Synthesis and Properties of Cross-Linkable High Molecular Weight Fluorinated Copolyimides

Hongyan Yao,[1] Yunhe Zhang,[1] Yu Liu,[1,2] Kaiyuan You,[1] Shanyou Liu,[1] Baijun Liu,[1] Shaowei Guan[1]

[1]Alan G. MacDiarmid Institute, Jilin University, Qianjin Street 2699, Changchun 130012, People's Republic of China
[2]Institute of Metal Research Chinese Academy of Sciences, Wenhua Road 72, Shenyang 110016, People's Republic of China
Correspondence to: S. Guan (E-mail: guansw@jlu.edu.cn)

Received 7 August 2013; accepted 30 October 2013; published online 17 November 2013
DOI: 10.1002/pola.27007

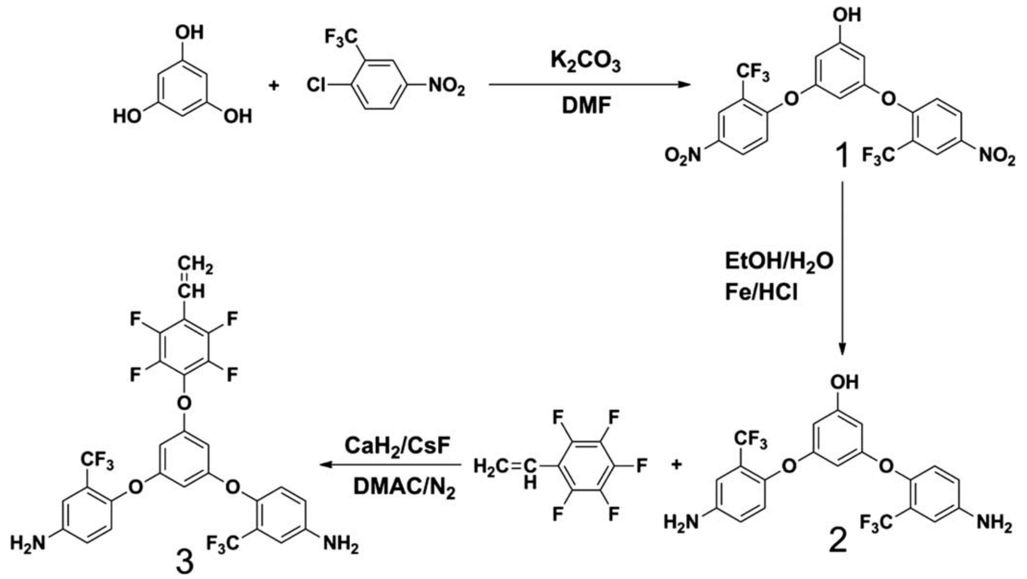
ABSTRACT: A series of novel high molecular weight fluorinated co-polyimides (Co-PIs) containing styryl side chain based on 1,3-bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)benzene (6FTFPB) were successfully synthesized. The weight-average molecular weights (M_ws) and polydispersities of the co-polyimides were in the range 8.93–10.81 $\times$ 10^4 and 1.33–1.82, respectively. The co-polyimide film showed excellent solubility in organic solvents, high tensile properties (tensile strength exceeded 91 MPa), excellent optical transparency (cut-off wavelength at 332–339 nm and light transparencies above 89% at a wavelength of 550 nm), and high thermal stability (5% thermal weight-loss temperature up to 510 °C). The casting and spinning films could be cross-linked by thermal curing. The cured films show better combination property (including excellent resistance to solvents) than that of co-polyimides. For instance, the glass transition temperature of Co-PI-1 (the molar weight ratio of 6FTFPB was 30%) increased from 217 to 271 °C, the tensile strength enhanced from 94 to 96 MPa, the 5% thermal weight-loss temperature improved from 514 to 525 °C. Moreover, after cured, Co-PI-1 film also has a coefficient of thermal expansion (CTE) value of 60.3 ppm $^{\circ}C^{-1}$, low root mean square surface roughness (R_q) at 4.130 nm and low dielectric constant of 2.60. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 349–359

KEYWORDS: crosslinking; fluoropolymers; polyimides; solubility; transparency; refractive index

INTRODUCTION As a kind of high-performance polymeric materials, aromatic polyimide (PI) has exhibited remarkably comprehensive characters, such as excellent thermal stability, high mechanical strength, good electric and optical properties.[1–5] In the past several decades, fluorinated polyimides with low moisture absorption, low refractive index, and low dielectric constant while maintaining many of advantages of polyimides have been prepared through introducing fluorine to the structure of the macromolecules. In addition, the incorporation of fluorine-containing substituents ($-CF_3$) is also known to enhance the solubility and optical transparency of polyimides.[6–8] Consequently, the fluorinated polyimides are of considerable interest for optical and electronic applications in recent years.

However, during the fabricated process of multilayer optoelectronic device, the polymeric material must have good resistance to organic solvents. In another word, the initial material could be dissolved in organic solvents, but insoluble after being films. For the purpose, the introduction of the cross-linkable structure becomes necessary. Styryl and phenylethynyl are both commonly used cross-linking groups. Compared to phenylethynyl, styryl can undergo cross-linking reaction by both thermal heating and UV irradiation. Besides, the thermal cross-linked reaction of styryl is readily accomplished by heating at a relative low temperature in the presence of a small amount of thermal initiator.[9,10]

Over the past decade, a great deal of effort has been concentrated on the introduction of cross-linkable structure to the end of oligomers, internal groups, or pendant groups of macromolecules. In recent years, phenylethynyl terminated imide oligomers have been widely studied.[11–17] However, to ensure the cross-linkable groups terminated oligomers have sufficient high cross-linking density, it is necessary to reduce the molecular weight of oligomers. Therefore, some properties such as mechanical strength and thermal properties should be sacrificed. For example, Yang et al. synthesized a series of phenylethynyl terminated imide oligomers based on a new endcapping agent. For these oligomers, the lower M_n oligomers showed lower T_g values, lower curing onset temperatures and stronger curing exothermal peaks. After thermal curing, the oligomer with the lowest molecular weights possessed the highest T_gs and worst mechanical properties which the tensile



SCHEME 1 Synthesis of the diamine monomer 1,3-bis (2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy) benzene (6FTFPB).

strength and elongation at break as low as 41.7 MPa and 6.2%, respectively.[16] To balance the relationship between the cross-linking density and molecular weight, some macromolecules containing cross-linkable group in the main chain have been synthesized.[18,19] But the cross-linked temperature of the macromolecules is much higher than the terminated oligomer, because the movement of cross-linkable internal groups is more difficult. As a strategy to solve the problem above, cross-linkable side chain copolymers have been extensively studied.[20–22] However, there are few studies on the polyimide which contain the cross-linkable side chain in the literature.

In our study, to introduce cross-linkable functionality into the side chain of fluorinated PIs and to ensure a suitable cross-linking density, a fluorinated diamine monomer 1,3-bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)-benzene (6FTFPB) was designed and prepared via a nucleophilic substitution between 5-bis(4-amino-2-trifluoromethylphenoxy)phenol and 2,3,4,5,6-pentafluorostyrene (as shown in Scheme 1). A series of novel cross-linkable fluorinated co-polyimides with styryl moieties in the side chain were prepared. By varying the feed ratio of diamine monomers, polymer films with different styryl content have been prepared. The solubility, thermal, mechanical, and optical properties of the PIs were evaluated. It was characterized that PIs exhibited good solubility, excellent mechanical properties, and high optical transparency. Moreover, we investigated the thermal crosslinking of the co-polyimides. After cured, the cross-linked PI films exhibited excellent chemical resistant, high thermal and mechanical properties, low dielectric constant, and excellent surface planarity.

