Synthesis and Properties of Novel Polyimide Optical Materials with Different Haloid Pendant

Yan Xing,[1] Dong Wang,[1,2] Hong Gao,[1] Zhenhua Jiang[1]

[1]Alan G. MacDiarmid Institute, Jilin University, Changchun, People's Republic of China 130012
[2]School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, People's Republic of China 100083

ABSTRACT: To investigate the difference of trifluoromethyl group and chlorine group affecting the optical properties of polyimides (PIs), two diamine monomers with different haloid pendants were designed and synthesized including (1,4-(4-amino-2-trifluoromethylphenoxy)-2-(3'5'-ditrifluoromethylphenyl)benzene and (1,4-(4-amino-2-trifluoromethylphenoxy)-2-(3'-trifluoromethyl-4'-chlorophenyl) benzene). From both diamines, two series of PIs with different haloid pendants were prepared via two-step chemical imidization methods with various dianhydride compounds. All the PIs have the high T_g, excellent thermal stability and good solubility, and can be formed the transparent, strong, and flexible films. All the PIs also are good transparent in UV-evisible absorption spectra, and have the low birefringences (0.0128–0.0157 at 650 nm) and low optical loss at communication windows. Two series of PIs exhibit the similar optical properties, except for refractive index. Based on the fantastic characterization, a series of optical materials with the tunable refractive indices were obtained by copolymerization. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 738–747, 2011

Key words: polyimides; haloid pendants; tunable refractive index

INTRODUCTION

Polyimides (PIs) with high thermal stability, ease of processing, loss moisture absorption, and relatively low cost compared with silica-based materials have been widely researched as a very promising materials in photonic applications, such as arrayed waveguide grating multiplexer (AWG), thermo-optical switches, tunable wavelength filters and variable optical attenuators.[1,2] Although these materials have potential advantages for optical applications, some properties such as good solubility, high optical transparency, low absorption loss and low birefringence need improvement.[3–5] The introduction of fluorinated groups in PIs is a very effective method, and the most research focuses on the PIs with trifluoromethyl groups (CF$_3$) due to their easier synthesis, excellent thermal stability and mechanical properties.[6–19] Usually, substitution of hydrogen by a fluorine atom can shift the associated vibrational overtone of C-H to longer wavelengths.[20–24] Furthermore, halogenations, particularly fluorination, can offer interesting opportunities for enhancing the solubility and raising the optical transparency. Moreover, the incorporation of noncoplanar moiety such as flexible ether group and bulky side groups in the polymers can disrupt the orientation of rigid groups of polymer chain and reduce intermolecular charge-transfer complex (CTC), furthermore attain good solubility and reduce the birefringence.[25–28]

Except for the fluorinated groups, the introduction of chlorine groups also can improve the polymer optical properties. According to the same rules about the polymers with carbon-fluorine bond (C-F), the polymers with carbon-chlorine bond (C-Cl) have low optical loss at 1310 and 1550 nm based on the calculation, and the C-Cl bond has the larger polarizability than the C-F bond.[29] Comparison to C-F bond, the incorporation of C-Cl bond into the polymer backbone should have the higher refractive indices.[30] If the monomers with different haloid groups were copolymerized into a series of copolymer, it will provides good methodology to control refractive index without additional optical loss. At this point, this method may be better than the previous methods that select the fluorinated and nonfluorinated monomers to copolymerize for controlling the refractive index.[31,32]

On the basis of the request for optical waveguide material, we attempt to synthesize the organosoluble PIs with different haloid groups (bulky trifluoromethyl/chloro side groups). In this article, two new diamines with different bulky side groups were synthesized and employed in a polycondensation

reaction with various commercially available aromatic dianhydrides to produce two series of PIs. The chemical composition of two series of PIs could be only distinguished from the Ph-Cl bond and Ph-CF3 bond. Their physical and optical properties were measured and the differences between two series of PIs were discussed, especially optical properties. Furthermore, the waveguide device was fabricated by reactive ion etching (RIE) from these polymers, and exhibited good optical propagation at wavelength of 1550 nm.

