Synthesis and Properties of New Poly(ether imides) Based on Pyridine-Containing Aromatic Dianhydride and Diamine Monomers

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ABSTRACT: A series of novel aromatic poly(ether imides) with inherent viscosities of 0.48–0.70 dL/g and weight-average molecular weights of 18,800–40,500 g/mol were successfully prepared from two dianhydride and two diamine monomers containing pyridine moiety via both two-step method and one-step method. Comparison of the one-step and the two-step methods for the preparation of poly(ether imides) was carried out and shown that poly(ether imides) obtained via one-step method exhibited higher molecular weights than the similar polymers prepared through two-step process. Poly(ether imide) resins obtained via both one-step and two-step methods with subsequent chemical dehydration showed good solubility not only in high boiling point solvents but also in low boiling point solvents. High-quality poly(ether imide) films could be obtained via the two-step method with subsequent thermal imidization, which exhibited excellent thermal properties with glass transition temperatures of 239–278°C, initial decomposition temperatures of 540–574°C, residual weight percent at 800°C of 64.5–69.3% under nitrogen, good thermo-oxidative stability with initial decomposition temperatures of 521–544°C, residual weight percent at 800°C of 33.6–51.1% under air atmosphere, outstanding mechanical properties with tensile strengths in the range of 104.6–109.4 MPa, tensile modulus in the range of 1.92–2.58 GPa, and elongation at break from 6.9 to 8.0%, as well as good transparency with cutoff wavelengths of 386–392 nm and low dielectric constants of 2.80–2.92 at 1 MHz. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1438–1447, 2009

Key words: polyimides; thermal properties; polycondensation; one-step method; pyridine moiety

INTRODUCTION

Aromatic polyimides have a variety of engineering and electrical applications due to their reasonably good thermal stability, mechanical properties and chemical resistance, and low dielectric constant.[1–3] However, most polyimides encounter processing difficulties because of their low solubility in common organic solvents and high melting or softening temperatures, which strictly limited their applications. Many efforts on the modification of the backbone structure of polyimides with the purpose of obtaining soluble and/or thermoplastic polyimides without sacrificing their excellent thermal and mechanical properties have been devoted to extend the utility of polyimides, such as the incorporation of flexible linkages, bulky pendent groups and aliphatic units, and disruption of their symmetry.[4–17] Approaches such as incorporation of flexible ether linkages and *meta*-oriented phenylene rings into polymer backbone lead to an increase in polymer chain flexibility and solubility, but at the same time, lead to an decrease in polymer thermal resistance and thermal stability,[11–16] thereby lowering their effective upper use temperature and making them rather unsuitable for the ever-increasing demand for higher use temperature materials for microelectronics applications.

In the past, it was shown that the incorporation of a rigid heteroaromatic pyridine ring to the polymer backbone could provide excellent thermal and thermo-oxidative stability,[18–20] which should be useful to decrease negative effects resulting from the introduction of flexible linkages mentioned above. Pyridine nuclear is a rigid ring with symmetry and aromaticity.[21,22] The rigidity based on symmetry and aromaticity of the pyridine ring would contribute to the thermal stability, chemical stability, and retention of mechanical property of the resulting polymer at elevated temperature, as well as the polarizability, resulting from the nitrogen atom in the pyridine

ring, could be suitable to improve their solubility in organic solvents and lower their dielectric constant.[23,24] Therefore, various pyridine-containing polyimides with good thermal stability and processability had been prepared in the past several years.[20–22,25–33] To our knowledge, the pyridine-containing polyimides were prepared via polycondensation of pyridine-containing diamines with commercial aromatic dianhydrides or polycondensation of pyridine-containing dianhydrides with commercial aromatic diamines to date; however, there are few studies on polycondensation of pyridine-containing diamines with pyridine-containing dianhydrides and related polyimides.

Thus, as part of our continuing efforts on soluble polyimides with high thermal stability and low dielectric constant for advanced microelectronics applications,[28–34] four kinds of new poly(ether imides) derived from two pyridine-containing diamines and two pyridine-containing dianhydrides were prepared. The resulting polymers were subjected to solubility and thermal, mechanical, optical, and dielectric property measurements. The structure–property relations of the poly(ether imides) based on the structure of pyridine-containing diamines and dianhydrides were investigated and also effects of one-step and two-step methods for the preparation of poly(ether imides) on their properties were discussed.

MATERIALS AND METHODS

Materials

2,6-Bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride (BPDA), 4-phenyl-2,6-bis[4-(3,4-dicarboxyphenoxy)phenyl]pyridine dianhydride (PPDA), 4-phenyl-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (PAPP), and 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP) were synthesized in the laboratory as reported elsewhere.[30–33] N,N-Dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), and m-cresol (Tianjin Chemical Reagents Corp., China) were purified by distillation under reduce pressure over calcium hydride and stored over 4 Å molecular sieves. Acetic anhydride, pyridine, benzoic acid and isoquinoline (Beijing Chemical Reagents Corp., China) were used without further purification.

