



Optically transparent and organosoluble poly(ether imide)s based on a bis(ether anhydride) with bulky 3,3',5,5'-tetramethylbiphenyl moiety and various fluorinated bis(ether amine)s

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Abstract

Novel optically transparent and organosoluble poly(ether imide)s (PEIs) were prepared from 4,4'-bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl dianhydride and various fluorinated bis(ether amine)s via chemical or thermal imidization. The effects of fluorinated groups and the imidization method on the properties of PEIs were investigated. Fluorinated PEIs prepared by the chemical imidization method exhibited essentially colorless characteristic with cutoff wavelengths lower than 380 nm, and yellowness index (b^* values) ranging from 5.2 to 7.3, which are close to that of transparent polyarylate polymer ($b^* = 3.3$). In addition, all fluorinated PEIs showed excellent solubility in common organic solvents. The thermal decomposition temperature at 10% weight loss is higher than 490°C, and the glass transition temperatures are in the range of 245–315°C. The fluorinated PEI series also exhibited low dielectric constants of 2.95–3.29 (1 MHz) and low moisture absorption in the range of 0.17–0.86 wt%, which are lower than the analogous nonfluorinated series.

Keywords

4,4'-Bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl dianhydride, fluorinated poly(ether imide)s, optically transparent, organosoluble

Introduction

Aromatic polyimides (PIs) are widely used in microelectronic and aerospace fields owing to reliable high thermal stability, good chemical resistance, and excellent mechanical properties.^{1–5} In addition, colorless PI films also exhibited special importance in some applications such as flexible solar radiation protectors,⁶ orientation films in liquid crystal display devices,⁷ optical waveguides for communication interconnects,⁸ and optical half-wave plates for planar lightwave circuits.⁹ For conventional PIs, there are some drawbacks such as poor organic solvent solubility and high softening temperatures due to their rigid backbones and strong interchain interactions. In addition, strong absorption in the visible region because of strong intermolecular charge transfer complexing (CTC) restricts their applications in optoelectronic and microelectronic fields.¹⁰

To overcome the drawbacks associated with conventional PIs, new diamine and dianhydride structure modifications are essentially needed. Incorporating flexible linkage (–O–), bulky, nonplanar, or asymmetry units in

the main chain had been proved to be successful approaches to obtain organosoluble PIs without sacrificing their original excellent properties.^{4,5} In addition, insertion of the fluorine-containing moiety could prevent the formation of CTC between PI chains but accompanied with high optical transparency, low dielectric constant, and low moisture uptake.¹¹ Fluorinated poly(ether imide)s (PEIs) derived from bis(ether anhydride)s and fluorinated bis(ether diamine)s usually exhibited improved optical

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transparency and organosolubility. The molecular design concepts are based on (1) fluorinated units such as bulky trifluoromethyl (CF₃) moiety can enhance the optical transparency and solubility due to the low polarizability of the C–F bond with increasing free volume^{10–12} and (2) flexible units such as ether linkage into diamine and dianhydride components can decrease the softening temperatures of PIs such as the commercial resin “Ultem 1000.”^{13–15}

To continue our works on developing optically transparent and organosoluble PIs with high thermal stability and low dielectric constants, a novel bulky bis(ether anhydride), 4,4'-bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl dianhydride (**I**) was designed and synthesized and its derived fluorinated PEIs were prepared by polycondensation reactions with CF₃-containing bis(ether amine)s. Incorporation of ether and tetramethylbiphenyl groups is expected to reduce the crystallinity and enhance the solubility.¹⁶ Moreover, the rigid biphenyl unit can suitably retain good mechanical property and high thermal stability as well. Solubility, thermal properties, mechanical properties, dielectric constant, and optical properties of the newly synthesized PEIs are investigated and compared with those of nonfluorinated analogs.

Experimental

Materials

3,3',5,5'-Tetramethylbiphenyl-4,4-diol (TMBP; Mitsubishi Petrochemical Co. Ltd, Japan), 4-nitrophthalodinitrile (NPDN; TCI, Japan), and acetic anhydride (Ac₂O; Fluka, St Louis, Missouri, USA) were used as-received without further purification. The CF₃-substituted bis(ether amine)s were synthesized according to the literatures,^{17–23} which included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**II_a**; mp: 133–134°C),¹⁷ 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene (**II_b**; mp: 116–117°C),¹⁸ 4,4-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**II_c**; mp: 155–156°C),¹⁹ 4,4-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (**II_d**; mp: 256–257°C),²⁰ 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**II_e**; mp: 131–132°C),²¹ 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-hexafluoropropane (**II_f**; mp: 65–66°C),²² and 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl] sulfone (**II_g**; mp: 219–220°C).²³ *N,N*-Dimethylacetamide (DMAc; Fluka) and *N,N*-dimethylformamide (DMF; Fluka) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of bis(ether anhydride) (**I**)

4,4'-Bis(3,4-dicyanophenoxy)-3,3',5,5'-tetramethylbiphenyl (**I'**). About 9.15 g (37.5 mmol) of TMBP, 13.0 g (75.0 mmol)

NPDN, and 10.4 g (37.6 mmol) of potassium carbonate (K₂CO₃) were mixed in a flask with 120 mL of anhydrous DMF. The reaction solution was stirred at room temperature for about 24 h. The mixture was then poured into 600 mL of water, the precipitated orange solid was collected, and washed thoroughly with methanol and water. The crude product was purified by recrystallization from dimethyl sulfoxide (DMSO) to give pure solid (17.0 g, 92%; mp: 234–235°C). Infrared (IR) (potassium bromide (KBr)): $\nu_{\max} = 2229 \text{ cm}^{-1}$ (C≡N), 1595, 1477 cm^{-1} (aromatic C=C), 1242 cm^{-1} (C–O). Proton nuclear magnetic resonance (¹H NMR; 500 MHz, deuterated chloroform synthesis of monomer **I** and PEI part (CDCl₃): $\delta = 7.76, 7.74$ (d, 2H, H_b, $J_{b-c} = 8.7$ Hz), 7.37 (s, 4H, H_d), 7.20–7.18 (4H, H_{c,a}), 2.17 (s, 12H, H_e). Carbon nuclear magnetic resonance (¹³C NMR; 125 MHz, CDCl₃): $\delta = 161.04$ (C⁶), 149.06 (C⁸), 138.69 (C⁴), 135.69 (C¹⁰), 131.00 (C⁷), 128.42 (C⁹), 119.80 (C¹¹), 119.65 (C^{11'}), 117.94 (C⁵), 115.43 (C¹), 115.05 (C²), 108.54 (C³), 16.35 (C¹²).