EXPERIMENTAL

Materials

2-Chloro-5-nitrotrifluromethlybenzene was obtained from Acros Organics. 1,4-Bis (3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA; Acros Organics, 97%) and 4,4-oxydiphthalic anhydride (ODPA; Acros Organics, 97%) were recrystallized from acetic anhydride before use. 4,4-(Hexafluoroisoprylidene) diphthalic anhydride (6FDA; Hoechst Celanese Corp., 99%) was used without purified N,N-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. (3,5-Ditrifluromethylphenyl)-1,4-hydroquinone and (3-trifluoromethyl-4-chloro phenyl)-1,4-hydroquinone were was synthesized according to the literature.[33,34]

Monomer synthesis

1,4-(4-Nitro-2-trifluoromethylphenoxy)-2-(3,5-ditrifluromethyl phenyl)benzene (I)

A mixture of (3,5-ditrifluromethylphenyl)-1,4-hydroquinone (64.4 g, 0.2 mol), 2-chloro-5-nitrotrifluromethlybenzene (90.0 g, 0.4 mol), anhydrous potassium carbonate (33.12 g, 0.24 mol), dried N,N-dimethylformamide (DMF) (500 mL) and toluene (70 mL) were charged into a three-necked round-bottom flask, equipped with a mechanical stirrer, a Dean-Stark strap, a reflux condenser and a nitrogen purge. The mixture was refluxed with stirring for 4 h. The water produced in the reaction was removed by distillation of the toluene/water azeotrope until the toluene was collected. Then the mixture was refluxed for another 8 h and cooled to room temperature. The mixture was poured into an excess of ice water to give a solid material, which was collected and washed with water, and then dried at 100°C *in vacuo*. Yield: 90%, mp: 167°C. IR (KBr, cm^{-1}): 1534 and 1356 (-NO$_2$ stretch), 1226 (Ph-O-Ph stretch), 1135 (C-F stretch).

1,4-(4-Nitro-2-trifluoromethylphenoxy)-2-(3-trifluoromethyl-4-chlorophenyl) benzene (II)

Monomer II was prepared by the same procedure as the monomer I, with the (3-trifluoromethyl-4-chloro-phenyl)-1,4-hydroquinone instead of (3,5-ditrifluromethyl phenyl)-1,4-hydroquinone. Yield: 87%, mp: 158°C. IR (KBr, cm^{-1}): 1531 and 1338 (-NO$_2$ stretch), 1239 (Ph-O-Ph stretch), 1130 (C-F stretch). ^{1}H NMR (500 MHz, DMSO-$d6$, δ, ppm): 8.55 (d, $J = 2.7$ Hz, 1H), 8.49 (quart, 1H), 8.47 (d, $J = 2.6$ Hz, 1H), 8.37 (quart, 1H), 7.93 (s, 1H), 7.8 (m, 2H), 7.71 (d, $J = 1.5$ Hz, 1H), 7.51 (m, 2H), 7.4 (d, $J = 9.2$ Hz, 1H), 7.17 (d, $J = 9.2$ Hz, 1H).

1,4-(4-Amino-2-trifluoromethylphenoxy)-2-(3,5-ditrifluromethylphenyl)benzene (III)

