated with both molecular packing and chain conformation (chain rigidity and linearity) of the polymers. The T_g values of series 4a, 4b, and 4c were, respectively, in the ranges of 208–230, 200–216, and 218–226 °C, which increased in the order of ODA > APB > 6FAPB. As we expected, the T_g values of these PEIs depended on the structures of the diamine components employed and decreased with increasing flexibility of the PEI

TABLE 4 Optical Properties and Dielectric Constants of the PEIs

Polymer	Refractive Index							
	n_{TE}[a]	n_{TM}[b]	n_{AV}[c]	Δn[d]	λ_0 (nm)	UV-Transmittance[e] (%)	ε_{opt}[f]	Water Uptake (%)
4aI	1.6028	1.5853	1.5970	0.0175	377	88	2.81	0.66
4aII	1.6053	1.5900	1.6002	0.0153	373	87	2.82	0.55
4aIII	1.5995	1.5848	1.5946	0.0147	369	89	2.80	0.38
4bI	1.5925	1.5763	1.5871	0.0162	372	89	2.77	0.64
4bII	1.5992	1.5821	1.5935	0.0171	369	87	2.79	0.53
4bIII	1.5898	1.5759	1.5852	0.0139	362	88	2.76	0.35
4cI	1.5838	1.5674	1.5792	0.0164	366	87	2.74	0.51
4cII	1.5908	1.5758	1.5851	0.0150	365	87	2.76	0.42
4cIII	1.5796	1.5674	1.5755	0.0122	357	88	2.73	0.23

[a] In-plane refractive index at 650 nm: n_{TE}.

[b] Out-of-plane refractive index at 650 nm: n_{TM}.

[c] Average refractive index: $n_{AV} = (2n_{TE} + n_{TM})/3$.

[d] Birefringence $\Delta n = n_{TE} - n_{TM}$.

[e] UV-transmittance at 800 nm (%).

[f] Dielectric constant estimated from the refractive index at 650 nm: $\varepsilon_{opt} = 1.10\, n^2_{AV}$.

backbones. 4aIII, 4bIII, and 4cIII, derived from 6FAPB exhibited low T_g because of the presence of two flexible ether units and two CF3 groups. In comparison with the analogous nonfluorinated PEIs, fluorinated PEI exhibited a lower T_g as a result of reduced interchain interactions and poor chain packing due to the bulky pendant CF3 groups.[24] Here, the PEIs series 4b exhibited lower T_g values than the PEIs series 4a, 4c. The phenomenon is possibly attributed to the different molecular packing density of the PEIs with different phenyl pendants. A possible explanation for the lower T_g values of 4b PEIs is that the substitution of methyl with trifluoromethyl or ditrifluoromethyl group would lead to an internal plasticization in addition to the geometry and free volume factors.[22,25]

Thermal stabilities of the PEIs were evaluated by TGA (Table 1). All the PEIs had excellent thermal stability, and no obvious decomposition was observed below 500 °C. Film samples of polyimides underwent 5% weight losses at 520–590 °C under nitrogen when subjected to TGA with a heating rate of 10 °C/min. Series 4b, 4c possessed higher decomposition temperatures than that of Series 4a. This result was attributed to the presence of stronger C—F bonds with higher stability than C—H under nitrogen. Their char yield at 800 °C in nitrogen was in the range of 47–67 wt %. The TGA data indicated that these PEIs had fairly high thermal stability regardless of the introduction of the pendant groups.

Mechanical Properties of the Polyimides

The mechanical properties of PEI films are summarized in Table 3. The PEI films have tensile strength of 88–117 MPa, tensile modulus of 2.14–2.47 GPa, and elongation at breakage of 15–27%. The tensile modulus of the PEIs enhanced with increasing in the imide concentration accompanied polymer backbones. PEI–4aI, 4bI, and 4cI, which had the highest imide concentration and the lowest ether concentration, exhibited the highest tensile modulus compared with PEIs from diamine II, III.