4,4'-Bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl (**I''**). A suspension of bis(ether dinitrile) **I'** (14.82 g; 30 mmol) in an ethanol/water mixture (120 mL/120 mL) containing 27 g (482 mmol) of dissolved potassium hydroxide (KOH) was boiled under reflux for about 30 h till the evolution of ammonia had ceased. Hot resulting clear solution was filtered to remove any possible insoluble impurities. The filtrate was allowed to cool and was then acidified by concentrated hydrochloric acid to a pH around 1–3. The white precipitated product was filtered off, washed with water till neutral, and dried it to obtain bis(ether diacid) **I''** (16.64 g, 98%; mp: 273–274°C). IR (KBr): $\nu_{\max} = 3600\text{--}2500 \text{ cm}^{-1}$ (O–H), 1707 cm^{-1} (C=O), 1606, 1471 cm^{-1} (aromatic C=C), 1221 cm^{-1} (C–O). ¹H NMR (500 MHz, deuterated DMSO (DMSO-*d*₆): $\delta = 7.76, 7.74$ (d, 2H, H_b, $J_{b-c} = 8.9$ Hz), 7.48 (4H, H_{c,a}), 6.92 (s, 4H, H_d), 2.10 (s, 12H, H_e). ¹³C NMR (125 MHz, DMSO-*d*₆): $\delta = 169.04$ (C¹¹), 167.70 (C^{11'}), 159.38 (C⁶), 149.60 (C⁸), 137.27 (C²), 137.13 (C⁴), 131.98 (C¹⁰), 131.15 (C⁷), 127.85 (C³), 124.85 (C⁹), 115.98 (C⁵), 113.74 (C¹), 16.16 (C¹²).

4,4'-Bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl dianhydride (**I**). A mixture of bis(ether diacid) **I''** (13.5 g; 23.85 mmol) dissolved in 35 mL of Ac₂O and 35 mL of glacial acetic acid was heated under reflux. The resulting hot clear solution was filtered to remove any insoluble impurities. The crystallized white solid was collected when the filtrate was cooled. The product was washed with dry toluene and dried it to give **I** (8.92 g, 70%; mp: 274–275°C). IR (KBr): $\nu_{\max} = 1849 \text{ cm}^{-1}$ (asymmetric C=O stretch), 1774 cm^{-1} (symmetric C=O stretch), 1617, 1477 cm^{-1} (aromatic C=C), 1278 cm^{-1} (C–O). ¹H NMR (500 MHz, deuterated chloroform CDCl₃): $\delta = 7.98, 7.96$ (d, 2H, H_b, $J_{b-c} = 8.4$ Hz), 7.45–7.43 (dd, 2H, H_c, $J_{c-b} = 8.4$ Hz, $J_{c-a} = 1.8$ Hz), 7.38 (s, 4H, H_d), 7.25–7.24 (d, 2H, H_a,

$J_{a-c} = 1.7$ Hz), 2.19 (s, 12H, H_c). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 164.43$ (C^6), 162.62 (C^{11}), 162.06 ($\text{C}^{11'}$), 149.36 (C^8), 138.54 (C^2), 134.21 (C^4), 130.88 (C^7), 128.30 (C^9), 127.82 (C^{10}), 123.86 (C^3), 123.11 (C^5), 110.41 (C^1), 16.28 (C^{12}).

PEI synthesis

Thermal imidization. General polymerization procedure is described by the following example: 0.3424 g (0.8 mmol) of diamine **II_a** was dissolved in 6.0 mL of dried DMAc in a 20 mL flask. After **II_a** was dissolved completely, an equimolar amount of bis(ether anhydride) **I** (0.4272 g; 0.8 mmol) was added in one portion. The mixture was stirred at room temperature for 12 h to yield a viscous poly(amic acid) (PAA) precursor solution (**III_a**). The **III_a** was poured into a glass culture dish and placed into an 80°C oven to remove the casting solvent. The semidried PAA films were further dried and imidized by sequential heating from 130°C to 250°C at the rate of 20°C 10 min⁻¹, then kept at 250°C for another 30 min. A flexible PEI film of **IV_a(H)** self-stripped off from the glass surface by immersion in water ($\eta_{\text{inh}} = 0.84$ dL g⁻¹).