EXPERIMENTAL

Materials

Phloroglucinol, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and 2-chloro-5-nitrobenzotrfluoride were purchased from Aldrich Chemical and used without further purification. 1,4-Bis-(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) was synthesized in our laboratory according to the literature.[7] *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and triethylamine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Measurements

Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min^{-1} using polystyrene as a standard. FTIR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 300 MHz for ^{1}H and 470 MHz for ^{19}F. The chemical shifts relative to tetramethylsilane (TMS) for ^{1}H NMR and CFCl$_3$ for ^{19}F NMR as internal reference are reported on the ppm scale. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 10 °C min^{-1} from 100 to 400 °C under nitrogen. Thermo gravimetric analysis (TGA) on a Perkin Elmer Pyris 1 thermal analyzer system was used to assess the thermal stability of the polyimides. Before the analysis, the polyimides were dried and kept in the TGA furnace at 100 °C under air for 30 min to remove water. The samples were evaluated over a temperature range of 100–800 °C at a heating rate of 10 °C min^{-1} under nitrogen. The coefficient of thermal expansion (CTE) of the PI films was measured by a thermal mechanical analysis (TMA) using a thermomechanical analyzer TMA/SDTA841e (Mettler Toledo) at a heating rate of 5 °C min^{-1}. The CTE values were calculated as a mean coefficient of linear thermal expansion in the temperature range of 50–250 °C after heating beyond T_g followed by cooling. The refractive indices of the polymer films were obtained using a Gaertener L116B spectroscopic ellipsometer. The dielectric constants of the polymer films (diameter = 13 mm and thickness = 0.5 mm, prepared by compression molding, and then coated with silver by a vacuum evaporation method) were obtained using an HP 4192A LF impedance gain-phase analyzer with an HP-6047C. UV transparencies were measured by a Shimadzu UV 2501-PC spectrophotometer. The mechanical tests in tension were performed using a Shimadzu AG-I at a constant crosshead speed of 10 mm min^{-1}. The photographs of the polyimide films were taken by Canon EOS 600D. Atomic force microscope (AFM) images were recorded with a Nanoscope IIIa scanning probe microscope from Digital Instruments using tapping mode under ambient conditions. The gel content of the crosslinked samples was determined according to ASTM D2765 method. Samples were extracted by Soxhlet's apparatus in DMAc for 48 h. The residue after extraction was taken as the gel component, and the gel content was calculated according to the following eq (1).

$$\text{Gel content} = \frac{W_2}{W_1} \times 100\% \quad (1)$$

where W_1 and W_2 are the weights of the samples before and after refluxed in DMAc for 48 h.

Monomer Synthesis

Synthesis of 3,5-Bis(4-nitro-2-trifluoromethylphenoxy) phenol (1)

A mixture of phloroglucinol (12.61 g, 0.10 mol), 2-chloro-5-nitrobenzotrfluoride (45.11 g, 0.20 mol), and K_2CO_3 (16.59 g, 0.12 mol) were dissolved in DMF (200 mL) and toluene (40 mL) in a 500 mL three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean-Stark trap, and a reflux condenser (Scheme 1). The apparatus was purged with nitrogen. The reaction mixture was refluxed at 120 °C for 5 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 151 °C and refluxed for 8 h under a nitrogen atmosphere. After being poured into deionized water (2 L), the precipitate was collected by filtration. The crude product was washed with deionized water to give earthy yellow powder. Yield: 89%. Mp (melting point): 169.4 °C. IR (KBr, cm^{-1}): 1530 and 1354 (—NO_2 stretch), 3446 (O—H), 1143 (C—F stretch).

^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.534–6.541 (d, J = 2.1 Hz, 2H), 6.610–6.624 (m, 1H), 7.331–7.365 (d, J = 10.2 Hz, 2H), 8.470–8.505 (m, 10.5 Hz, 4H), 10.489 (s, 1H, OH). Mass spectrum: m/z 501.9.

Synthesis of 3,5-Bis (4-amino-2-trifluoromethylphenoxy)phenol (2)

A total of 3,5-bis(4-nitro-2-trifluoromethylphenoxy)phenol (28.90 g, 0.057 mol), Fe (38.51 g, 0.68 mol), and 50% aqueous ethanol (180 mL) were mixed in a 250 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser (Scheme 1). The mixture was refluxed with stirring. To the solution, a mixture of HCl (2 mL, 0.023 mol) and 40 mL of 50% aqueous ethanol was then slowly added after which, the reaction mixture was further refluxed for 5 h and 0.96 g NaOH was added. The hot mixture was then filtered, and the filtrate was then distilled to remove the solvent *in vacuo*. The crude product was purified by recrystallization from ethanol and deionized water to give a brownish red solid. Yield: 84%. Mp: 176.8 °C. IR (KBr, cm^{-1}): 3430, 3353, and 3300 (N—H stretch), 1127 (C—F stretch).

^{1}H NMR (300 MHz, DMSO-d_6) δ: 5.486 (s, 4H, NH_2), 5.850–5.881 (m, 3H), 6.795–6.833 (m, 2H), 6.887–6.929 (m, 4H), 9.627 (s, 1H, OH). ^{19}F NMR (470 MHz, DMSO-d_6) δ: −60.703 (s, 6F). Mass spectrum: m/z 443.7.

Synthesis of 1,3-Bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)benzene (3)

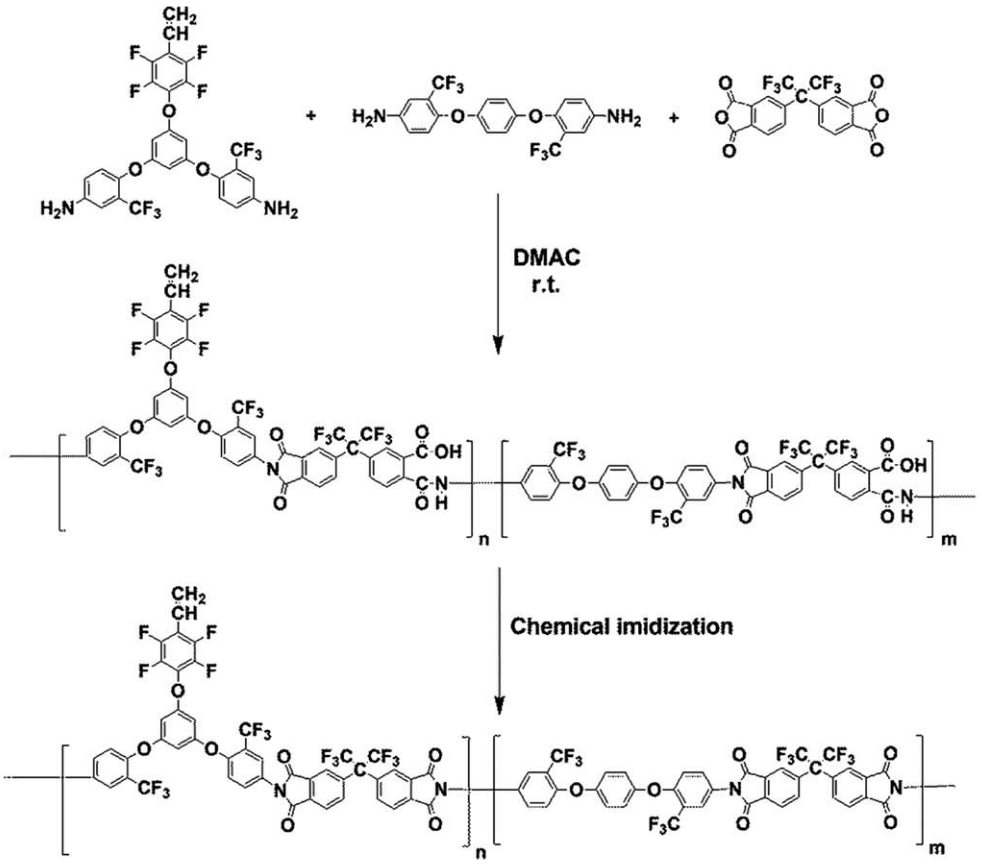
3,5-Bis(4-amino-2-trifluoromethylphenoxy)phenol (1.31 g, 2.9 mmol), 2, 3, 4, 5, 6-pentafluorostyrene (0.6867 g, 3.5 mmol), calcium hydride (0.2482 g, 5.8 mmol), and cesium fluoride (0.0448 g, 0.29 mmol) were added into a 25 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a water condenser (Scheme 1). Then, DMAc (13 mL) was added into the flask under the nitrogen atmosphere. The mixture was heated to 80 °C with stirring under nitrogen in the dark for 18 h. After cooled to room temperature, it was poured into 150 mL deionized water, washed with deionized water, extracted with ether, dried with anhydrous $MgSO_4$, and then filtrated. The solvent was evaporated under vacuum, and the residue was then purified by column chromatography (petroleum ether/ethyl acetate, 4/5) to afford the pure products. Yield: 68%. Mp: 145.8 °C. IR (KBr, cm^{-1}): 3485 and 3379 (N—H stretch), 1635 (C—C), 1127 (C—F stretch).