The previously obtained dinitro compound (I) (14.0 g, 0.02 mol), Fe powder (13.44 g, 0.24 mol) and 50% aqueous ethanol (60 mL) were mixed in a 250 mL, three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed with stirring. To this solution was then slowly added a mixture of concentrated HCl (0.7 mL) and 50% aqueous ethanol (10 mL). The reaction solution was refluxed for 3 h, then NaOH (0.37 g) was added. The solution was filtered, and the filtrate was distilled to remove the solvent in vacuum. The crude product was purified by recrystallization from ethanol to give a gray solid. Yield: 47%, mp: 154°C. IR (KBr, cm^{-1}): 3472 and 3382 (N-H stretch), 1238 (Ph-O-Ph stretch), 1131 (C-F stretch). ^{1}H-NMR (500 MHz, CDCl$_3$, δ, ppm): 8.04 (s, 2 H), 7.81 (s, 1H), 7.07 (d, $J = 2.6$ Hz, 1H), 6.97 (d, $J = 2.3$ Hz, 1H), 6.92 (d, $J = 2.1$ Hz, 1H), 6.89 (d, $J = 9$ Hz, 2H), 6.82 (m, 2H), 6.70 (m, 2H), 3.73 (s, 4 H). ^{13}C-NMR (75 MHz, CDCl$_3$, δ, ppm): 154.1, 149.5, 146.0, 145.8, 142.7, 142.3, 138.9, 131.3, 130.7, 129.5, 123.7, 122.4, 121.8, 121.3, 119.9, 119.4, 119.2, 119.1, 119.0, 113.2. ELEM. ANAL. Calcd. For C$_{28}$H$_{16}$F$_{12}$N$_2$O$_2$ (640.10): C, 52.51%; H, 2.52%; N, 4.37%. Found: C, 52.54%; H, 2.58%; N, 4.35%.

1,4-(4-Amino-2-trifluoromethylphenoxy)-2-(3-trifluromethyl-4-chlorophenyl) benzene (IV)

Monomer IV was prepared by the same procedure as the monomer III, with the dinitro monomer II instead of monomer I. Yield: 52%, mp: 142°C. IR (KBr, cm^{-1}): 3490 and 3398 (N-H stretch), 1239 (Ph-O-Ph stretch), 1127 (C-F stretch). ^{1}H NMR (500 MHz, DMSO-$d6$, δ, ppm): 7.99 (s, 1H), 7.79 (m, 2H), 7.12 (d, $J = 3$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 1H), 6.92 (d, $J = 2.7$ Hz, 1H), 6.88 (m, 2H), 6.81 (m, 2H), 6.75 (s, 2H), 5.42 (d, 4H). ^{13}C-NMR (75 MHz, CDCl$_3$, δ, ppm): 154.1, 149.3, 146.3, 146.1, 142.62(C^{13}), 142.1, 135.8, 133.5, 131.4, 131.2, 128.5, 124.5, 123.1, 120.3, 119.7, 119.4, 119.2, 118.6, 113.1. ELEM. ANAL. Calcd. For C$_{27}$H$_{16}$F$_9$N$_2$O$_2$ (606.08): C, 53.44%; H, 2.66%; N, 4.62%. Found: C, 53.60%; H, 2.63%; N, 4.61%.

Polymer synthesis

Utilizing III and IV as the diamine monomers, six polyimides were synthesized by polycondensation with dianhydride monomer HQDPA (a), ODPA (b) and 6FDA (c), respectively. The resulting PIs were abbreviated to III-a - III-c and IV-a - IV-c, successively.

In a typical experiment, PI-IV-b, which derived from diamine IV and OPDA (b), was prepared as follows: diamine IV (1.82 g, 3 mmol) was dissolved in dried DMAc (10 mL) in a three-necked flash fitted with a nitrogen inlet pipet and mechanical stirrer. After the diamine was dissolved completely, OPDA (b, 3 mmol, 0.93 g) was added in one portion. Then the reaction was allowed to carry through 18 h at room temperature to yield a viscous polyamide acid solution (PAA solution) with 15% of solid content. Then a mixture of acetic anhydride and pyridine (volume ratio 5 : 4) was added to the PAA solution. The PAA solution was imidized by stirring in oil bath at 60°C for 6 h, the solution containing polyimide was poured into ethanol to produce a precipitate, the precipitate was collected by filtration and washed with ethanol thoroughly, and it was dried at 80°C for 24 h and 120°C for 6 h under vacuum. IR (KBr, cm^{-1}): 1788 and 1726 (asymmetric, symmetric imide C=O stretch), 1619-1481 (aromatic C=C stretch), 1377 (C—N stretch), 1239 (Ph-O-Ph stretch), 1100-1300 cm^{-1} (C—O and C—F stretching). ^{1}H NMR (500 MHz, DMSO-$d6$, δ, ppm): 8.25 (m, J = 6.5, 2H), 8.16 (m, J = 7.4, 4H), 8.03 (s, 1H), 8.00 (s, 1H), 7.88 (m, J = 8.6, 2H), 7.78 (d, J = 8.9, 2H), 7.67 (d, J = 9.0, 1H), 7.62 (s,1H), 7.39 (s, 2H), 7.33 (d, J = 8.6, 1H), 7.17 (d, J = 8.9, 1H).