Dielectric Constants of the Polyimides

The dielectric constants for the PEI thin films were evaluated by optical method (2.73–2.82), as listed in Table 4. The dielectric constant (ε_{opt}) of the materials at optical frequencies could be estimated from the refractive index (n_{AV}) according to Maxwell's equation, $\varepsilon_{opt} \approx n^2$. The ε_{opt} at around 1 MHz is evaluated to be $\varepsilon_{opt} \approx 1.1n^2$, including an additional contribution of approximately 10% from the IR absorption.[26–28] The estimated values are lower than Kapton films (ξ_{cap} = 3.5 at 1 kHz) and Ultem (ξ_{cap}= 3.15 at 1 kHz).[29,30] The low dielectric constants were attributed to the bulky pendant groups, which has low polarizability and large free volume of the polymer.

Considering the type of dianhydride backbone, the dielectric constant form lists in the following order: 4a > 4b > 4c. The decreased dielectric constants could be explained by the attribution of the bulky ditrifluoromethyl phenyl pendant groups, which has lower polarizability and larger free volume of the polymer chain than trifluoromethyl phenyl

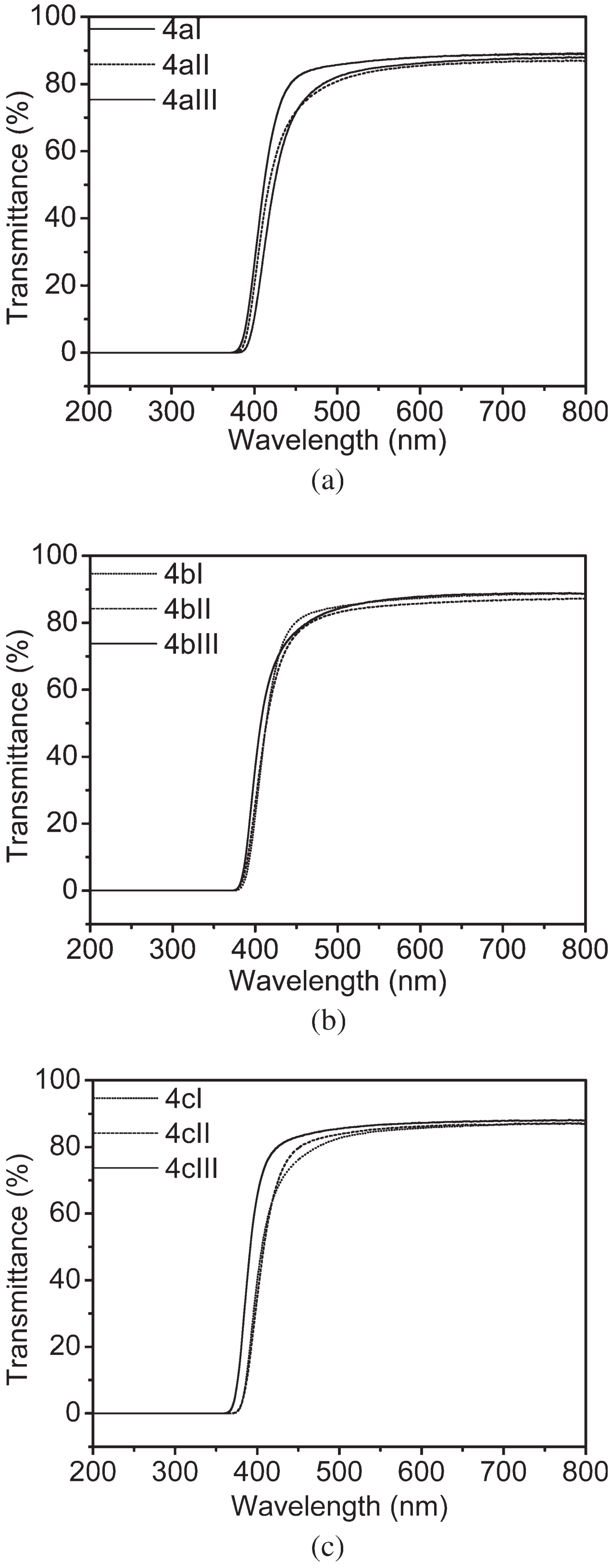
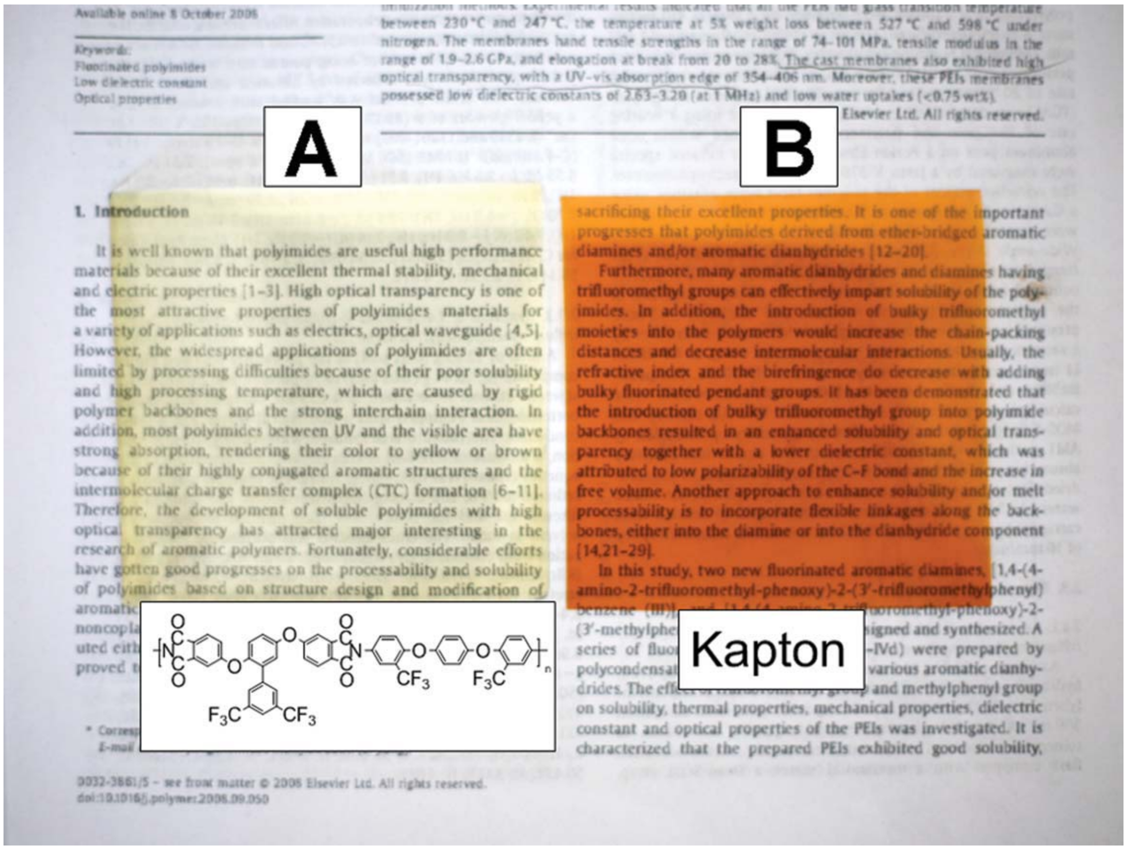


FIGURE 3 UV-Visible spectra of the PEI films.