Chemical imidization. A similar PAA solution was prepared as above, then 0.8 mL mixture of Ac_2O and pyridine (volume ratio: 2:1) was added to the PAA solution and stirred at 80–100°C for 1 h. The polymer solution was poured into a glass culture dish, which was placed in a 100°C oven for 1 h to evaporate the solvent and form a thin film. Finally, the PEI film **IV_a(C)** was obtained by sequentially heating to 200°C and holding at that temperature for 1 h to remove the residual solvent ($\eta_{\text{inh}} = 0.79$ dL g⁻¹). IR (PAA film): $\nu_{\text{max}} = 3500\text{--}2500$ cm⁻¹ (O–H), 1718 cm⁻¹ ($\text{C}\equiv\text{O}$), 1489 cm⁻¹ (aromatic $\text{C}\equiv\text{C}$), 1252 cm⁻¹ (C–O), 1134 (C–N). IR (PEI film): $\nu_{\text{max}} = 1780$ (asymmetric C=O stretch), 1726 (symmetric imide C=O stretch), 1377 (C–N stretch), 1242 (C–O), 1138 (C–N), 1092, 744 cm⁻¹ (imide ring deformation). ^1H NMR (500 MHz, deuterated chloroform $\delta = 7.91$, 7.90 (2H, d, $J_{b-c} = 8.3$ Hz, H_b), 7.75 (2H, d, $J_{a-c} = 2.2$ Hz, H_a), 7.54–7.51 (2H, dd, $J_{c-b} = 8.7$ Hz, $J_{c-a} = 2.2$ Hz, H_c), 7.37 (4H, H_d), 7.30–7.27 (4H, $H_{f,e}$), 7.14 (4H, H_h), 7.05–7.02 (2H, d, $J_{g-f} = 8.7$ Hz, H_g), 2.20 (12H, H_i). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 166.53$, 166.40 ($\text{C}^{21,21'}$), 163.48 (C^5), 154.96 (C^{17}), 152.29 (C^{17}), 149.61 (C^{14}), 138.40 (C^1), 134.35 (C^{11}), 131.26 (C^{10}), 131.04 (C^8), 128.21 (C^9), 126.25 (C^3), 126.13 (C^2), 125.63, 125.59 ($\text{C}^{12,4}$), 124.20 (C^{13}), 122.10 (C^{20} , quartet, $^1J_{C-F} = 271.3$ Hz), 121.55 (C^{18}), 121.49 (C^{15} , quartet, $^2J_{C-F} = 30$ Hz), 118.70 (C^{16}), 109.66 (C^6), 16.34 (C^{19}).

Measurements

IR spectra were measured on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer (Japan). Elemental

analyses were performed on a Heraeus VarioEL-III CHN analyzer (Germany). ^1H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer (Billerica, Massachusetts, USA). The inherent viscosities were determined at a 0.5 g dL⁻¹ concentration with an Ubbelohde viscometer (SCHOTT, Germany) at 30°C and DMAc as the solvent. number-average molecular weights (M_n) and weight-average molecular weights (M_w) were obtained via gel permeation chromatography (GPC) on a Waters 2410 instrument (Milford, Massachusetts, USA) with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min⁻¹ using polystyrene as a standard. Thermogravimetric analysis (TGA) was conducted with a TA Instruments (TGA 2050; New Castles, Delaware, USA). Measurements were carried out on 9–11 mg film samples tested under flowing nitrogen or air atmosphere (90 cm³ min⁻¹) with a heating rate of 20°C min⁻¹. Melting points were measured by differential scanning calorimeter (DSC) on a TA Instruments DSC 2010 under flowing nitrogen atmosphere at a heating rate of 5°C min⁻¹. Glass transition temperatures (T_g) were conducted by DSC at a heating rate of 15°C min⁻¹. Mechanical properties of the films were measured with an Instron model 1130 tensile tester (Norwood, Massachusetts, USA) with a 5-kg load cell at a crosshead speed of 5 cm min⁻¹ on strips approximately 30–60 μm thick and 0.5 cm wide with a 2-cm gauge length. At least five individual determinations were used for general average value. The color intensity was evaluated by a Macbeth color-eye colorimeter using Commission International de l'Eclairage (CIE) LAB color difference equation. Measurements were performed with films 30–60 μm thick with an observational angle of 10° and a CIE-D illuminant. Ultraviolet–visible (UV-Vis) spectra were determined by a Shimadzu UV-1601 UV-Vis spectrophotometer (Japan). The dielectric property was tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric analyzer (Palo Alto, California, USA) from the polymer film samples tested in a dry chamber at room temperature. Gold electrodes were vacuum deposited on both surfaces of dried films. 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.

Results and discussion

Synthesis of bis(ether anhydride) (**I**)

The new bis(ether anhydride) (**I**) was synthesized with a three-stage synthetic procedure,^{24,25} as shown in Figure 1. The synthesis started from the nucleophilic nitro displacement reaction of TMBP with NPDN in DMF in the presence of K_2CO_3 as the base at room temperature to obtain the intermediate bis(ether dinitrile) (**I'**). The purified compound **I'** was then hydrolyzed to afford bis(ether diacid) (**I''**) by KOH in ethanol and the generated tetracarboxylic

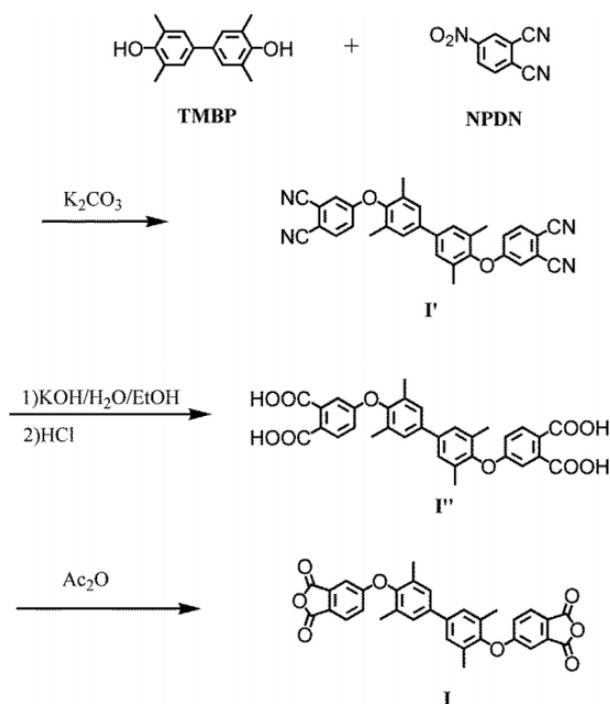


Figure 1. Synthesis of 4,4'-bis(3,4-dicarboxyphenoxy)-3,3',5,5'-tetramethylbiphenyl dianhydride (**I**).