Similarly, all other PI films were prepared with the aforementioned procedure.

Copolymer synthesis

The copolyimides were prepared from both amines (III and IV) with OPDA. The content of III was varied (20–80 mol % based on IV). The copolyimides were prepared by the same procedure as the homopolymers.

Film preparation

A polymer solution was made by the dissolution of about 1 g of the polyimide sample in 10 mL of DMAc. The homogeneous solution was poured into a glass plate, which was placed in a 75°C oven overnight for the slow release of the solvent, and then the film was stripped off from the glass substrate and further dried *in vacuo* at 140°C for 8 h, 200°C for 2 h. The obtained films were about 49−65 μm thick and were used for X-ray diffraction measurements, tensile test, and near infrared measurements.

Instrumentation

IR spectra (KBr) were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker 510 NMR spectrometer and Bruker Avance 300 NMR spectrometer with tetramethyl silane as a reference. Elemental analysis were performed on an Elemental Analysis MOD-1106. Inherent viscosities were determined on 0.5 g/dL concentration of polymer in DMAc using an Ubbelohde capillary viscometer at 25°C. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821^e instrument at a heating rate of 20°C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10°C/min on a PERKIN ELMER TGA-7. UV transparencies were measured by a Shimadzu UV 2501-PC spectrophotometer. The refractive indices were obtained using a Gaertener L116B spectroscopic ellipsometer. Near infrared spectra were measured by a Jasco V-570 UV/VIS/NIR spectrophotometer. The birefringences of the polymer films, at the 650 nm wavelength, were determined from coupling angles of TE (transverse electric) or TM (transverse magnetic) optical guided modes with a gadolinium gallium garnet (GGG) prism. Wide-angle X-ray diffraction (WAXD) measurements at room temperature were made using a Rigaku/max-rA diffractometer equipped with a Cu Kα radiation source. The mechanical tests in tension were carried out using a SHIMADZU AG-I at a constant crosshead speed of 10 mm/min.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The CF$_3$-containing diamine III and chloro/CF$_3$-containing diamine IV were prepared in two steps according to a well-established procedure.[6] The first step involved a nucleophilic aromatic substitution reaction between 2-chloro-5-nitrotrifluromethylbenzene with (3,5-ditrifluromethylphenyl)-1,4- hydroquinone and (3-trifluoromethyl-4-chlorophenyl)-1,4-hydroquinone in the presence of potassium carbonate. In the nucleophilic substitution reaction, the reaction temperature and the amount of K$_2$CO$_3$ could be reduced to avoid coloring of the dinitro compound.[35] In this study, the substitution reaction under 150°C for 12 h had better results. The diamine III and IV were readily obtained by the Fe/HCl reduction of the intermediate dinitro compound I and II in refluxing ethanol and water solution
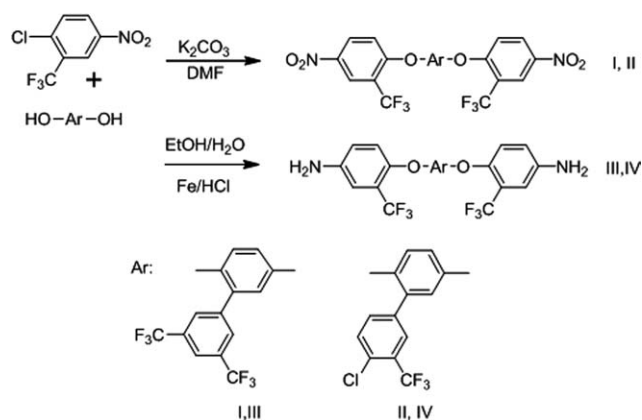
Scheme 1   Synthesis of monomers.