Measurements

Fourier transform infrared (FTIR) spectra were recorded in the range 4000–500 cm^{-1} for the resulted polymers in KBr disks by a Micolet NEXUS 670 spectrometer. ^{1}H-NMR spectra were measured on a JEOL EX-600 spectrometer by using tetramethylsilane as the internal reference. Elemental analysis was determined on a Perkin–Elmer model 2400 CHN analyzer. Differential scanning calorimetry (DSC) analyses were performed on a NETZSCH STA 449C instrument at a heating rate of 20°C/min under flowing nitrogen. Glass transition temperature (T_g) was taken as the midpoint of the inflection observed on the curve of heat capacity versus temperature. Thermogravimetric analysis (TGA) was conducted with a NETZSCH STA 449C instrument at a heating rate of 20°C/min under nitrogen or air. Dynamic thermogravimetric analysis (DTGA) was performed on a NETZSCH STA 449C instrument at heating rates of 5, 10, 20, and 40°C/min under nitrogen, respectively. The mechanical properties of polyimide films were measured on an Instron 1122 testing instrument with 100 mm × 5 mm specimens in accordance with GB 1040-79 at a drawing rate of 50 mm/min. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Lambda 35 UV–vis spectrophotometer at room temperature in air. The values of inherent viscosity (η_{inh}) were determined by an Ubbelohde viscometer at 30°C by using DMAc as a solvent, and polymer solution concentration was 0.5 g/dL. The weight-average molecular weights (M_w) were determined on a Brookhaven DI-200SM laser scattering instrument via small-angle laser scattering method. Qualitative solubility was determined with 10 mg polymer in 1 mL of solvent at room temperature for 24 h, or heating at 80°C. Dielectric constants of polyimide films were determined on an Agilent 4291B instrument at frequencies of 1 and 10 MHz at room temperature. Water uptake was measured by weighing the changes of a sample (30 mm × 30 mm) before and after immersion in water at 25°C for 24 h.

Polymerization

Two-step method

An equimolar amount of diamine and dianhydride monomer was reacted under constant flow of nitrogen. A typical procedure is as follows.

First, poly(amic acid) (PAA) solution was synthesized in the following procedure: 0.6316 g (1.0 mmol) of PPDA was gradually added to a stirred solution of 0.5896 g (1.0 mmol) FAPP in 7.0 mL NMP in a 25-mL three-necked flask equipped with a magnetic stirrer and a nitrogen inlet at 5°C. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h, forming a viscous solution of PAA precursor in NMP. The PAA was subsequently converted into polyimide by either a thermal or a chemical imidization process.

The chemical imidization was carried out by adding 1 mL of a mixture of acetic anhydride/pyridine

(3/2, v/v) into the PAA solution with stirring at ambient temperature for 1 h; the mixture was then stirred at 100°C for 4 h to yield a homogeneous poly(ether imide) solution, which was slowly poured into 100 mL ethanol to give a fibrous precipitate. The poly(ether imide) resin was obtained by filtrating, washing thoroughly with hot methanol, and drying at 80°C in vacuum overnight, which was marked as PI-A$_{TC}$ (subscript TC: Two-step method, chemical imidization). The yield was more than 93%. The inherent viscosity of the polymer PI-A$_{TC}$ in DMAc was 0.53 dL/g, measured at a concentration 0.5 g/dL at 30°C. FTIR (KBr, cm^{-1}): 1777 and 1724 (C=O), 1374 (N—H). Anal. calcd. for (C$_{75}$H$_{43}$F$_3$N$_4$O$_8$)$_n$: C, 76.01%; H, 3.66%; N, 4.73%. Found: C, 75.92%; H, 3.67%; N, 4.65%.

The thermal imidization was carried out by pouring the PAA solution into a glass plate, which was then dried in an oven with the following programmed procedure: 80°C/2 h, 120°C/1 h, 150°C/1 h, 180°C/1 h, 250°C/1 h, 280°C/0.5 h. The poly (ether imide) film could be easily obtained via the thermal imidization. The obtained film was stripped from the glass substrate by immersing the glass plates in hot water, which was marked as PI-A$_{TT}$ (subscript TT: Two-step method, thermal imidization). FTIR (KBr, cm^{-1}): 1778 and 1721 (C=O), 1380 (N—H). Anal. calcd. for (C$_{75}$H$_{43}$F$_3$N$_4$O$_8$)$_n$: C, 76.01%; H, 3.66%; N, 4.73%. Found: C, 75.87%; H, 3.71%; N, 4.69%.

PI-B$_{TC}$ (BPDA-FAPP), PI-C$_{TC}$ (PPDA-PAPP), PI-D$_{TC}$ (BPDA-PAPP), PI-B$_{TT}$, PI-C$_{TT}$, and PI-D$_{TT}$ were prepared by using a similar procedure, respectively.

Poly(ether imide) PI-B$_{TC}$. Inherent viscosity in DMAc: 0.52 dL/g. FTIR (KBr, cm^{-1}): 1779, 1721, 1377. Anal. calcd. for (C$_{71}$H$_{39}$F$_3$N$_4$O$_{10}$)$_n$: C, 73.19%; H, 3.37%; N, 4.81%. Found: C, 73.10%; H, 3.42%; N, 4.80%.

Poly(ether imide) PI-B$_{TT}$. FTIR (KBr, cm^{-1}): 1779, 1722, 1378. Anal. calcd. for (C$_{71}$H$_{39}$F$_3$N$_4$O$_{10}$)$_n$: C, 73.19%; H, 3.37%; N, 4.81%. Found: C, 73.01%; H, 3.40%; N, 4.74%.

Poly(ether imide) PI-C$_{TC}$. Inherent viscosity in DMAc: 0.64 dL/g. FTIR (KBr, cm^{-1}): 1777, 1723, 1376. Anal. calcd. for (C$_{74}$H$_{44}$N$_4$O$_8$)$_n$: C, 79.56%; H, 3.97%; N, 5.02%. Found: C, 79.48%; H, 3.96%; N, 4.97%.

Poly(ether imide) PI-C$_{TT}$. FTIR (cm^{-1}): 1777, 1721, 1377. Elemental analysis: Calculated for (C$_{74}$H$_{44}$N$_4$O$_8$)$_n$: C, 79.56%; H, 3.97%; N, 5.02%; Found: C, 79.44%; H, 4.03%; N, 4.94%.

Poly(ether imide) PI-D$_{TC}$. Inherent viscosity in DMAc: 0.48 dL/g. FTIR (KBr, cm^{-1}): 1777, 1720, 1379. Anal. calcd. for (C$_{70}$H$_{40}$N$_4$O$_{10}$)$_n$: C, 76.63%; H, 3.67%; N, 5.11%. Found: C, 76.55%; H, 3.70%; N, 5.09%.