Available online 8 October 2006

Keywords:
Fluorinated polyimides
Low dielectric constant
Optical properties

1. Introduction

It is well known that polyimides are useful high performance materials because of their excellent thermal stability, mechanical and electric properties [1–3]. High optical transparency is one of the most attractive properties of polyimides materials for a variety of applications such as electrics, optical waveguide [4,5]. However, the widespread applications of polyimides are often limited by processing difficulties because of their poor solubility and high processing temperature, which are caused by rigid polymer backbones and the strong interchain interaction. In addition, most polyimides between UV and the visible area have strong absorption, rendering their color to yellow or brown because of their highly conjugated aromatic structures and the intermolecular charge transfer complex (CTC) formation [6–11]. Therefore, the development of soluble polyimides with high optical transparency has attracted major interesting in the research of aromatic polymers. Fortunately, considerable efforts have gotten good progresses on the processability and solubility of polyimides based on structure design and modification of aromatic
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doi:10.1016/j.polymer.2006.09.050

between 230 °C and 247 °C, the temperature at 5% weight loss between 527 °C and 598 °C under nitrogen. The membranes hand tensile strengths in the range of 74–101 MPa, tensile modulus in the range of 1.9–2.6 GPa, and elongation at break from 20 to 28%. The cast membranes also exhibited high optical transparency, with a UV–vis absorption edge of 354–406 nm. Moreover, these PEIs membranes possessed low dielectric constants of 2.63–3.20 (at 1 MHz) and low water uptakes (<0.75 wt%).
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sacrificing their excellent properties. It is one of the important progresses that polyimides derived from ether-bridged aromatic diamines and/or aromatic dianhydrides [12–20].

Furthermore, many aromatic dianhydrides and diamines having trifluoromethyl groups can effectively impart solubility of the polyimides. In addition, the introduction of bulky trifluoromethyl moieties into the polymers would increase the chain-packing distances and decrease intermolecular interactions. Usually, the refractive index and the birefringence do decrease with adding bulky fluorinated pendant groups. It has been demonstrated that the introduction of bulky trifluoromethyl group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lower dielectric constant, which was attributed to low polarizability of the C–F bond and the increase in free volume. Another approach to enhance solubility and/or melt processability is to incorporate flexible linkages along the backbones, either into the diamine or into the dianhydride component [14,21–29].

In this study, two new fluorinated aromatic diamines, [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-trifluoromethylphenyl) benzene (III)], and [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-methylphe
igned and synthesized. A series of fluor
-IVd) were prepared by polycondensat
various aromatic dianhydrides. The effe
and methylphenyl group on solubility, thermal properties, mechanical properties, dielectric constant and optical properties of the PEIs was investigated. It is characterized that the prepared PEIs exhibited good solubility,

FIGURE 4 Photographs of a piece of the PEI-4cIII film (89 μm thick) and a piece of the Kapton film (90 μm thick).

pendant and methyl phenyl pendant groups. PEI having diamine III exhibited lowest dielectric constants because of presence of bulky CF_3 groups. As expected, the fluorinated PEI series 4c exhibited lower water absorptions (0.23–0.51%) than series 4b (0.35–0.64%) and 4a (0.38–0.66%) due to content of two hydrophobic CF_3 groups. The low water absorptions ensure that these polymers have stable dielectric performance.

Optical Properties of the Polyimides

Thin films (pale-yellow, ~90 μm thick) were measured for optical transparency with UV-visible spectroscopy. Figure 3 shows the UV-visible transmittance spectra of the PEI films, the cut-off wavelength (absorption edge, λ_0) values and the percentages transmittance at 800 nm from these spectra are listed in Table 4. All the PEIs had shorter λ_0 than 380 nm, and exhibited high optical transparency of 87–89%. Because of the highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation of PI, most polymers between UV and the visible area had strong absorption. However, these PEIs which had flexible group like ether linkage and CF_3 group with bulky side groups in the center of dianhydride reduced the intermolecular CTC between altermating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The ODA, APB, and 6FAPB produced nearly colorless polyimide films and these could be explained from the decreased intermolecular interactions.[31] Moreover, CF_3 group might weaken chain-to-chain cohesive force due to lower polarizability of the C—F bond. The decrease in intermolecular CTC formation was understandable also from the significant solubility of the PEIs prepared from dianhydrides. All the series 4c revealed shorter λ_0 than their respective series 4b and 4a. A photograph of one piece of the PEI 4cIII is shown in Figure 4(A). For comparison, another photograph of a commercially Kapton film is shown in Figure 4(B) either. The films were photographed against a special background to highlight the transparency. It is easy to find that PEI 4cIII film exhibited much lighter color than Kapton film.