1H NMR (300 MHz, DMSO-d_6) δ: 5.501 (s, 4H, NH_2), 5.809–5.848 (d, J = 11.7 Hz, 1H), 5.942–5.956 (m, 1H), 6.027–6.087 (d, J = 18 Hz, 1H), 6.367 (s, 2H), 6.652–6.816 (m, 3H), 6.876 (s 2H), 6.917–6.946 (d, J = 8.7 Hz, 2H). ^{19}F NMR (470 MHz, DMSO-d_6) δ: −60.818 (s, 6F), −144.294 (2F, m), −156.465 (2F, m). Mass spectrum: m/z 617.9. ELEM. ANAL Calcd for $C_{28}H_{16}F_{10}N_2O_3$: C 54.38, H 2.61, N 4.53; found: C 54.51, H 2.64, N 4.23.

Polymer Synthesis

Synthesis of the Fluorinated Homo-PIs

Homo-PI-1: A three-necked flask was charged with diamine 6FAPB (0.6425 g, 1.5 mmol) and 9 mL of DMAc. The solution was stirred under a nitrogen atmosphere until diamine dissolved completely, and then 6FDA (0.6664 g, 1.5 mmol) was added (Scheme 2). The reaction mixture was stirred at ambient temperature for 24 h under a nitrogen atmosphere to form poly(amic acid) solution with 15 wt % solid content. Chemical imidization was performed via the addition of 1.5 g of triethylamine and 4.5 g of acetic anhydride into the PAA solution at ambient temperature. The mixture was stirred at 60 °C for 6 h to yield a polyimide solution. Then the solution was poured into anhydrous ethanol to give a precipitate and



Co-Polyimide	n/m
1	0/10
2	3/7
3	5/5
4	7/3
5	10/0

SCHEME 2 Synthesis of the Co-PIs.

washed thoroughly with anhydrous ethanol. Finally, the product was dried at 80 °C *in vacuo* for 24 h. Yield: 91.6%. Homo-PI-2 was synthesized in an analogous procedure. ELEM. ANAL Calcd for $C_{47}H_{18}F_{16}N_2O_7$: C 54.99, H 1.77, N 2.73; found: C 55.35, H 1.73, N 2.37.

Synthesis of the Cross-linkable Fluorinated Co-PIs

A typical synthetic procedure for the preparation of cross-linkable fluorinated co-polyimide (Co-PI-2) is as follows (Scheme 2). To a solution of 6FTFPB (0.4638 g, 0.75 mmol) and 6FAPB (0.3212 g, 0.75 mmol) in DMAc (10 mL), 6FDA (0.6664 g, 1.5 mmol) was added. The mixture was stirred in nitrogen at room temperature for 24 h to yield a viscous poly(amic acid) (PAA) solution with 15 wt % solid content. Chemical imidization was performed via the addition of 1.5 g of triethylamine and 4.5 g of acetic anhydride into the PAA solution at ambient temperature. The mixture was stirred at 60 °C for 6 h to yield a polyimide solution. Then it was poured into anhydrous ethanol to give a precipitate. Co-PI-2 was collected by filtration, washed thoroughly with anhydrous ethanol, and dried at 80 °C *in vacuo* for 24 h. Yield: 94.2%. Other Co-PIs were synthesized in an analogous procedure.

Film Preparation for the Measurement of Optical and Mechanical Properties

Polyimides (0.5 g) were dissolved in DMAc (5 mL) overnight. Afterwards, the solutions were then filtered through a Teflon syringe filter with a pore size of 0.22 μm and cast directly onto clean glass plates with a programmed procedure (25 °C, 6 h; 60 °C, 6 h; 80 °C, 6 h; 120 °C, 6 h) in a vacuum oven to remove the solvents. After dried thoroughly, tough and flexible films of PIs were obtained (Fig. 7). The thicknesses of the films were in the range of ~30 μm. To measure the properties of cured films, the polyimide films were put into a vacuum oven and treated at 260 °C for 2 h to obtain the cured films.

Film Preparation for the Measurement of Refractive Index

The polymer solutions were prepared in DMAc (1 g/10 mL). The solutions were then filtered through a Teflon syringe filter with a pore size of 0.22 μm and spincoated onto a SiO_2/Si substrate with a programmed procedure (25 °C, 6 h; 60 °C, 6 h; 80 °C, 6 h; 120 °C, 6 h) under vacuum. Thermal curing of the films was then performed by heating slowly to 260 °C and maintaining this temperature for 2 h in a vacuum oven.

RESULTS AND DISCUSSION

Synthesis and Characterizations of the Monomer

To improve chemical stabilities of the resulting materials, many monomers have been designed to contain either thermal or photochemical reactive groups that can undergo intermolecular reactions under external stimuli to form

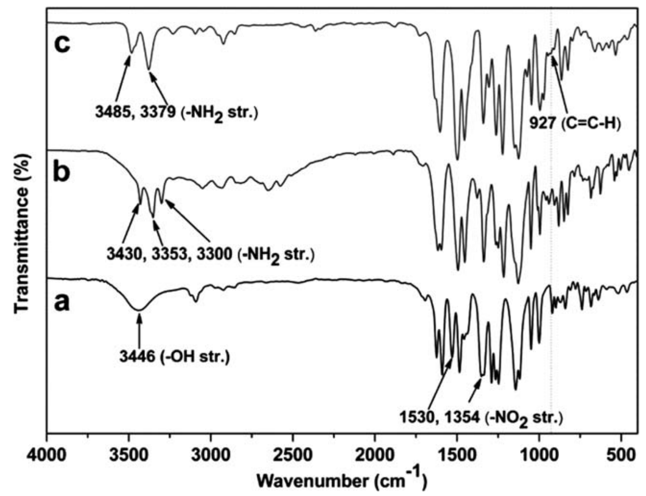


FIGURE 1 FTIR spectra of organic monomers. (a) 3,5-Bis(4-nitro-2-trifluoromethylphenoxy)phenol. (b) 3,5-Bis(4-amino-2-trifluoromethylphenoxy)phenol. (c) 1,3-Bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)benzene.

cross-linked polymer networks. A novel diamine monomer with styryl side chain was designed and prepared as shown in Scheme 1. Monomer 6FTFPB was prepared by a three-stage synthetic procedure starting with nucleophilic substitution reaction of phloroglucinol and 2-chloro-5-nitrobenzotrfluoride. Then the product of first step was deoxygenized by Fe/HCl in ethanol/deionized water at 90 °C. Finally, as described similarly in the literature,[9,10] the monomer 6FTFPB was also synthesized through a nucleophilic substitution reaction.