Poly(ether imide) PI-D$_{TT}$. FTIR (KBr, cm^{-1}): 1778, 1721, 1378. Anal. calcd. for (C$_{70}$H$_{40}$N$_4$O$_{10}$)$_n$: C, 76.63%; H, 3.67%; N, 5.11%. Found: C, 76.46%; H, 3.69%; N, 5.06%.
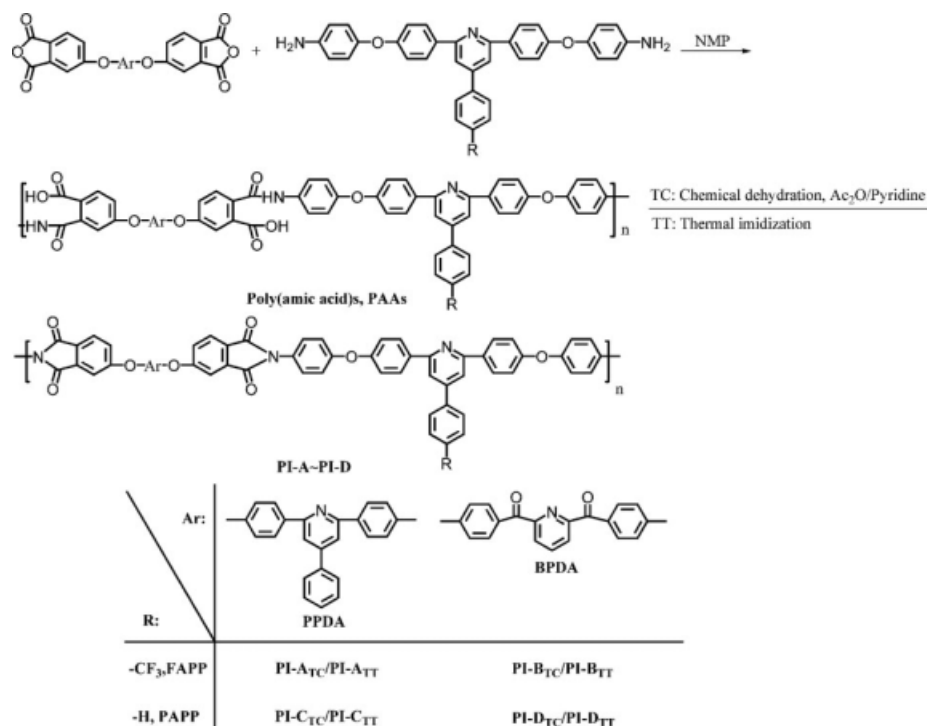
One-step method

A typical one-step method procedure is as follows: A 50-mL three-necked flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet was charged with 0.5896 g (1.0 mmol) FAPP, 0.6316 g (1.0 mmol) PPDA, and 11 mL m-cresol. The mixture was heated at 80°C with stirring until all solid dissolved. Benzoic acid (0.2500 g) was then added to the mixture, which was heated at 80°C for 1 h and then at 180°C for 2 h. Next, 0.2600 g of isoquinoline was added to the reaction mixture, which was then heated at 180°C for another 6 h. The reaction mixture was cooled to room temperature and precipitated into an excess of ethanol. The precipitation was filtrated, washed thoroughly with hot methanol, and dried in a vacuum oven at 100°C overnight, and finally, the poly(ether imide) resin PI-A$_O$ (subscript O: One-step method) was obtained in high yield more than 94%. The inherent viscosity of the polymer PI-A$_O$ in DMAc was 0.69 dL/g. FTIR (KBr, cm^{-1}): 1777 and 1721 (C=O), 1383 (N—H). ^{1}H-NMR (600 MHz, CDCl$_3$, δ, ppm): 8.26–8.25 (d, J = 9 Hz, 2H), 8.19–8.18 (d, J = 7.8 Hz, 4H), 8.11–8.10 (d, J = 7.8 Hz, 4H), 7.89–7.88 (d, J = 8.4 Hz, 2H), 7.80 (m, 6H), 7.74–7.73 (d, J = 6 Hz, 2H), 7.34 (s, 4H), 7.69–7.68 (d, J = 7.2 Hz, 2H), 7.48–7.45 (m, 5H), 7.31–7.30 (m, CDCl$_3$), 7.16–7.15 (d, J = 7.8 Hz, 2H), 7.11–7.09 (d, J = 7.8 Hz, 2H), 7.07–7.06 (d, J = 7.8 Hz, 2H). Anal. calcd. for (C$_{75}$H$_{43}$F$_3$N$_4$O$_8$)$_n$: C, 76.01%; H, 3.66%; N, 4.73%. Found: C, 75.88%; H, 3.69%; N, 4.71%.

Poly(ether imide) PI-B$_O$. Inherent viscosity in DMAc: 0.58 dL/g. FTIR (KBr, cm^{-1}): 1776 and 1722 (C=O), 1380 (N—H). ^{1}H-NMR (600 MHz, CDCl$_3$, δ, ppm): 8.40–8.39 (d, J = 7.8 Hz, 1H), 8.33–8.31 (d, J = 7.8 Hz, 2H), 8.27–8.26 (d, J = 7.8 Hz, 4H), 8.15–8.13 (d, J = 7.2 Hz, 4H), 7.79–7.78 (d, J = 7.8 Hz, 2H), 7.76 (s, 2H), 7.73–7.70 (m, 4H), 7.54–7.55 (d, J = 6 Hz, 2H), 7.43–7.42 (d, J = 6 Hz, 2H), 7.35 (CDCl$_3$), 7.24 (s, 2H), 7.10–7.06 (m, 8H), 7.00–6.99 (d, J = 8.4 Hz, 4H). Anal. calcd. for (C$_{71}$H$_{39}$F$_3$N$_4$O$_{10}$)$_n$: C, 73.19%; H, 3.37%; N, 4.81%. Found: C, 73.03%; H, 3.39%; N, 4.79%.