Figure 1   IR spectra of dinitro (II), diamino (IV) and PI-IV-b.

(Scheme 1). The structures of the obtained compounds in each step were confirmed by spectroscopic techniques.

Using the IV series as the examples, Figures 1 and 2 showed the IR and ^{1}H NMR spectra of the intermediate dinitro compound II and diamine IV, respectively. The monomer II gave two characteristic bands at 1531 and 1338 cm^{-1} (NO$_2$ asymmetric and symmetric stretching). After the reduction, the characteristic absorptions of the nitro group disappeared and the amino group of the compound IV showed a pair of N-H stretching bands in the region of 3400–3500 cm^{-1} (3449, 3392 cm^{-1}). All of the above compounds exhibited the characteristic absorptions at 1223–1126 cm^{-1} due to ether linkages, and around 1135 cm^{-1} corresponding to CF$_3$ groups. The ^{1}H NMR and ^{13}C NMR spectra confirmed that the nitro groups were completely converted into amino groups by the high field shift of the aromatic protons. The peaks at around 5.4 ppm were assigned to the —NH$_2$ groups. Figure 3 showed the ^{1}H NMR spectra of the diamine IV and the chemical structure of monomer IV could be confirmed too.
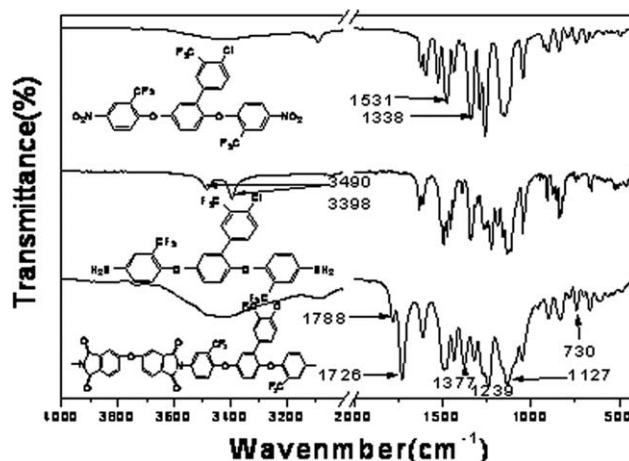
Polymer synthesis

All the polymers were synthesized from diamines (III and IV) and three different dianhydrides (a-c) by a conventional two-step procedure of ring-opening polycondensation at room temperature to form PAA and sequential chemical imidization to obtain the corresponding PIs, as shown in Scheme 2. According to Table I, the polymers gave moderate inherent viscosities of 0.57–0.75 dL/g in DMAc. The molecular weights of the soluble PIs were measured by GPC and the number-average molecular weights (M_n) and polydispersities (M_w/M_n) of the resulting PIs were in the range of 49,000–94,000 and 1.93–2.13, respectively, (Table I).