compound **I''** was subsequently cyclodehydrated by Ac_2O to yield the target bis(ether anhydride) (**I**). The structural analysis of the bis(ether anhydride) (**I**) and its precursor compounds (**I'** and **I''**) was carried out by FTIR, ^1H , and ^{13}C NMR spectroscopies. Based on the observation on FTIR spectra of **I'**, **I''**, and **I**, the cyano groups ($\text{C}\equiv\text{N}$ stretching) of **I'** gave a characteristic band at 2229 cm^{-1} . After hydrolysis, the characteristic band of the cyano groups was absent, but the resulting carboxyl groups displayed the typical O–H and C=O stretching bands in the region of $2500\text{--}3600\text{ cm}^{-1}$ and 1707 cm^{-1} . The IR spectrum of **I** showed characteristic anhydride absorption at 1849 and 1774 cm^{-1} (asymmetric and symmetric carbonyl stretching) after cyclodehydration from precursor **I''**. In addition, the ^1H and ^{13}C NMR spectra of the target bis(ether anhydride) **I** together with its precursor compounds **I'** and **I''** are illustrated in Figures 2 to 4, respectively. In the ^1H NMR spectra, the aromatic protons of **I'**, **I''**, and **I** resonated in the region of 7.18–7.76, 6.92–7.76, and 7.25–7.98 ppm, and their methyl protons appeared in the region of 2.17, 2.10, and 2.19 ppm. A slight downfield shift of the protons on the outer benzene ring was observed after the cyano group was converted to the carboxyl group and anhydride group. In the ^{13}C NMR spectra, the most relevant change on passing from **I'** to **I''** was the disappearance of the resonance peaks for the cyano carbons at 119–120 ppm and the appearance of carbonyl peaks at 167–169 ppm. After dehydration, the resonance signals of the carbonyl groups slightly shifted to 162–163 ppm. In addition, 10 signals of aromatic carbons were observed in the range

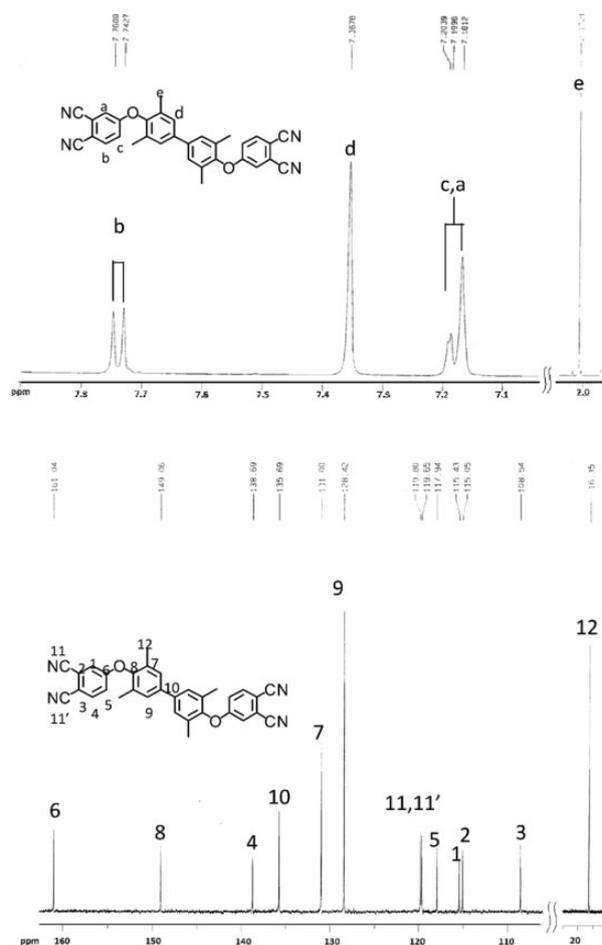


Figure 2. ^1H and ^{13}C NMR spectra of **I'** in CDCl_3 . ^1H NMR: proton nuclear magnetic resonance; ^{13}C NMR: carbon nuclear magnetic resonance; CDCl_3 : deuterated chloroform.

of 109–164 ppm and the peak of the methyl carbons appeared at around 16 ppm. Thus, these spectra are in good agreement with the expected structures of **I'**, **I''**, and **I**.

Synthesis of PEIs

A series of fluorinated PEIs (**IV**) was synthesized by a conventional two-step procedure of ring opening polyaddition from bis(ether anhydride) **I** with various fluorinated diamines **II_{a-g}** at room temperature to form the PAA solutions and sequential thermal (**H**) or chemical (**C**) imidization to give the corresponding PEI films (Figure 5). The results of elemental analysis of the **IV(C)** series are listed in Table 1, and the found values were in good agreement with the calculated values of the proposed structures. The inherent viscosity and GPC data of the **IV(C)** series are listed in Table 1 as well. The inherent viscosities were in the range of $0.42\text{--}1.05\text{ dL g}^{-1}$ as measured in DMAc solvent. The molecular weights were in the range of $1.89\text{--}4.09 \times 10^4$ for M_n and $3.35\text{--}6.50 \times 10^4$ for M_w with polydispersity index (M_w/M_n) values of 1.59–1.84, respectively. The lower inherent