The structures of these monomers were confirmed by FTIR, LC-MS, ^{1}H NMR, and ^{19}F NMR spectroscopy. Figure 1 shows the FTIR spectra of monomers 1, 2, and 3. The nitro group of 1 gave characteristic absorption bands at 1354 and 1530 cm^{-1} (NO$_2$ asymmetric and symmetric stretching). In addition, the hydroxyl of 1 exhibited characteristic absorption in the region of 3307–3614 cm^{-1} (O—H stretch). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group exhibited a pair of N—H stretching bands in the region of 3304–3437 cm^{-1}. Finally, after the second step of nucleophilic substitution reaction, the vinyl group of monomer 3 gave absorption band at 927 cm^{-1} (C═C—H out of plane vibrations). The ^{1}H NMR and ^{19}F NMR spectra of 6FTFPB are shown in Figure 2. As shown in Figure 2(a), the signals at 5.5 ppm were assigned to the protons in the amino groups of monomer 6FTFPB, while those characteristic signals at 5.8–6.1 ppm were ascribed to the protons on the vinyl group of the tetrafluorostyro units. To confirm the structure of monomer 6FTFPB further, ^{19}F NMR measurement was also performed. The signals at −156.53 and −144.36 ppm corresponded to the aromatic fluorine atoms, and the peak at −60.70 ppm was assigned to the fluorine atoms of —CF$_3$. These results indicated that we had successfully synthesized the 1,3-bis (2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)benzene.

Synthesis and Characterizations of the Polymer

Two Homo-PIs and a series of Co-PIs in Scheme 2 were prepared via the conventional two-step method by reacting equimolar amounts of the diamines with 6FDA to form the poly (amic-acid) at ambient temperature and sequential chemical imidization by adding mixture of acetic anhydride and triethylamine into PAA solution at ambient temperature followed by heating at 60 °C for 6 h to obtain polyimides. The molecular weights of PIs were determined by GPC and the results are summarized in Table 1. The weight-average molecular weights (M_ws) and polydispersities were recorded in the range of 8.93–10.81 × 10^4 and 1.33–1.82, respectively.

The chemical structures of the PIs were characterized with FTIR and NMR spectroscopy. The typical FTIR spectrum of Co-PI-1 is shown in Figure 6. All the PIs exhibited characteristic absorption bands of the imide ring near 1788 and 1734 cm^{-1} due to C═O asymmetric and symmetric stretching, and 1375 cm^{-1} ascribing to C—N stretching. Furthermore, there

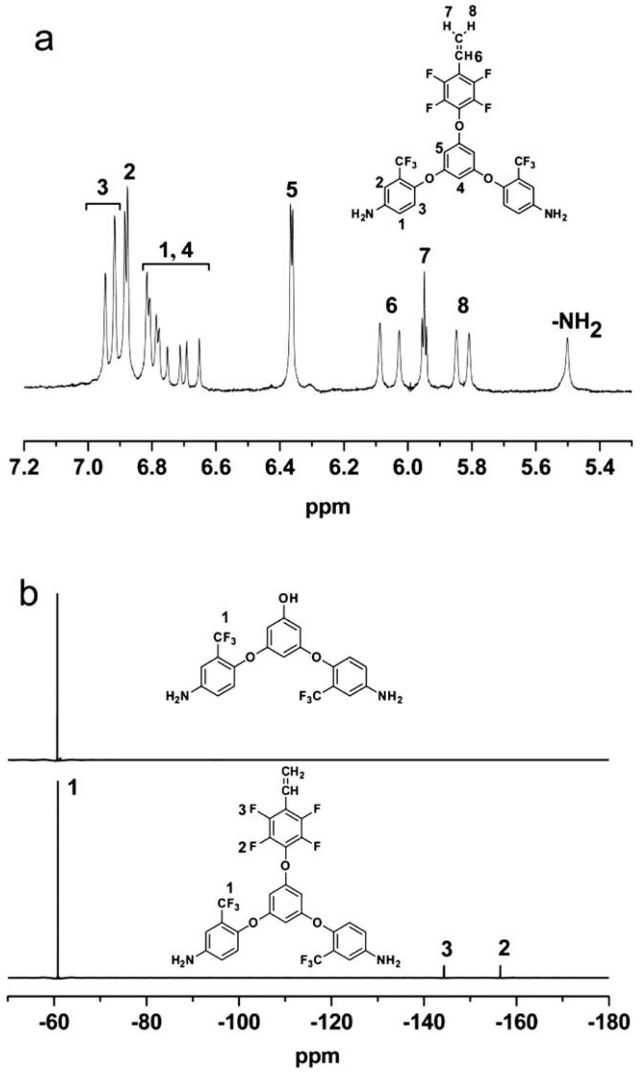


FIGURE 2 (a) ^{1}H NMR and (b) ^{19}F NMR spectra of the 6FTFPB in DMSO-d_6.

TABLE 1 GPC Data and Monomer 6FTFPB Content of PIs

Polymers (n/m)	6FTFPB Content (mol %)[a]	6FTFPB Content from ^{1}H NMR[b]	Yield (%)	M_n[c] ($\times 10^4$)	M_w[c] ($\times 10^4$)	PDI[d] (M_w/M_n)
Homo-PI-1 (0/10)	0	0	91.6	5.76	10.04	1.74
Co-PI-1 (3/7)	30	32.5	93.4	7.73	10.31	1.33
Co-PI-2 (5/5)	50	50.7	94.2	5.47	8.93	1.63
Co-PI-3 (7/3)	70	70.6	89.7	5.13	9.34	1.82
Homo-PI-2 (10/0)	100	100	88.2	6.99	10.81	1.55

[a] Feed molar ratio of 6FTFPB relative to the total diamines.

[b] Feed molar ratio of 6FTFPB relative to the total diamines calculated by the ^{1}H NMR of PIs.

[c] M_n, M_w values were determined by GPC in THF with PS as standard.

[d] PDI values (M_w/M_n) were determined by GPC in THF with PS as standard.

was not an amide carbonyl peak at 1650 cm^{-1}, thus indicating complete imidization during polycondensation. From the ^{1}H NMR and ^{19}F NMR (Fig. 3), the polymer structures were found in good agreement with the designed structures. In the ^{1}H NMR spectra, three resonances at 5.79, 6.04, and 6.67 ppm were observed and attributed to the protons on the vinyl moiety of tetrafluorostyrol groups. No other aliphatic resonances could be found, indicating that the tetrafluorostyrol units were introduced successfully into fluorinated polymers and were stable to the polymerization and imidization conditions used. Meanwhile, it was observed that these signals attributed to the vinyl group of the tetrafluorostyrol units increased with the increasing feed ratio of monomer 6FTFPB in the Co-PIs. In addition, the protons 3 and 3′ were in the same position of the two kinds of diamines, but due to locating in the polymer segment of different chemical environments, their chemical shifts are different. The peak area of 3 and 3′ was changed as the proportion of the two kinds of diamines varied in the polymerization. According to the ^{1}H NMR, the actual content of monomer 6FTFPB in the Co-PIs was equal to the ratio of the peak area of 3 and the sum of the peak area of 3 and 3′. The value of the content of monomer 6FTFPB was calculated and summarized in the Table 1. On detailed examination of the ^{19}F NMR spectra, it was observed that two little peaks around at −60.8 and −63.0 ppm were attributed to F3, F3′ and F4, F4′ which belonged to the fluorine atoms of —CF_3, respectively. The two peaks at −143.9 and −155.9 ppm were ascribed to the F1 and F2 of the tetrafluorostyrol units, respectively. Compared to the signals of F3, F3′ and F4, F4′, they increased proportionally with the increase of the feed ratio of monomer 6FTFPB. All the characterizations show that the series of polyimides were synthesized successfully.