Poly(ether imide) PI-C$_O$. Inherent viscosity in DMAc: 0.70 dL/g. FTIR (KBr, cm^{-1}): 1777 and 1723 (C=O), 1376 (N—H). ^{1}H-NMR (600 MHz, CDCl$_3$, δ, ppm): 8.32–8.31 (d, J = 6.6 Hz, 2H), 8.25–8.24 (d, J = 5.4 Hz, 4H), 8.17–8.16 (d, J = 5.4 Hz, 4H), 7.95–7.93 (d, J = 7.2 Hz, 2H), 7.86 (m, 6H), 7.82 (m, 4H), 7.73–7.70, 7.50–7.46 (m, 10H), 7.35 (CDCl$_3$), 7.22–7.21 (d, J = 5.4 Hz, 4H), 7.16–7.15 (d, J = 5.4 Hz, 4H), 7.13–7.12 (d, J = 5.4 Hz, 1H). Anal. calcd. for (C$_{74}$H$_{44}$N$_4$O$_8$)$_n$: C, 79.56%; H, 3.97%; N, 5.02%. Found: C, 79.41%; H, 4.01%; N, 4.98%.

Poly(ether imide) PI-D$_O$. Inherent viscosity in DMAc: 0.51 dL/g. FTIR (KBr, cm^{-1}): 1776 and 1723 (C=O),

Scheme 1 Two-step method for the preparation of polyimides.

1376 (N—H). ^{1}H-NMR (600 MHz, CDCl$_3$, δ, ppm): 8.40–8.38 (d, J = 8.4 Hz, 1H), 8.30–8.29 (d, J = 5.4 Hz, 2H), 8.26–8.25 (d, J = 7.8 Hz, 4H), 8.11–8.10 (d, J = 8.4 Hz, 4H), 7.77–7.76 (d, J = 7.8 Hz, 2H), 7.74 (s, 2H), 7.69–7.68 (d, J = 6.0 Hz, 4H), 7.52–7.39 (m, 5H), 7.36 (CDCl$_3$), 7.36–7.34 (d, J = 8.4 Hz, 2H), 7.24 (s, 2H), 7.16–7.08 (m, 8H), 6.98–6.97 (d, J = 9.0 Hz, 4H). Anal. calcd. for (C$_{70}$H$_{40}$N$_4$O$_{10}$)$_n$: C, 76.63%; H, 3.67%; N, 5.11%. Found: C, 76.52%; H, 3.719%; N, 5.08%.

RESULTS AND DISCUSSION

Preparation of poly(ether imides)

In this article, both the two-step method and the one-step method were employed in the preparation of poly(ether imides), as shown in Schemes 1 and 2, respectively. In the two-step method, a diamine reacted with a dianhydride at low temperature in NMP to produce a PAA solution, which was then converted to related poly(ether imide) by chemical dehydration in the presence of acetic anhydride and pyridine or thermal dehydration. In the one-step method, poly(ether imides) were prepared by a high-temperature polycondensation reaction in high boiling point solvent *m*-cresol with the presence of benzoic acid and isoquinoline, in which process chain growth and imidization occur spontaneously. An acidic catalyst such as benzoic acid was added, which promotes the formation of the *trans*-isoimide. It has been proposed that a basic catalyst such as

isoquinoline was needed to convert the *trans*-isoimide into polyimide.[34,35]