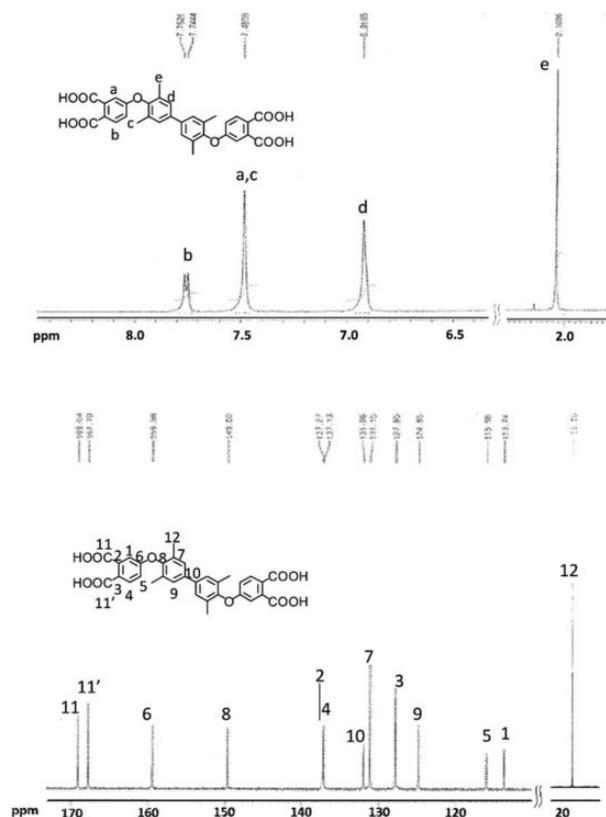


Figure 3. ^1H and ^{13}C NMR spectra of **I'** in $\text{DMSO}-d_6$. ^1H NMR: proton nuclear magnetic resonance; ^{13}C NMR: carbon nuclear magnetic resonance; $\text{DMSO}-d_6$: deuterated dimethyl sulfoxide.

viscosity and average molecular weight of PEI **IV_b** are possible consequences of the *ortho* substitution pattern of diamine **II_b** in combination of bis(ether anhydride) **I** in forming cyclic oligomers of the intermediate PAA; there is no reason to believe that there is any change in distribution of species on imidization.²⁶ The complete imidization of the polymer was confirmed with FTIR and NMR spectra. Figure 6 depicts a typical IR spectra of the PAA **III_a** and PEI **IV_a**. The PAA showed characteristic absorptions at 3500–2500 (O–H and N–H stretching) and 1718 cm^{-1} (carboxyl group of C=O stretching). After dehydration, the above peaks disappeared and came out imide carbonyl symmetrical and asymmetrical stretching around 1726 and 1780 cm^{-1} and imide-ring deformation of 1092 and 744 cm^{-1} . The ^1H and ^{13}C NMR spectra of the representative PEI **IV_a** are shown in Figure 7. Assignments of carbon and proton NMR spectra were in good agreement with the proposed structure. For example, the protons of methyl group appeared in 2.20 ppm in ^1H NMR spectrum and the carbonyl carbons $\text{C}^{21,21'}$ appeared in the downfield region, together with total 22 signals in the ^{13}C NMR spectrum.

Solubility

The solubility for the PEI samples was determined at a concentration of 10% in variety of organic solvents and the

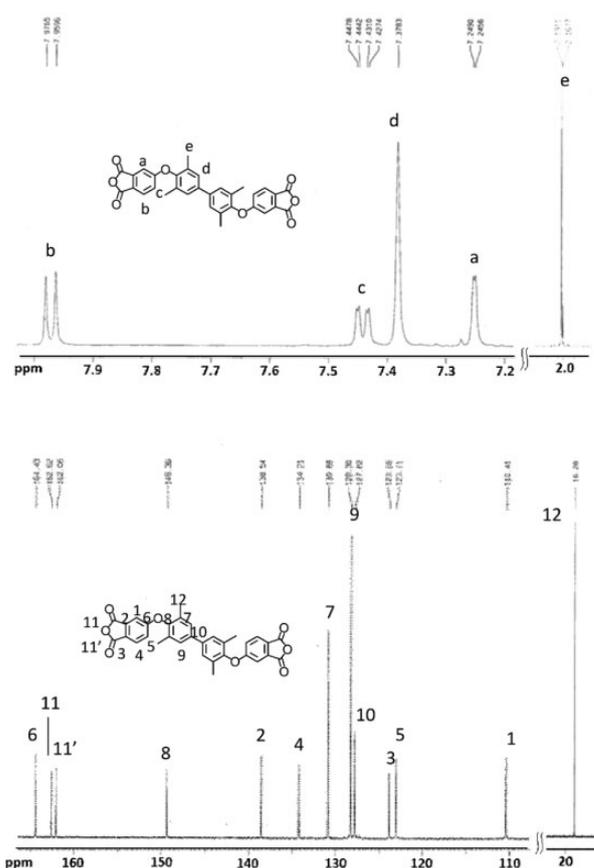


Figure 4. ^1H and ^{13}C NMR spectra of **I** in CDCl_3 . ^1H NMR: proton nuclear magnetic resonance; ^{13}C NMR: carbon nuclear magnetic resonance; CDCl_3 : deuterated chloroform.

results are listed in Table 2. All the fluorinated polymers showed an excellent solubility in aprotic polar solvents such as *N*-methyl-2-pyrrolidone, DMAc, and DMF and were also soluble in low-boiling solvents such as THF, dichloromethane, and chloroform. When comparing the solubility for the **IV(C)**, **IV(H)**, and **V(H)** series PEIs, it was observed that the fluorinated **IV** series showed significantly better solubility than the corresponding non-fluorinated **V** analogs. This could be attributable to the presence of bulky CF_3 groups, which disrupted regularity and dense chain packing with decreasing chain–chain interactions.^{11,27} In addition, the PEIs with *ortho*-substituted phenylene (from **II_b**) and hexafluoroisopropylidene units (from **II_f**) generally showed higher solubilities.