Solubility of the Polymers

The solubility of synthesized PIs was tested in various organic solvent and the results are summarized in Table 2. The PIs showed an excellent solubility in aprotic polar solvents such as DMSO, DMAc, DMF, and NMP and were also soluble in less polar solvents like THF, $CHCl_3$, and acetone at room temperature. The solubility of polyimides is enhanced due to the introduction of bulky pendant trifluoromethylphenyl group and tetrafluorostyrol units which could inhibit close packing and reduced the interchain interactions to enhance solubility.

Thermal Cross-linking and Thermal Properties of the Polymers

Thermal properties of the PIs were evaluated by DSC, TGA, and TMA. The thermal behavior data of all the PIs are summarized in Table 3. DSC experiments were conducted at a

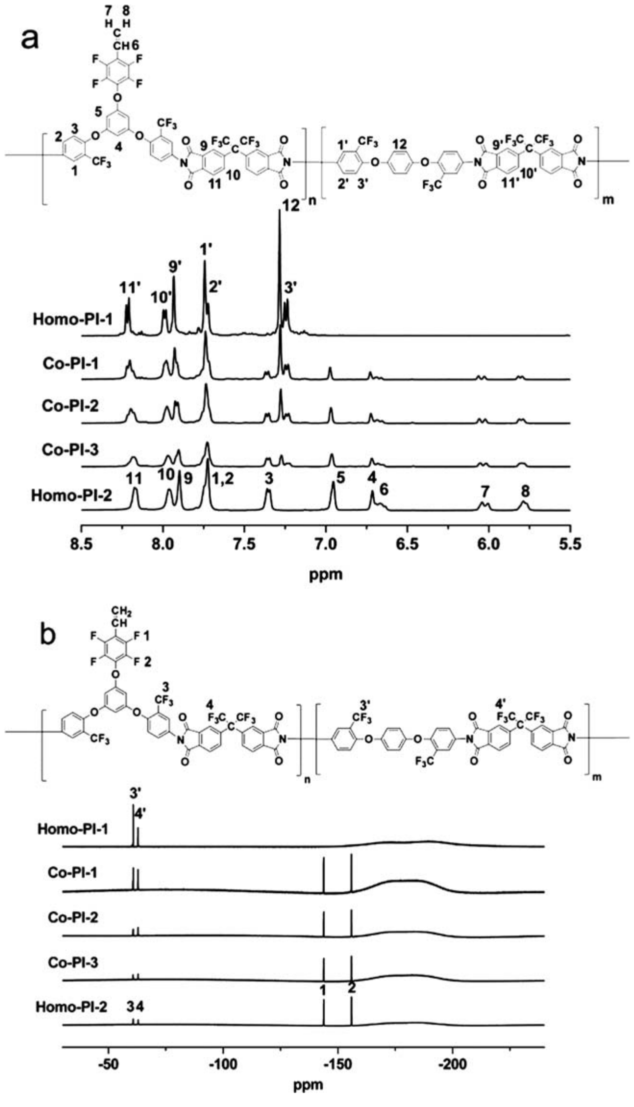


FIGURE 3 (a) ^{1}H and (b) ^{13}C NMR spectra of the PIs in DMSO-d_6.

TABLE 2 Solubility of the PIs in Organic Solvents

Polymers	Solvent[a]							
	NMP	DMAc	DMF	DMSO	THF	$CHCl_3$	Acetone	Ethanol
Homo-PI-1	++	++	++	++	++	++	++	−
Co-PI-1	++	++	++	++	++	++	++	−
Co-PI-2	++	++	++	++	++	++	++	−
Co-PI-3	++	++	++	++	++	++	++	−
Homo-PI-2	++	++	++	++	++	++	++	−

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

[a] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; $CHCl_3$: chloroform.

heating rate of 10 °C min^{-1} in nitrogen. All the PIs' DSC heating scans exhibited only one distinct T_g in the range of 197–230 °C. According to Fox equation, the T_g of a random copolymer can be predicted based on the feed ratio of the monomers using eq (2):[22]

$$\frac{1}{T_g} = \frac{W_{t1}}{T_{g1}} + \frac{W_{t2}}{T_{g2}} \tag{2}$$

where T_g is the glass transition temperature of the copolymer, W_{t1} is the sum of the weight fractions of the repeat units which contain 6FTFPB relative to the all repeat units, W_{t2} is the sum of the weight fractions of the repeat units which contain 6FAPB relative to the all repeat units, T_{g1} and T_{g2} are the glass transition temperatures of the Homo-PIs derived from monomer 6FTFPB with 6FDA (T_{g1} = 197 °C) and from 6FAPB with 6FDA (T_{g2} = 230 °C), respectively. Figure 4 displayed the measured T_g and the predicted trend line according to the Fox equation. A good agreement of the T_gs of the resulting copolymers with the values predicted by the Fox equation was observed. Thus, it can be concluded that the two diamine monomers have been randomly incorporated into the polymers.

The tetrafluorostyrol units in the fluorinated polymers can undergo cross-linking reactions by both thermal heating and UV irradiation. We investigated the thermal crosslinking of the co-polyimides emphatically. The thermal crosslinking of Co-PI-1 was studied by heating the polymer films at 260 °C for 1 h or 2 h in vacuum in the absence of any initiator. As shown in Figure 5, an intense exothermic peak was regarded as the reaction of the vinyl moiety for the uncross-linked polymer. After thermal curing of the Co-PI-1, the T_g increased from 217 to 271 °C. But the T_gs of Co-PI-3 and Homo-PI-2 were not observed in the DSC curve, possibly because the cross-linking density of the two polyimides is large enough to limit the molecular chain movement. The characteristic absorption of the vinyl group near 928 cm^{-1} out of plane vibrations of the vinyl group ($CH_2{=}CH$) was selected to monitor the reaction by FTIR spectroscopy. Figure 6 exhibits the comparisons of FTIR spectra of Co-PI-1 film before and after curing. The absorption peak near 928 cm^{-1} disappeared totally after curing 260 °C for 2 h. ASTM D2765 method was experimentally used to detect the extent of the cross-linking reaction. The cured films were extracted in DMAc for 48 h using Soxhlet's apparatus. And then the gel contents of the polymers were calculated according to eq

TABLE 3 Mechanical Properties, Thermal Properties and Gel Content of PIs

Polymers	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (GPa)	T_g[a] (°C)	$T_{5\%}$[b] (°C)	CTE (ppm °C^{-1})[c]	Gel content[d] (%)
Homo-PI-1	98	14.7	3.7	230	497	76.7	0
Co-PI-1	94 (96)	14.9 (12.5)	3.6 (3.9)	217 (271)	514 (525)	60.3	91.5
Co-PI-2	92 (97)	8.6 (6.4)	3.5 (4.0)	207 (283)	512 (530)	62.8	98.0
Co-PI-3	91 (96)	7.5 (6.7)	3.3 (3.8)	204 (–)	511 (530)	61.6	99.7
Homo-PI-2	87 (92)	5.5 (3.2)	3.1 (3.7)	197 (–)	514 (535)	62.7	99.8

The data in the parentheses were the data of the polyimides after curing at 260 °C for 2 h under vacuum.