The chemical structures of PIs were characterized by FTIR, ^{1}H NMR, and elemental analysis. Using the IV series as the examples, Figures 1 and 2 showed the IR and ^{1}H NMR spectra of the PI-IV-b, respectively. The FTIR spectra of the PI-IV-b exhibited characteristic imide group absorptions at around 1788 and 1726 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretching), 1377 cm^{-1}
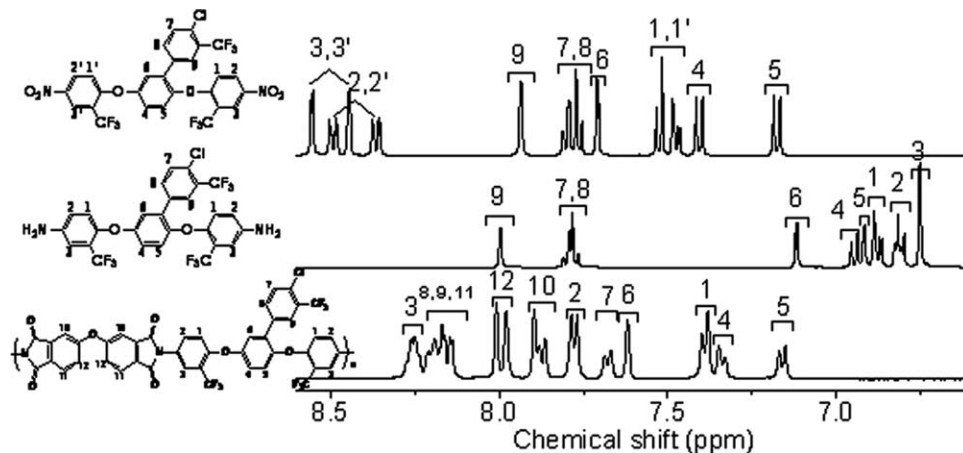
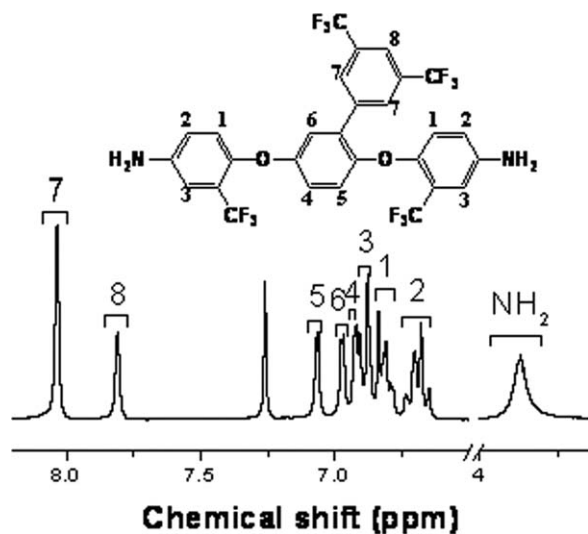Figure 2 ^{1}H NMR spectra of dinitro (II), diamino (IV) and PI-IV-b.

Figure 3 H NMR spectra of diamino (IV).

(C—N stretch) and 730 cm^{-1} (imide ring deformation), and the strong absorption bands in the region of 1100–1300 cm^{-1} was attributed to the C—O and C—F stretching (Fig. 1). The ^{1}H NMR spectra of IVb were shown in Figure 2. All the protons resonated in the region of 7.10–8.3 ppm. The aforementioned showed that the PIs (III-based PIs and IV-based PIs) had been synthesized successfully.