Optical and mechanical properties

The color intensities of the polymer films were elucidated from the yellowness (b^*), redness (a^*), and lightness (L^*) indices observed by a Macbeth color-eye colorimeter. The results are listed in Table 3. The **IV(C)** series PEIs were almost colorless and exhibited a very low yellowness index (b^*) of 5.2–7.3 close to that of a transparent polyarylate polymer ($b^* = 3.3$). The fluorinated films prepared by the

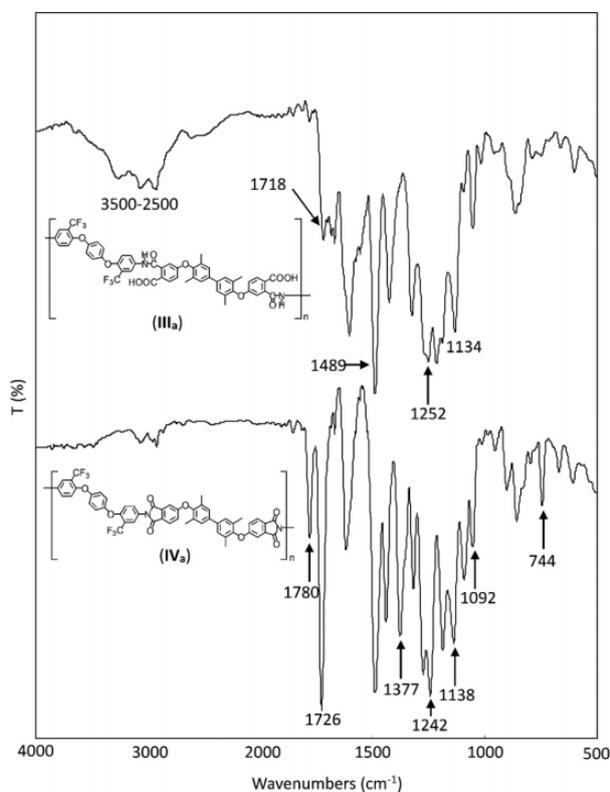


Figure 6. FTIR spectra of poly(amic acid) **III_a** and poly(ether imide) **IV_a**. FTIR: Fourier transform infrared.

properties, with strengths at break of 85–105 MPa, elongations at break of 9–68%, and initial moduli of 1.6–2.1 GPa; thus, they could be considered as strong materials. The high extensibility of the PEI films of **IV_c** and **IV_d** is similar to that reported in the literature.²⁸ A possible reason has been proposed that, in the polymer film as cast, the bisphenoxybiphenyl unit in the diamine residue adopts a conformation that causes the polymer chain to coil strongly, through the disposition of aromatic rings adjacent to the ether linkages, but that under stress these conformations are modified to give a more linear in-chain unit; the effective uncoiling of the long bisphenoxybiphenyl unit about its ether linkages could provide a mechanism for considerable chain extension.

Thermal properties

The thermal behavior data of the polymers were evaluated by DSC and TGA. The relevant data are summarized in Table 5. DSC experiments were carried out at a heating rate of 15°C min⁻¹ under nitrogen atmosphere. Rapid cooling from 400°C to room temperature producing predominantly amorphous samples, so the T_g of all the PEIs could be easily read in the subsequent heating traces. The T_g values of the **IV** series PEIs were in the range of 245–315°C, correlated with diamine structures. Polymer **IV_b** exhibited lower T_g than **IV_a** because of the more flexible backbone arising

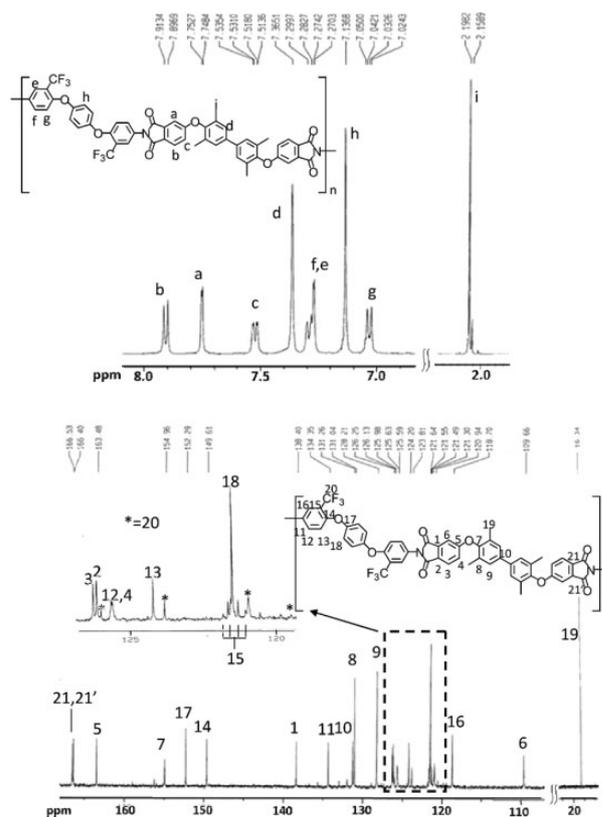


Figure 7. ¹H and ¹³C NMR spectra of PEI **IV_a** in CDCl₃. ¹H NMR: proton nuclear magnetic resonance; ¹³C NMR: carbon nuclear magnetic resonance; CDCl₃: deuterated chloroform.

from *ortho*-substituted phenylene units. PEI **IV_d** showed the highest T_g of 315°C because of the increase of chain rigidity caused by the tetramethyl substitution *ortho* to the ether linkages in the diamine moiety. PEI **IV_d** exhibited an increased T_g by 30°C than its analogous **IV_c** without the methyl substituents was due to the hindrance effect of the chain rotation in the substituted polymer. PEIs **IV_e** and **IV_f** exhibited relatively lower T_g than others due to their more flexible backbones arising from the isopropylidene and hexafluoroisopropylidene linkages. **IV_g** displayed a relatively higher T_g than **IV_e** and **IV_f** films, attributed to the polar sulfonyl group. Furthermore, **IV** series showed slightly lower T_g than those of the corresponding nonfluorinated **V** counterparts for almost all cases. This might be due to the decreased electronic interactions and less dense packing caused by the incorporation of bulky pendent CF₃ groups.