The elemental analysis values of the resulted polymers showed in Materials and Methods were in good agreement with the calculated ones according to their respective structures, and the FTIR spectra of these polymers exhibited characteristic absorption
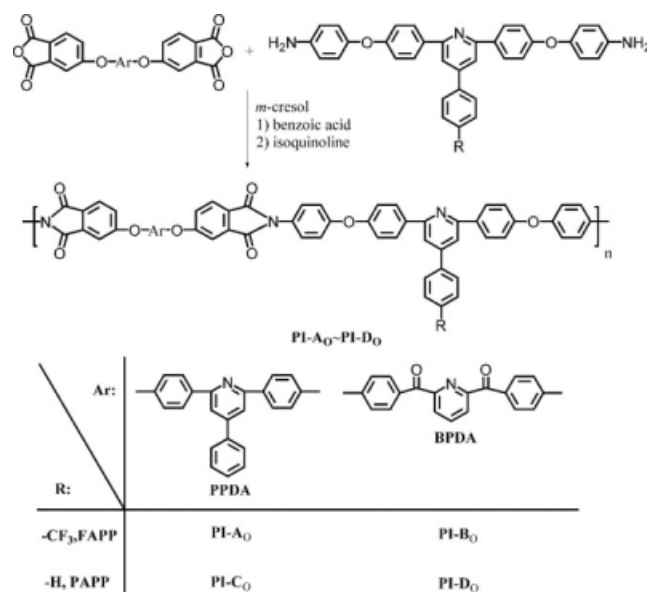
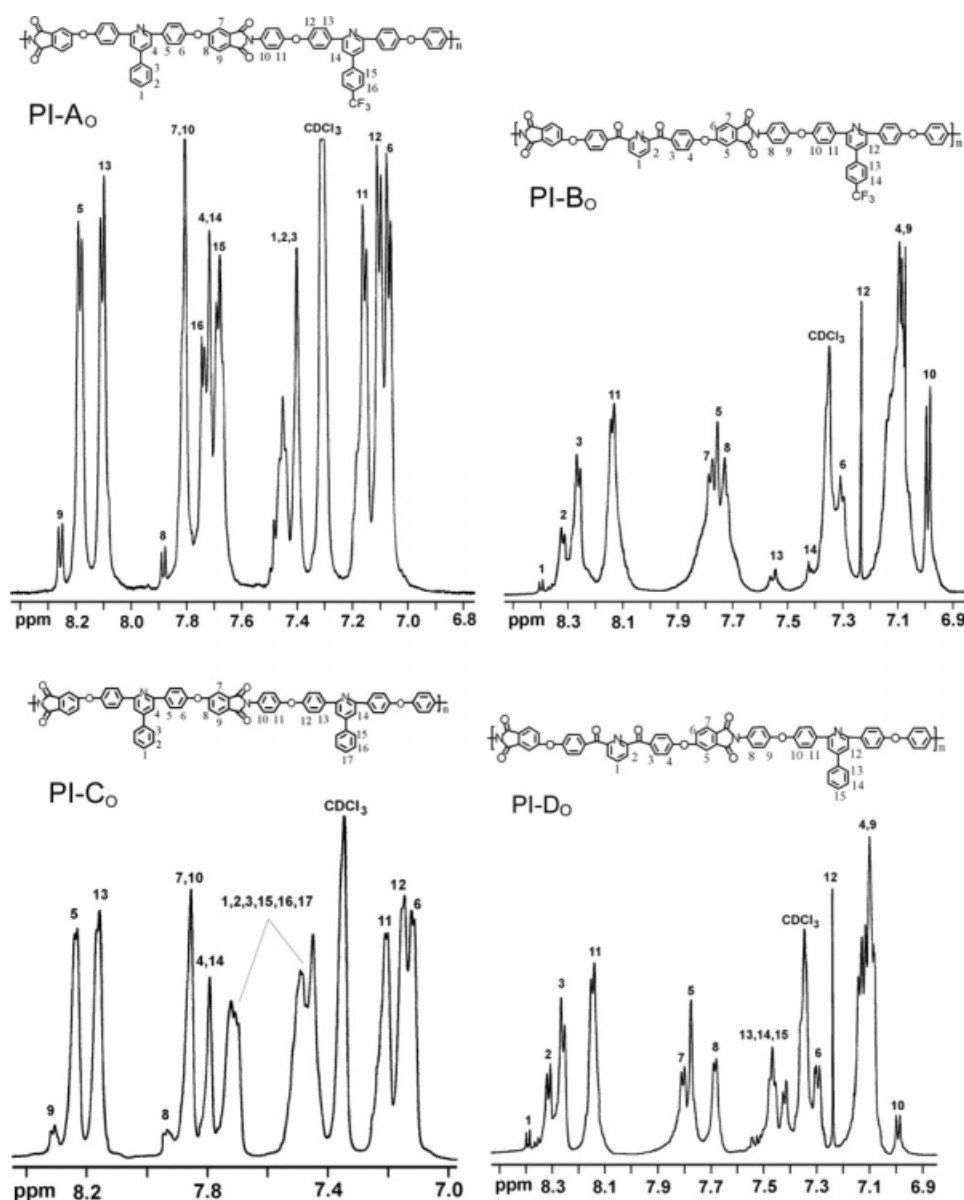**Scheme 2** One-step method for the preparation of polyimides.

Figure 1 ^{1}H-NMR spectra of polyimides PI-A$_O$-PI-D$_O$.

bands around 1780 and 1720 cm^{-1} due to the asymmetric and symmetric stretches of the carbonyl groups of imide ring. The absorption band around 1375 cm^{-1} due to the stretch of C—N bond confirmed the formation of the imide. The results of elemental analysis and FTIR spectra indicated that polymers with complete imidization were obtained, and also the fact that polymers obtained via the one-step method and the two-step method exhibited similar elemental analysis results and that FTIR spectra explained that complete imidization could be achieved via both one-step method and two-step method in all cases. Structures of the poly(ether imides) obtained via one-step method were also confirmed by their ^{1}H-NMR spectra, in which all pro-

tons in the polymer backbone can be assigned, as shown in Figure 1.

The inherent viscosity of the poly(ether imide) resins measured at a concentration of 0.5 g/dL in DMAc at 30°C and the M_w determined via small-angle laser scattering method are summarized in Table I. It can be seen that the obtained poly(ether imides) exhibited inherent viscosities in the range of 0.48–0.70 dL/g in DMAc and M_w in the range of 18,800–40,500 g/mol. The molecular weights of these poly(ether imides) were sufficient to cast tough and flexible films, which was consistent with the fact that clear, flexible, and tough poly(ether imide) films could be obtained by casting PAA solutions on glass substrate followed by thermal curing. It can also

TABLE I
Yields, Inherent Viscosities, and Weight-Average Molecular Weights of Polyimides

Polymer code	Yield (%)	$\eta_{inh}{}^a$ (dL/g)	$M_w{}^b$ (g/mol)	Film quality
PI-A$_O$	96	0.69	40,500	–
PI-A$_{TC}$	94	0.53	24,700	–
PI-A$_{TT}$	–^{c}	–	–	C, F, and T^d
PI-B$_O$	96	0.58	30,600	–
PI-B$_{TC}$	95	0.52	22,500	–
PI-B$_{TT}$	–	–	–	C, F, and T
PI-C$_O$	95	0.70	35,000	–
PI-C$_{TC}$	93	0.64	31,800	–
PI-C$_{TT}$	–	–	–	C, F, and T
PI-D$_O$	94	0.51	22,900	–
PI-D$_{TC}$	94	0.48	18,800	–
PI-D$_{TT}$	–	–	–	C, F, and T

^{a} Measured at a concentration of 0.5 g/dL in DMAc at 30°C.
^{b} Weight-average molecule weight measured via small-angle laser scattering method using polymer solution in DMAc.
^{c} Not detected.
^{d} C: clear; F: flexible; and T: tough.

found that poly(ether imides) obtained via the one-step method showed slightly higher viscosities and therefore better growth of molecular weights than the two-step method.