[a] Glass transition temperature measured by DSC with a heating rate of 10 °C min^{-1} in nitrogen.

[b] Temperature at 5% weight-loss were recorded by TGA at a heating at 10 °C min^{-1} in nitrogen.

[c] Coefficient of thermal expansion of cured PI films measured by TMA in a temperature range of 50–250 °C at a heating rate of 5 °C min^{-1} in N_2.

[d] Gel content for cured samples.

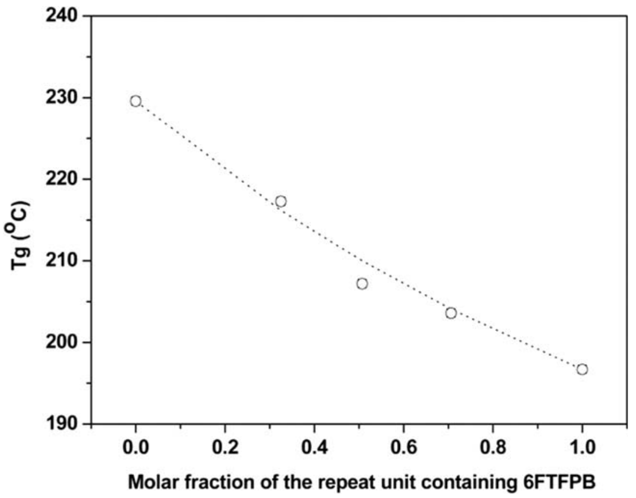


FIGURE 4 Correlation between T_g of PIs and the molar fraction of the repeat unit containing 6FTFPB: (○) experimentally determined T_g values from DSC. The dotted line represents the calculated values according to the Fox equation.

(1). The result indicated that the gel contents of the copolymers were all more than 90%, confirming the formation of a highly cross-linked network with good solvent resistance and the cross-linking films was suitable for multi-layer process.

The thermal stability (T_d, temperature at 5% weight-loss) of PIs was investigated by TGA at a heating rate of 10 °C min^{-1} under nitrogen. The T_ds of uncured Co-PIs were recorded in the range of 511–514 °C. Compared to uncured PIs, the cured Co-PIs have higher T_ds which were in the range of 525–534 °C. This reason is that the Co-PIs have undergone cross-linking reaction for treatment at 260 °C for 2 h. The TGA data indicated that these cured Co-PIs had high thermal stability.

The coefficients of thermal expansion (CTE) of the cured PI films were determined to range from 60.3 to 76.7 ppm °C^{-1}. The CTE is dependent on both backbone chemistry and the morphology and strongly influenced by molecular orientation. In general, polymers consisting of rigid backbone structures and causing a higher degree of in-plane chain orientation have shown relatively low CTE value.[23–26] Compared to Homo-PI-1, other PIs not only possess flexible molecular structures, but also have cross-linkable styryl side groups. The styryl groups underwent cross-linking reaction and formed dense cross-linked structures when cured at 260 °C. Lower CTE of the cross-linked PIs might attribute to the cross-linked structures which limited the macromolecular chain segmental motion. The CTE of all of the PIs are about 60 ppm °C^{-1}, although the content of styryl side groups increase from Co-PI-1 to Homo-PI-2. The phenomena could be ascribed to that the crosslinking densities of these PIs are high enough, when the content of styryl groups is beyond 30%. It is consistent with the results of the gel content characterization. After been extracted by Soxhlet's apparatus in DMAc for 48 h, the gel component of cross-linked PIs was more than 90%. The results also indicated that the cross-linked PIs have excellent chemical resistance.

Mechanical Properties of the Polymers

The mechanical properties of PI films are summarized in Table 3. Before thermal cured, the PI films have tensile strength of 87–98 MPa, tensile modulus of 3.1–3.7 GPa, and elongation at breakage of 5.5–14.9%. By contrast, the mechanical properties of polyimides which were cured at 260 °C for 2 h were 92–99 MPa, 3.7–4.0 GPa, 3.2–14.5%, respectively. Among them, Co-PI-1 offered the best mechanical properties after crosslinking. These results indicate that the incorporation of the tetrafluorostyrol group into the structure of the polyimides retains the good tensile properties.

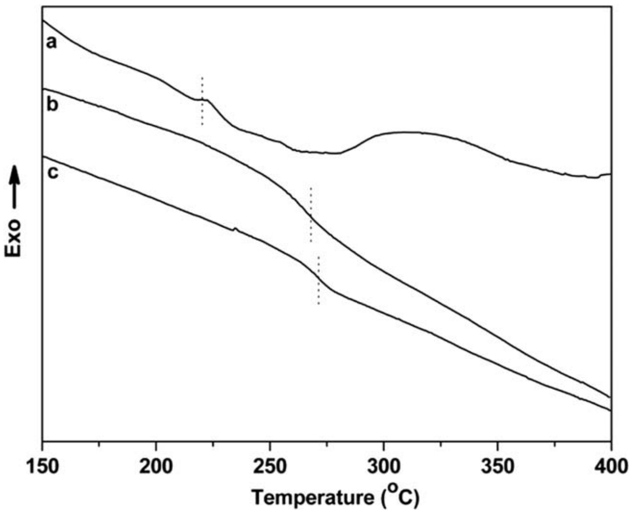


FIGURE 5 DSC curves of Co-PI-1 (a) before curing; (b) after curing at 260 °C for 1 h under vacuum; and (c) after curing at 260 °C for 2 h under vacuum.

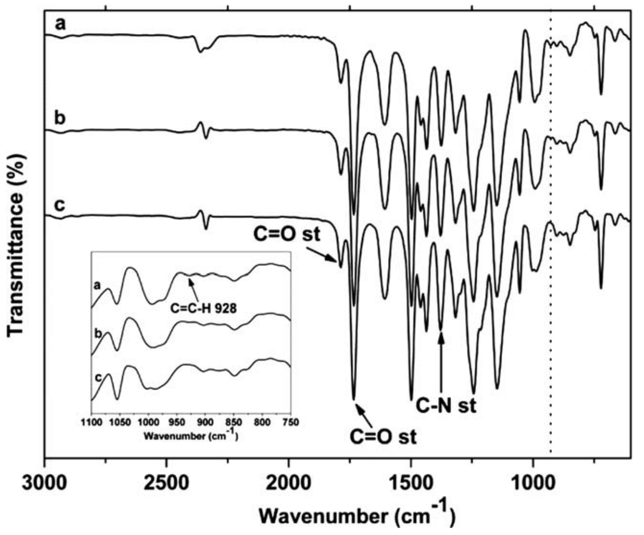


FIGURE 6 FTIR spectra of Co-PI-1 (a) before curing; (b) after curing at 260 °C for 1 h under vacuum; and (c) after curing at 260 °C for 2 h under vacuum.