It was reported that the replacement of C—H bonds with C—F bonds gives high optical transparency of the polymeric material in the near-infrared (NIR) telecommunication region.[32] The propagation losses of the fluorinated PEIs series 4b and 4c were measured by the near-infrared (NIR) absorption spectra, and the spectra are shown in the Figure 5. There were C—H bond vibrational absorptiong peaks ($2\nu_{C—H}$ 1650 nm and $3\delta_{C—H}$, 1100 nm) and related peak ($2\nu_{C—H} + \delta_{C—H}$, 1400 nm). However, it had small light absorptions at telecommunication wavelengths of 1310 and 1550 nm due to high fluorine content. Furthermore, the near-infrared absorption of series 4c was weaker than that of series 4b at the key telecommunication wavelengths of 1310 and 1550 nm because of the presence of two —CF_3

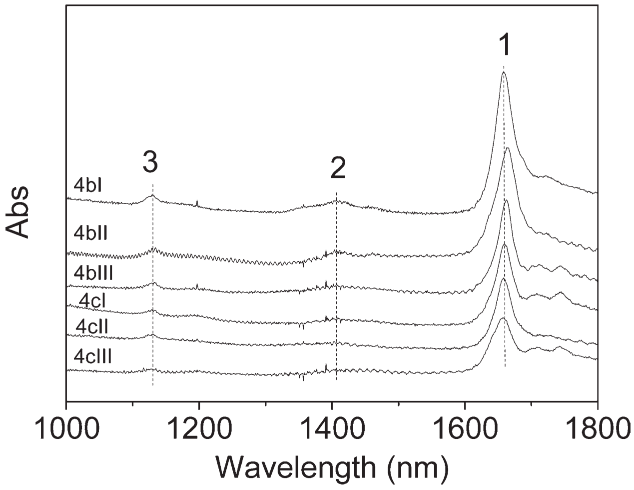

FIGURE 5 Near-IR spectra of the PEIs series 4b and 4c.

groups. The wavelength of 1310 or 1550 nm will be used for optical telecommunication, so these PEIs are expected to be applicable to optoelectronic materials.[33]

The average refractive indices (n_{AV}) estimated from the n_{TE} and n_{TM} values ranged between 1.5764 and 1.5970. PEI-4cIII had the lowest refractive index due to its high fluorine contents. The birefringences ($\Delta n = n_{TE} - n_{TM}$) of the PEIs were in the range of 0.0122–0.0175. The fact that n_{TE} values were slightly higher than the n_{TM} ones for all PEIs films reflects the preferential chain orientation parallel to the film plane. It is well known that the birefringence of polymers can be affected by chain flexibility and geometry of the repeat units.[34,35] The values of Δn were far lower than conventional aromatic PIs.[36] The negligibly small birefringence implied that these polymers with pendant groups had low anisotropy and the polymer chains were randomly oriented in the film.

CONCLUSIONS

Three series of soluble poly(ether imide)s (PEIs) were prepared from the dianhydrides (4a, 4b, and 4c) and diamines by two-step chemical imidization methods, respectively. Because of the presence of pendant groups and aryl ether groups along the polymer backbone of the repeat unit, the obtained PEIs successfully reduced overall charge-transfer complex formation both inter and intramolecular electronic interactions. Thus, the prepared PEIs displayed excellent solubility, fantastic optical property and low dielectric constant. In addition, PEI series 4c also exhibited better stability, higher optical transparency and lower water absorption than series 4a and 4b. As a result, these PEIs, especially for series 4c, may be considered as promising processable high temperature materials for applications in microelectronic and optical devices.

We thank the National Science Foundation of China (Nos. 50773025 and 50803025) for the financial support.

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