Polymer properties

The qualitative solubility was determined with 10 mg poly(ether imide) in 1 mL of solvent at room temperature for 24 h, or heating at 80°C; the results were listed in Table II. All the poly(ether imides) exhibited good solubility in common organic solvents, such as NMP, DMAc, DMF, m-cresol, tetrahy-drofuran (THF), and chloroform, at room temperature or upon heating at 80°C. The good solubility should be governed by the introduction of the flexible ether groups, the bulk pendent phenyl group, and the trifluoromethyl group in the polyimide backbone. Good solubility of these poly(ether imides) in low boiling point solvents, such as THF and chloroform, indicated that they should have potential applications in areas where temperature is sensitive. The fact that poly(ether imides) PI-A$_O$~PI-D$_O$ obtained via one-step method showed similar solubility with poly(ether imides) PI-A$_{TC}$~PI-D$_{TC}$ obtained via chemical imidization in the two-step method indicated that both of the two methods could prepare the poly(ether imide) resins with good solubility in this case.

The thermal properties of the resulted poly(ether imides) were evaluated by DSC and TGA, as summarized in Table III. T_g of these polymer films was found to be in the range of 239–272°C. PI-A$_{TT}$ and PI-C$_{TT}$ derived from the dianhydride PPDA showed higher T_g values than PI-B$_{TT}$ and PI-D$_{TT}$ derived from dianhydride BPDA, which indicated that incorporation of the pendent phenyl group together with the decrease of flexible carbonyl group in the polymer backbone could endow the polymer with better thermal resistance. This can be explained that the steric hindrance of pendent group restricts the rotation of the polymer chain.[36,37] Comparison between poly(ether imides) based on the same dianhydride (i.e., PI-A$_{TT}$ to PI-C$_{TT}$ and PI-B$_{TT}$ to PI-D$_{TT}$) exhibited that T_g values of the fluorinated poly(ether imides) was more than 6°C lower than that of the nonfluorinated analogies. This can be interpreted that the incorporation of the bulky trifluoromethyl group in the pendent phenyl group of the polymer backbone

TABLE II
Solubility of Polyimides

Polymer code^a	Organic solvents^{b,c}							
	m-Cresol	NMP	DMAc	DMF	DMSO	Toluene	THF	CHCl$_3$
PI-A$_O$	++	++	++	+−	+−	−−	++	++
PI-A$_{TC}$	++	++	++	+−	+−	−−	++	++
PI-B$_O$	++	++	++	+−	+−	−−	++	++
PI-B$_{TC}$	++	++	++	+−	+−	−−	++	++
PI-C$_O$	++	++	++	+−	+−	−−	+	++
PI-C$_{TC}$	++	++	++	+−	+−	−−	+	++
PI-D$_O$	++	++	++	+−	+−	−−	+	++
PI-D$_{TC}$	++	++	++	+−	+−	−−	+	++

^{a} Measured samples were polyimide resins obtained via one-step method or chemical imidization of two-step method.
^{b} Qualitative solubility was determined with 10 mg polyimide in 1 mL of solvent at room temperature or upon heating at 80°C; ++: soluble at room temperature, +: soluble on heating at 80°C, +−: partially soluble on heating at 80°C, −: insoluble.
^{c} NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethyl-formamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

TABLE III
Thermal Properties of Polyimides

Polymer code	$T_g{}^a$	In $N_2{}^b$				In Air			
		T_d (°C)	T_5 (°C)	T_{10} (°C)	$R_w{}^c$ (%)	T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%)
PI-A$_O$	–	–	–	–	–	539	565	576	44.9
PI-A$_{TC}$	–	–	–	–	–	542	572	594	45.0
PI-A$_{TT}$	272	574	525	601	69.3	544	567	579	47.6
PI-B$_{TT}$	239	542	536	571	66.5	535	529	563	34.9
PI-C$_{TT}$	278	574	522	585	64.5	533	543	575	33.6
PI-D$_{TT}$	249	540	531	564	67.0	521	541	576	51.1

[a] T_g, glass-transition temperature measured by DSC at a heating rate of 20°C/min.
[b] T_d, initial decomposition temperature; T_5, T_{10}, 5 or 10% weight loss temperature.
[c] R_w, residual weight (%) at 800°C.

increased the free volume, decreased the packing density, and thereby caused the reduction of the T_g values of the fluorinated poly(ether imides).[38]

TGA in nitrogen and air at a heating rate of 20 °C/min was applied to evaluate the thermal and thermo-oxidative stability of the resulted poly(ether imide) films, as shown Table III. The initial decomposition temperatures (T_d) of the four kinds of polymer films in nitrogen and air were in the range of 540–574 °C and 521–544 °C, respectively, and the 10% weight loss temperatures that are important criterion for evaluation of thermal stability were in the range of 564–601 °C and 563–579 °C in nitrogen and air, respectively, and also the char yields of these films at 800 °C were 64.5–69.3% and 33.6–47.6% in nitrogen and air, respectively. Accordingly, the obtained polyimide films exhibited excellent thermal and thermo-oxidative stability, which should contribute to the incorporation of rigid pyridine ring.

To investigate the effects of polymerization methods on polymer thermal stability, TGA measurements for PI-A$_O$ obtained via the one-step method and PI-A$_{TC}$ obtained via the two-step method with subsequently chemical dehydration were also carried out under air. Results listed in Table III showed that PI-A$_O$, PI-A$_{TC}$, and PI-A$_{TT}$ showed similar T_d, T_5, T_{10}, and R_w values, which indicated that polymerization methods showed little effect on polymer thermal stability in this case.