The temperatures at a 10% weight loss (T_{10}) of the PEIs under nitrogen and air atmospheres stayed within the range of 490–524°C and 491–523°C, respectively. In addition, their char yields at 800°C under nitrogen atmosphere are more than 54% (Table 5). As expected, the methyl-substituted **IV_d** began to decompose at lower temperatures compared to other PEIs. **IV_g** also exhibited relatively lower T_{10} value due to the C–S weak linkage of the sulfone linkage. For comparison, TGA thermograms of **IV_a** and its

Table 2. Solubility behavior of PEIs in various organic solvents.

Polymer	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH ₂ Cl ₂	CHCl ₃
IV _a (C)	+++	+++	+++	+	+	++	+++	+++	+++	+++
IV _b (C)	+++	+++	+++	+	++	+++	+++	+++	+++	+++
IV _c (C)	+++	+++	++	–	+	+++	+++	+++	+++	+++
IV _d (C)	+++	+++	++	–	+	+++	+++	+++	+++	+++
IV _e (C)	+++	+++	++	–	+	+++	+++	+++	+++	+++
IV _f (C)	+++	+++	+++	+	++	+++	+++	+++	+++	+++
IV _g (C)	+++	+++	+++	+	+	+++	+++	+++	+++	+++
IV _a (H)	+++	+++	+++	+	+	+++	+++	+++	+++	+++
IV _c (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
V _a (H)	–	–	–	–	–	–	–	–	–	–
V _b (H)	+	–	–	–	–	–	–	–	–	–
V _c (H)	–	–	–	–	–	–	–	–	–	–
V _d (H)	–	–	–	–	–	–	–	–	–	–
V _e (H)	–	–	–	–	–	–	–	–	–	–
V _f (H)	+	+	+	–	–	++	–	++	++	++
V _g (H)	–	–	–	–	–	–	–	–	–	–

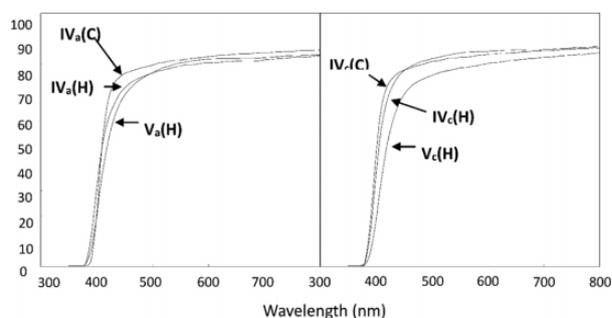
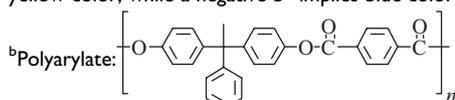
+++ : soluble at a concentration of 10% (100 mg sample in 1 mL of the solvent); ++ : soluble at 5%; + : soluble at 1%; – : insoluble; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran; C: chemical imidization method; H: thermal imidization method.

Table 3. Color coordinates and the cutoff wavelength (λ_0) from ultraviolet–visible spectra for **IV** and **V** series.

Polymer	Film thickness (μm)	Color coordinates ^a			λ_0 (nm)
		b*	a*	L*	
Blank	–	1.0	–0.4	96.2	–
Polyarylate ^b	51	3.3	–0.77	98.9	–
IV _a (C)	54	5.2	–1.6	95.3	374.5
IV _b (C)	58	5.9	–1.7	95.1	379.5
IV _c (C)	56	5.3	–1.7	95.5	375.5
IV _d (C)	57	7.3	–2.4	95.2	374.0
IV _e (C)	55	6.1	–1.8	95.0	380.0
IV _f (C)	58	5.6	–1.5	95.3	372.0
IV _g (C)	54	5.4	–1.4	95.1	375.0
IV _a (H)	55	16.9	–4.1	88.2	376.5
IV _c (H)	52	12.4	–3.0	88.8	376.0
V _a (H)	73	26.6	–5.1	90.6	386.0
V _b (H)	53	22.1	–3.8	88.1	382.0
V _c (H)	54	15.5	–4.3	94.1	378.0
V _d (H)	57	20.4	–4.7	92.9	375.0
V _e (H)	55	16.8	–3.0	91.9	374.5
V _f (H)	74	15.3	–2.8	91.4	374.0
V _g (H)	57	34.8	0.4	83.8	384.0
Kapton	41	83.8	5.0	88.1	444.0

C: chemical imidization method; H: thermal imidization method.

^aThe color parameters were calculated according to a CIE LAB equation. L* is lightness; 100 means white, while 0 implies black. A positive a* means red color, while a negative a* indicated green color. A positive b* means yellow color, while a negative b* implies blue color.

**Figure 8.** Ultraviolet–visible spectra of **IV_a**, **IV_c** and **V_a** PEI films.**Table 4.** Tensile properties of the PEIs.

Polymer ^a	Strength at yield (MPa)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
IV _a	92	85	11	1.8
IV _b	–	100	9	2.0
IV _c	–	103	54	1.7
IV _d	–	104	68	1.7
IV _e	–	94	11	2.1
IV _f	–	96	15	1.6
IV _g	–	105	9	2.0

^aThe PEI samples were prepared by the chemical imidization method.

analogous **IV'_a** without methyl substituents are illustrated in Figure 9. Under nitrogen atmosphere, **IV_a** showed a distinct decomposition in the temperature range from 450°C to 670°C. However, the char yield of **IV_a** at 800°C was higher than that of **IV'_a**. This might be explained by the fact that the methyl substituents decompose at an early stage resulting in

Table 5. Thermal properties of the PEIs.