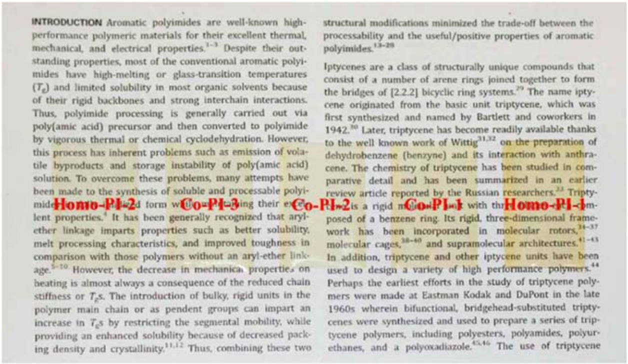


FIGURE 7 Photographs of the PIs (~30-μm thick). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Optical and Dielectric Properties of the Polymers

All the PIs could be processed into transparent and flexible films by casting from the DMAC polymer solutions and the photographs of these films are shown in Figure 7. The corresponding UV–vis spectra of the PIs films (~30-μm thick) are shown in Figure 8. The cut-off wavelength values and the percentages transmittance at 400 nm and 550 nm from these spectra are listed in Table 4. All the PIs had λ_0 about 332–339 nm, and exhibited high optical transparency about 90% at a wavelength of 550 nm. These results indicated that the PI films are light-colored films. Because of the highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation of PI, most polyimides have strong absorption in the UV and visible area. However, our polyimide materials with the bulky and electron-withdrawing —CF_3 groups in their diamine moieties possessed light color. It could be explained by the decreased CTC formation of polymer chains through higher steric hindrance and lower inductive effect. Moreover, the influence of —CF_3 groups on the film transparency was the weakening intermolecular dispersion forces due to low polarizability of the C—F bond.[27] The color of the PI films decreased in the order: Homo-PI-2 > Co-PI-3 > Co-PI-2 > Co-PI-1 > Homo-PI-1 (Fig. 7), which is relevant to the transmittance order at 400 nm wavelength. The regularity is also consistent with the side groups and fluorine content in the PIs. Besides, we also investigated the relationship between transparency of the films and their thickness. The corresponding UV–vis spectra of these PI films with different thickness are shown in Figure 8(b). According the data from this figure, the dependence of the cutoff wavelength, transmittance at 400 nm, and the thickness of films could be summarized as

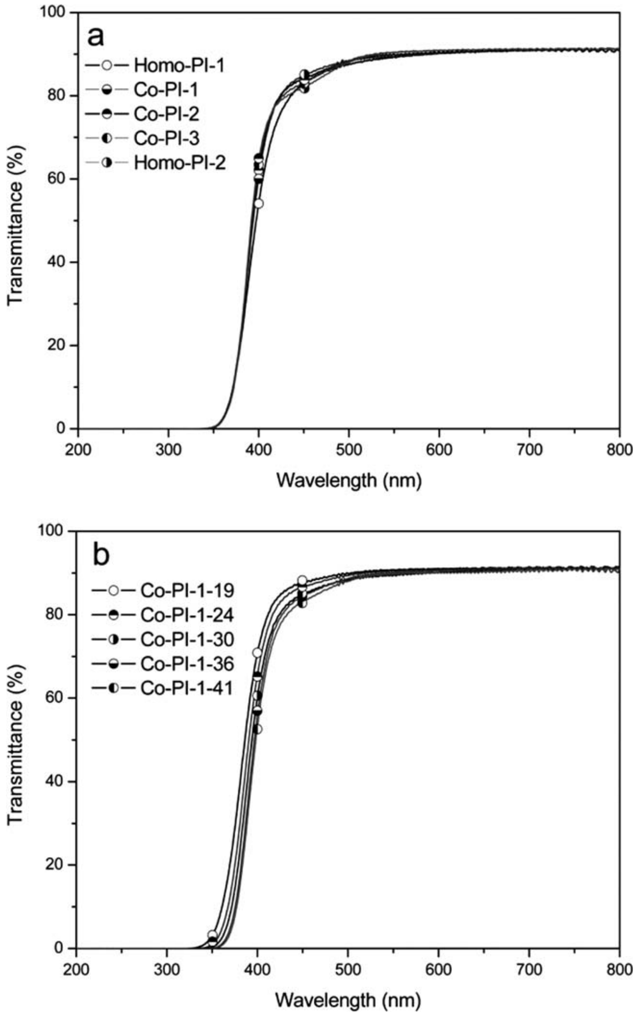


FIGURE 8 Transmittance UV–visible spectra of PIs films (a) PIs films (~30-μm thick), (b) Co-PI-1 films with different thickness: (19–41 μm).

TABLE 4 Optical and Dielectric Properties of PIs

Polymers	Refractive index		Dielectric constant[c]	λ_o[d] (nm)	Transmittance at 400 nm (%)	Transmittance at 550 nm (%)	Film thickness (μm)
	n[a] 1,310 nm	n[b] 1,550 nm					
Homo-PI-1	1.5332	1.5310	2.62	339	54	89	29
Co-PI-1	1.5319	1.5295	2.60	338	60	89	30
Co-PI-2	1.5311	1.5287	2.78	334	62	90	30
Co-PI-3	1.5311	1.5288	2.67	335	63	90	29
Homo-PI-2	1.5307	1.5284	2.74	332	65	90	31

[a] Refractive indices of polyimides at 1,310 nm: $n_{1,310nm}$.

[b] Refractive indices of polyimides at 1,550 nm: $n_{1,550nm}$.

[c] Dielectric constant of cured PI films at 1 MHz.

[d] Cut-off wavelength defined as the point at which the transmittance becomes less than 1%.

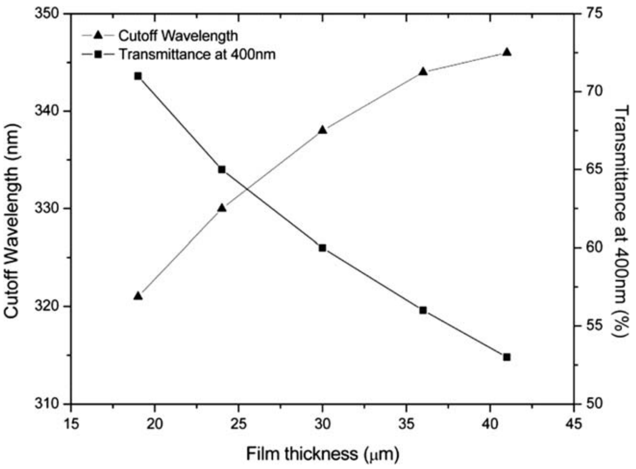


FIGURE 9 Cutoff wavelength and transmittance at 400 nm of Co-PI-1 films with different thickness: (19–41 μm).

presented in Figure 9. With the increase of the thickness of PI films, the cutoff wavelength increases from 321 to 346 nm and transmittance at 400 nm decreases from 71 to 53%. The results indicated that the transparency of films is dependent on their thickness heavily.

The refractive indices were measured using spectroscopic ellipsometer. These results are summarized in Table 4. All the PIs showed very low refractive indices in the range of 1.5307–1.5332 at 1310 nm and 1.5284–1.5310 at 1550 nm, respectively. As the refractive indices could change with the free volume (packing density), polarizability of the material, temperature, and humidity,[28] it seems easy to explain that the very low refractive index of the co-polyimides are attributed to the smaller electronic polarizability and large free volume of the C—F compared to C—H bond. In addition, the variation of refractive index at 633 nm with 6FTFPB content is shown in Figure 10. As expected, the refractive indices decreased regularly with 6FTFPB content increasing, due to the fluorine content of 6FTFPB was higher than 6FAPB.

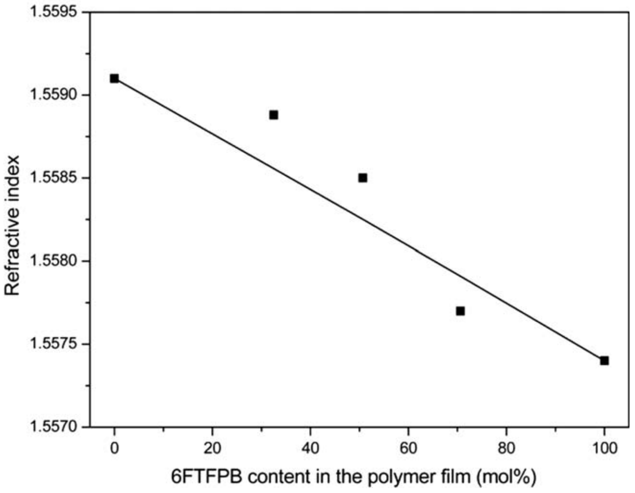


FIGURE 10 Variation of refractive index at 633 nm with 6FTFPB content; (a) before curing; (b) after curing at 260 °C for 2 h under vacuum.