To understand the thermal decomposition behavior of the resulted polymers, the thermal degradation kinetics of polyimide films PI-A$_{TT}$ and PI-B$_{TT}$ was studied by DTGA.[39,40] The DTGA curves (Fig. 2) were obtained at different scanning temperature rates (β). According to Ozawa's suggestion and the approximation given by Doyle,[41] the following equation was given:

$$\log F_{(\alpha)} = \log(AE/R\beta) - 2.315 - 0.4567(E/RT) \quad (1)$$

Considering the random degradation for polymer, eq. (1) can be changed to

$$\log \beta = \log(AE/RF_{(\alpha)}) - 2.315 - 0.4567(E/RT) \quad (2)$$

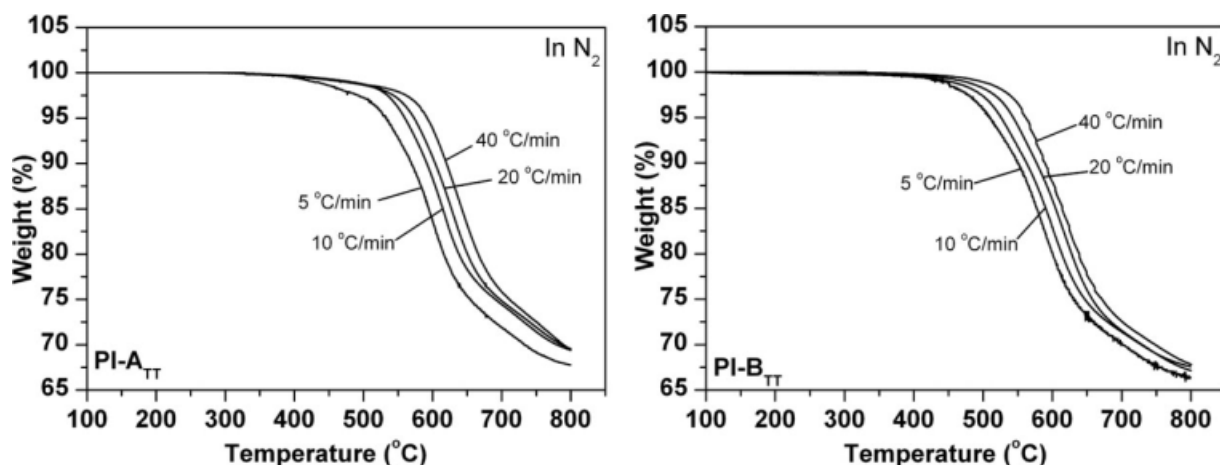where α is the conversion defined as the volatilized mass at time t divided by the initial mass, and R, A,

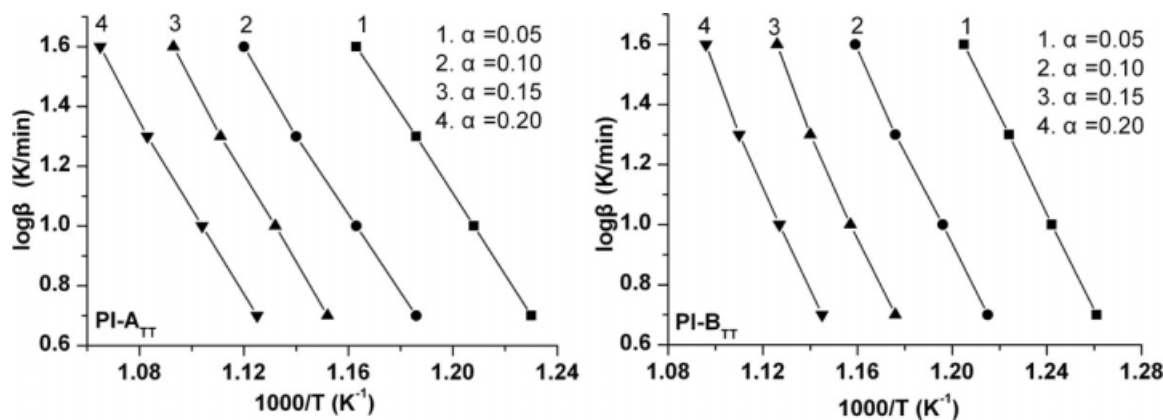**Figure 2** DTGA curves of polyimide films PI-A$_{TT}$ and PI-B$_{TT}$.

Figure 3 Plots of log β vs. $1000/T$ at constant values of conversion (α) for the degradation of PI-A$_{TT}$ and PI-B$_{TT}$.

E, and T represent the gas constant, preexponential factor, activation energy, and absolute temperature, respectively. According to eq. (2), the curve of log β vs. $1/T$ for a constant value of conversion α should give a straight line, and several curves of log β ∼ 1000/T based on various α values were plotted, as shown in Figure 3. The parallel relationship of the straight lines for various α values indicated that the thermal degradation of polyimide films PI-A$_{TT}$ and PI-B$_{TT}$ was in good agreement with randomly thermal initiation process.[39] Equation (3) could be obtained from eq. (1):

$$\log A = 2.315 + 0.4567(E/RT) - \log(E/R\beta F_{(\alpha)}) \quad (3)$$

For a random initiation model of polymer thermal degradation, eq. (4) was obtained:

$$F_{(\alpha)} = -\ln(1 - \alpha) \quad (4)$$

Hence, eq. (3) could become

$$\log A = 2.315 + 0.4567(E/RT) \\ - \log\{E/R\beta[-\ln(1 - \alpha)]\} \quad (5)$$

According to eq. (2), slopes for the straight lines with a constant α values were $0.4567E/R$; thus, a series of E values could be calculated, and the corresponding A values could be obtained by eq. (5) by

using the obtained E values and other parameters, such as T, R, α, and β, as shown in Table IV. For thermal degradation of PI-A$_{TT}$ and PI-B$_{TT}$, the average activation energy and preexponential factor were 701.6 kJ/mol and 1.63×10^{15} min^{-1}, and 835.3 kJ/mol and 1.88×10^{19} min^{-1}, respectively.

The mechanical properties of these poly(ether imide) films were presented in Table V. The polymer films had a tensile strength ranging from 104.6 to 109.4 MPa, tensile modulus ranging from 1.92 to 2.58 GPa, and elongation at break ranging from 6.9 to 8.0%. Thus, they could be considered as strong and flexible materials.