Polymer ^a	T_g (°C) ^b	T_{10} (°C) ^c		Char yield (%) ^d
		Under nitrogen atmosphere	Under air atmosphere	
IV _a	269	517	512	57
IV _b	254	504	508	58
IV _c	285	524	523	62
IV _d	315	493	491	62
IV _e	249	502	514	55
IV _f	245	519	523	54
IV _g	267	490	498	55
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V _a	270	530	528	63
V _b	264	512	506	59
V _c	303	533	508	59
V _d	326	498	495	53
V _e	275	530	531	58
V _f	280	540	522	68
V _g	285	518	527	60

T_g : glass transition temperature; T_{10} : 10% weight loss temperature.

^aIV series were obtained from chemical imidization method and V series were obtained from thermal imidization method.

^bBaseline shift in the second heating DSC traces, with a heating rate of 15°C min⁻¹.

^cTemperatures at which 10% weight loss were recorded by TG at a heating rate of 20°C min⁻¹.

^dResidual weight (%) when heated at 800°C under nitrogen atmosphere.

benzyl radicals, which might couple forming a cross-linked polymer network.¹⁶ Similar behavior was also observed under the air atmosphere.

Electrical and moisture absorption properties

The dielectric constants and moisture absorption for all PEIs are presented in Table 6. The IV series PEIs exhibited lower dielectric constants (2.95–3.29 at 1 MHz) than the corresponding nonfluorinated V series (3.20–3.41 at 1 MHz). The presence of bulky CF₃ groups resulted in less packing density of the polymer chains, and the strong electronegativity of fluorine atoms decreased the polarizability of C–F bonds, thus leading to the decrease in dielectric constants. In addition, the IV_f with additional hexafluoroisopropylidene linkage in the diamine component exhibited the lowest dielectric constants due to the higher fluorine content in the polymer chain. As expected, the IV series PEIs exhibited lower moisture absorption (0.17–0.86%) than the V series ones (0.37–1.04%) because of the hydrophobicity of CF₃ group. The relative low moisture absorption characteristics also can ensure these polymers have stable dielectric performance.

Conclusions

Novel optically transparent and organosoluble fluorinated PEIs were successfully synthesized from a tetramethyl-

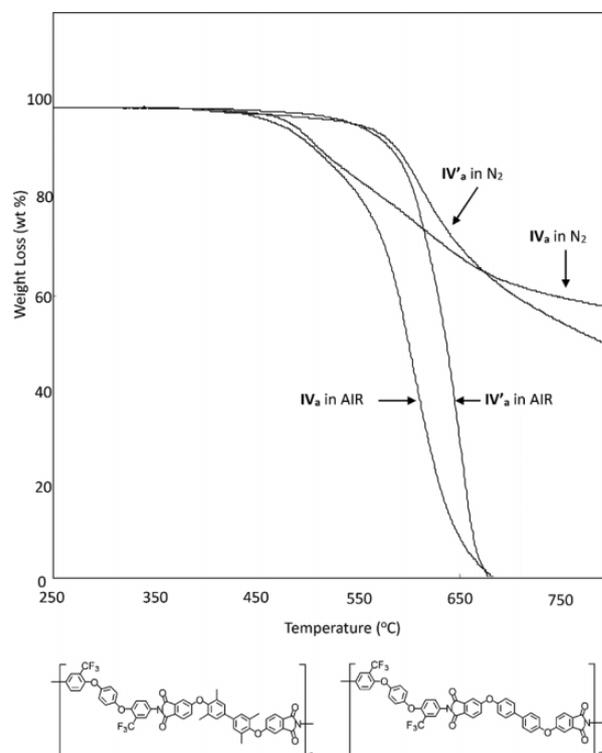


Figure 9. Typical TGA curve of IV_a and IV'_a with a heating rate of 20°C min⁻¹. TGA: thermogravimetric analysis.

Table 6. Moisture absorption and dielectric constants of the PEIs.

Polymer ^a	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (dry)			
			1 kHz	10 kHz	1 MHz	40 MHz
IV _a	47	0.31	3.33	3.29	3.26	3.28
IV _b	54	0.65	3.42	3.37	3.29	3.32
IV _c	72	0.42	3.26	3.26	3.20	3.23
IV _d	68	0.32	3.31	3.25	3.20	3.24
IV _e	64	0.21	3.16	3.16	3.10	3.13
IV _f	83	0.17	3.07	3.02	2.95	2.99
IV _g	59	0.86	3.29	3.24	3.17	3.20
<hr/>						
V _a	87	0.79	3.48	3.47	3.41	3.44
V _b	72	0.89	3.45	3.41	3.32	3.35
V _c	34	0.60	3.39	3.35	3.28	3.32
V _d	53	0.80	3.42	3.40	3.33	3.36
V _e	41	0.50	3.37	3.36	3.33	3.31
V _f	94	0.37	3.31	3.25	3.20	3.25
V _g	76	1.04	3.36	3.34	3.30	3.31

^aIV series were obtained from chemical imidization method and V series were obtained from thermal imidization method.

biphenyl bis(ether anhydride) and various fluorinated bis(ether amine)s via thermal or chemical imidization. The combination of flexible ether linkage and bulky CF₃

substituent onto the PI backbones could reduce overall charge transfer complex formation and improve the solubility to organic solvents. In particular, the PEI films based on chemical imidization process had low yellowness index (b^*) around 5, which is close to the value of a transparent polyarylate polymer ($b^* = 3.3$). The highly transparent and organosoluble films were achieved without much sacrifice in thermal stability and mechanical properties. In addition, the **IV** series PEI films exhibited relatively higher transmittance, better solubility, lower moisture, and dielectric constant than the nonfluorinated **V** series analogs. Thus, these properties suggest the potential usefulness of these PEIs in microelectronic and optoelectronic applications. Among those fluorinated PEIs, **IV_c** exhibited the most balanced performance on optical, thermal, mechanical, and solubility properties. It might be further evaluated as flexible and colorless substrates for optoelectronic applications.

Declaration of Conflicting Interests

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