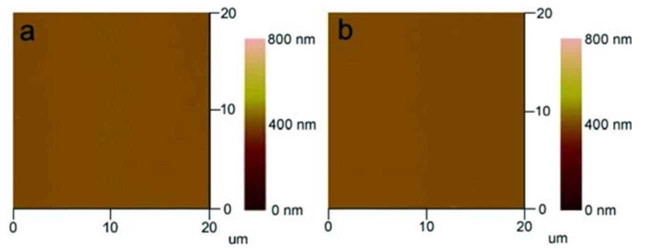


FIGURE 11 AFM images of the Co-PI-1 films coated on silicon wafer substrates: (a) height images of uncured film; (b) height images of cured film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The dielectric constants for the cured PI films were evaluated by capacitance method and were listed in Table 4. All the cured PIs showed low ε values in the range of 2.60–2.78 due to the existence of bulky CF_3 groups in the main chain, which brought about less efficient chain packing and an increased free volume.

Morphology Analyses of the Films

The height AFM images of uncured and cured Co-PI-1 films are summarized in Figure 11. The root mean square surface roughness (R_q) for the films is 1.940 nm and 4.130 nm, respectively. It indicated that the cured films with excellent surface planarity could be obtained. Above all, the Co-PIs are expected to be applicable polymeric materials for optoelectronic devices.[29]

CONCLUSIONS

A series of novel high molecular weight cross-linkable fluorinated co-polyimides were successfully synthesized using newly designed 1, 3-bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,4,5-tetrafluorophenoxy)benzene with 6FAPB and 6FDA. The co-polyimides showed excellent solubility in common organic solvents, high tensile properties, excellent optical transparency, and high thermal stability. The co-polyimides could be cross-linked thermally, yielding materials with outstanding chemical resistance. The cross-linking density of the copolymers was readily controlled by adjusting the feed ratio of 6FTFPB to 6FAPB. After curing, the glass transition temperature of co-polyimides obviously increased except Co-PI-3 and Homo-PI-2 whose T_gs could not be observed owing to their high cross-linking density. All the tensile strength, Young's Modulus, and the 5% thermal weight-loss temperature of the co-polyimides were enhanced. Furthermore, despite the root mean square surface roughness changed slightly, the cross-linked films still possessed excellent surface planarity. In addition, the cross-linked PI films show low dielectric constant ranging 2.60–2.78. These attracting properties make our Co-PIs potential matrixes for constructing optoelectronic devices. The next work of the application for fabricating the optical waveguide is under way in our group.

ACKNOWLEDGMENT

The authors would like to thank the China Natural Science Foundation (Grant nos. 51173062 and 51203172) for financial support of this work.

REFERENCES AND NOTES

1 D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem. Int. Ed.*, **1990**, *29*, 138–175.

2 D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Polyimides; Chapman and Hall: New York, **1990**.

3 M. K. Ghosh, K. L. Mittal, Polyimides: Fundamentals and Applications; Marcel Dekker: New York, **1996**, pp 697–884.

4 B. V. Kotov, B. M. Rumyantsev, V. I. Berendyaev, E. V. Lunina, B. P. Bespalov, E. L. Frankevich, M. M. Triebel, *Synth. Met.*, **2001**, *121*, 1553–1554.

5 Y. R. Wang, S. G. Xu, T. Chen, H. W. Guo, Q. Y. Liu, B. X. Ye, Z. Zhang, Z. Q. He, S. K. Cao, *Polym. Chem.*, **2010**, *1*, 1048–1055.

6 K. Xie, J. G. Liu, H. W. Zhou, S. Y. Zhang, M. H. He, S. Y. Yang, *Polymer*, **2001**, *42*, 7267–7274.

7 K. Xie, S. Y. Zhang, J. G. Liu, M. H. He, S. Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2581–2590.

8 S. H. Hsiao, C. P. Yang, C. K. Lin, *J. Polym. Res.* **1995**, *2*, 1–12.

9 Y. H. Qi, J. F. Ding, M. Day, J. Jiang, C. L. Callender, *Chem. Mater.* **2005**, *17*, 676–682.

10 Y. H. Qi, J. F. Ding, M. Day, J. Jiang, C. L. Callender, *Polymer* **2006**, *47*, 8263–8271

11 M. E. Wright, D. A. Schorzman, A. M. Berman, *Macromolecules* **2002**, *35*, 6550–6556.

12 X. H. Rao, H. W. Zhou, G. D. Dang, C. H. Chen, Z. W. Wu, *Polymer* **2006**, *47*, 6091–6098.

13 Y. F. Liu, Z. Wang, H. L. Yang, L. X. Gao, G. Li, M. X. Ding, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4227–4235.

14 H. J. Sun, H. T. Huo, H. Nie, S. Y. Yang, L. Fan, *Eur. Polym. J.* **2009**, *45*, 1169–1178.

15 Y. Yang, L. Fan, M. Ji, S. Y. Yang, *Eur. Polym. J.* **2010**, *146*, 2145–2155.

16 Y. Yang, L. Fan, X. M. Qu, M. Ji, S. Y. Yang, *Polymer* **2011**, *52*, 138–148.

17 Y. H. Zhang, P. Luo, H. Y. Yao, S. W. Guan, *React. Funct. Polym.* **2012**, *72*, 621–626.

18 M. E. Rezac, E. T. Sorensen, H. W. Beckham, *J. Membr. Sci.* **1997**, *136*, 249–259.

19 Y. C. Xiao, T. S. Chung, H. M. Guan, M. D. Guiver, *J. Membr. Sci.* **2007**, *302*, 254–264.

20 X. Y. Ma, Z. H. Lv, D. Wang, S. W. Guan, C. H. Chen, G. B. Wang, D. M. Zhang, Z. H. Jiang, *J. Photochem. Photobiol. A* **2007**, *188*, 43–50.

21 Z. H. Jiang, X. Y. Ma, C. H. Chen, X. F. Li, S. W. Guan, D. Wang, Chinese Patent, Z. L., 10011381. X., **2004**.

22 G. H. Li, J. Y. Wang, G. P. Yu, X. G. Jian, L. H. Wang, M. S. Zhao, *Polymer* **2010**, *51*, 1524–1529.

23 T. Takeichi, M. Zuo, M. Hasegawa, *J. Polym. Sci. Part B: Polym. Phys.* **2001**, *39*, 3011–3019.

24 Y. Terui, S. Matsuda, S. Ando, *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 2109.

25 J. Ishii, A. Takata, Y. Oami, R. Yokota, L. Vladimirov, M. Hasegawa, *Eur. Polym. J.* **2010.**, *46*, 681.

26 M. Hasegawa, Y. Sakamoto, Y. Tanaka, Y. Kobayashi, *Eur. Polym. J.* **2010**, *46*, 1510.

27 S. Ando, T. Matsuura, S. Sasaki. *Polym. J.* **1997**, *29*, 69–76.

28 J. W. Kang, J. P. Kim, J. S. Lee, J. J. Kim, *J. Lightwave. Technol.*, **2005**, *23*, 364–373.

29 T. Matsuura, S. Ando, S. Sasaki, F. Yamamoto, *Macromolecules* **1994**, *27*, 6665–6670.