The dielectric properties of the poly(ether imide) films were measured with a dielectric analyzer at frequencies of 1 and 10 MHz, as shown in Table VI. The dielectric constants of these polymer films at 1 and 10 MHz were in the range of 2.80–2.92 and 2.77–2.85, respectively, and the dielectric dissipation factors at 1 and 10 MHz were in the range of 0.0065–0.0090 and 0.0061–0.0074, respectively. Fluorinated poly(ether imide) films PI-A$_{TT}$ and PI-B$_{TT}$ exhibited lower dielectric constant values than non-fluorinated ones, PI-C$_{TT}$ and PI-D$_{TT}$, which can be explained by the contribution of the —CF$_3$ groups in the backbone. For each poly(ether imide), the dielectric constant at 1 MHz is higher than that at 10 MHz. This variation was attributed to the frequency dependence of the polarization mechanisms, which comprise the dielectric constant. The dielectric

TABLE IV
The Calculated Activation Energy (E) and Preexponential Factor (A) for the Thermal Degradation of PI-A$_{TT}$ and PI-B$_{TT}$ Films

Conversion value (α)	PI-A$_{TT}$		PI-B$_{TT}$	
	E (kJ/mol)	A (min^{-1})	E (kJ/mol)	A (min^{-1})
0.05	661.7	1.03×10^{15}	790.3	1.23×10^{19}
0.10	665.3	9.55×10^{14}	782.6	1.58×10^{19}
0.15	741.8	1.70×10^{15}	874.4	2.11×10^{19}
0.20	737.7	2.84×10^{15}	893.9	2.61×10^{19}
Average	701.6	1.63×10^{15}	835.3	1.88×10^{19}

TABLE V
Mechanical Properties of Polyimide Films

Polymer code	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-A$_{TT}$	107.7	1.92	7.2
PI-B$_{TT}$	109.4	2.04	8.0
PI-C$_{TT}$	106.9	2.58	6.9
PI-D$_{TT}$	104.6	2.49	7.1

TABLE VI
Dielectric Properties, Optical Properties, and Water Uptake of Polymimde Films

Polymer code	Film thickness (μm)	ε^a 1 MHz	tan δ^a 1 MHz	ε'^a 10 MHz	tan δ'^a 10 MHz	λ_{cut}^b (nm)	Water uptake (%)
PI-A$_{TT}$	43	2.80	0.0090	2.79	0.0074	386	0.69
PI-B$_{TT}$	49	2.81	0.0065	2.77	0.0069	389	0.73
PI-C$_{TT}$	45	2.92	0.0067	2.85	0.0061	391	0.76
PI-D$_{TT}$	48	2.86	0.0068	2.83	0.0064	392	0.87

[a] ε, tan δ: dielectric constant and dielectric dissipation factor at 1 MHz; ε', tan δ': dielectric constant and dielectric dissipation factor at 10 MHz.
[b] The cutoff wavelength.

constant values of these poly(ether imide) films were fairly low, which are lower than that of commercially available polyimide film, Kapton H (3.5, 75 μm, 1 MHz), and comparable to those of many previously reported semifluorinated polyimides (2.89–3.0, 1 MHz).[21,42] The results suggested that incorporation of bulky trifluoromethyl group or pendent phenyl group in the polymer backbone could improve the dielectric performance, which can be explained that incorporation of the bulky trifluoromethyl or pendent phenyl group prohibits close packing of the polymer chains and reduces interchain charge transfer of the highly polar dianhydride groups; in addition, the large fluorine atoms increased the free volume fraction in the polymer, thereby essentially reducing the number of polarizable groups in a unit volume and leading the decrease of polymer dielectric constant. The polar pyridine moieties maybe also have contributed to the dielectric constant due to its low polarizability resulting from the high polarity of pyridine ring.[24] Table VI also showed that these poly(ether imide) films exhibited low water uptake of 0.69–0.87%, which prevented the negative influence of the moisture from surrounding environment on dielectric properties. Because of the hydrophobic trifluoromethyl groups in the polymer backbone, the fluorinated poly(ether imide) films PI-A$_{TT}$ and PI-B$_{TT}$ exhibited lower water uptake than the nonfluorinated films PI-C$_{TT}$ and PI-D$_{TT}$.

The optical properties of the resulted polyimide films were investigated via testing their transmission UV–vis spectra. As shown in Table VI, all the films were entirely transparent and exhibited cutoff wavelengths (λ_{cut}) shorter than 400 nm, ranging from 386 to 392 nm. The fluorinated polyimide films PI-A$_{TT}$ and PI-B$_{TT}$ exhibited lower λ_{cut} values than the nonfluorinated films PI-C$_{TT}$ and PI-D$_{TT}$. This may be interpreted by reduction in the intermolecular charge–transfer complex between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The bulky and electron-withdrawing trifluoromethyl group in the diamine moieties was

presumably effective in decreasing charge–transfer complexes between polymer chains through steric hindrance and the inductive effect by decreasing the electron-donating property of diamine moieties. The electron-donating ether linkages in the dianhydride moiety also contribute somewhat toward decreasing the overall electron affinity of the phthalimide units, and subsequently, lowering the intermolecular charge–transfer interaction.

CONCLUSION

Four kinds of pyridine-containing poly(ether imides) were successfully prepared via both the one-step method and the two-step method. It was observed that poly(ether imides) obtained via the one-step method exhibited higher molecular weight than the similar polymers prepared through the two-step process; however, their solubility and thermal properties showed little difference. Transparent, flexible, and tough poly(ether imide) films were obtained by casting PAA solutions on glass substrate followed by thermal curing, which showed excellent thermal and mechanical properties, and good dielectric properties and transparency, as well as low water uptake.

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