The incorporation of fluorine atoms in the polymers can affect the refractive index and the optical loss. It was reported that the refractive index of polymers is related to the free volume, the electronic polarizability, and the difference between the used optical wavelength and the maximum absorption wavelength. The birefringence of polymer materials comes mainly from the preferred orientation of rigid groups and polymer chains, although the orientation may be induced by stress during the formation of the final polymer films.[36] Usually it was the direct connection between the CF3 groups and main chain in the fluorinated PIs with CF3 groups. Lee et al.[36]
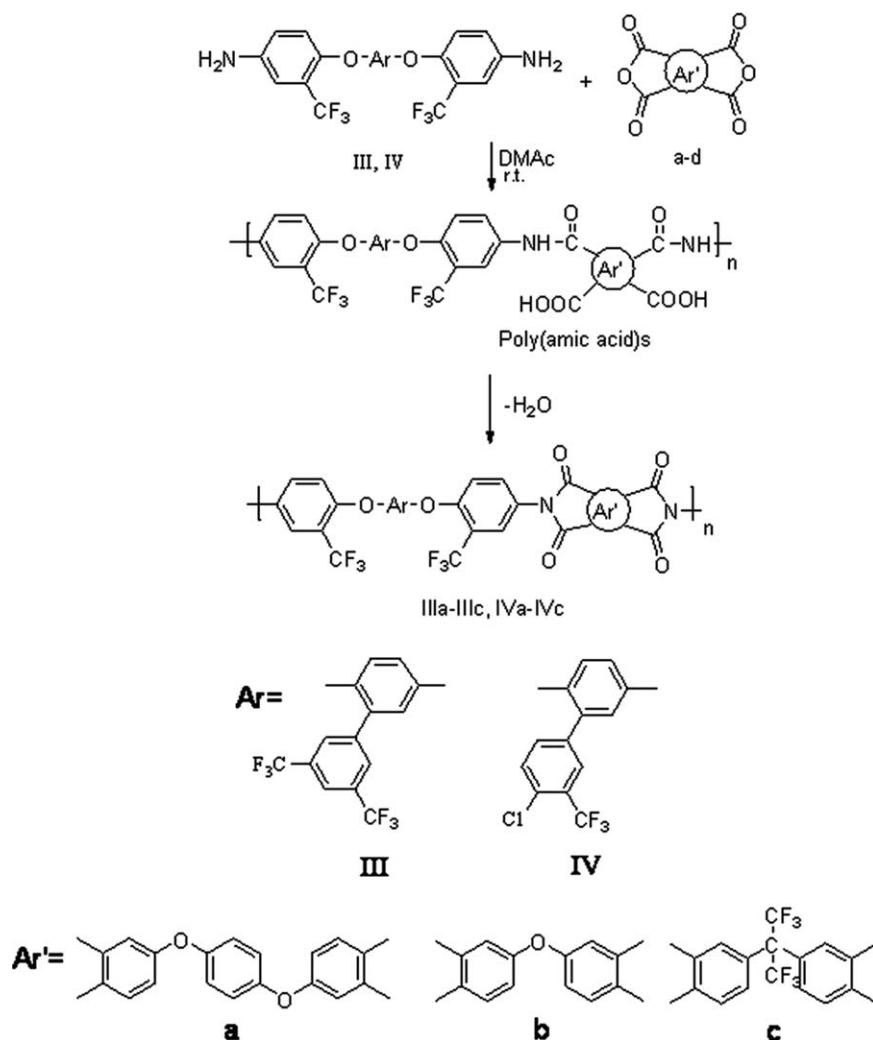
Scheme 2 Synthesis of polyimides.

TABLE I
Molecule Weight and Thermal Properties of Polyimides

Polymers	Inherent viscosity (dL/g)[a]	$M_n \times 10^3$	$M_w \times 10^3$	M_w/M_n	DSC T_g[b] (°C)	TGA $T_{5\%}$[c] (°C)	$T_{10\%}$[c] (°C)	Char yield[d] (%)
IIIa	0.59	25	53	2.13	240	590	615	44.8
IIIb	0.75	37	78	2.10	243	536	552	47.2
IIIc	0.62	50	64	2.10	246	573	598	45.6
IVa	0.67	21	49	1.93	236	544	571	44.2
IVb	0.57	45	94	2.12	239	550	573	45.9
IVc	0.64	41	90	2.08	244	531	548	44.1

[a] Determined with 0.5% solutions in a solvent (DMAc) at 25°C.
[b] Baseline shift in the second heating DSC traces, with a heating rate of 20°C/min.
[c] Temperature at 5% and 10% weight loss.
[d] Residual weight (%) when heated to 800°C.

prepared terphenyl dihydroxy monomer substituted with CF3 moieties as a counterpart of pentafluorophenyl sulfide. In the polymer structure, it has two bulky side phenyl groups containing four CF3 moieties, which can increase the free volume of the polymer, and they decrease the refractive index due to the greater steric volume of fluorine in comparison to hydrogen. In the chemical structures of our synthesized PIs, there were not only the CF3 groups that were linked directly to the main chain, but also the CF3 groups that were linked to the main chain by the bulk phenyl groups. Surely, the latter must be huger pendant than the former, and it will improve the solubility of PIs and other properties. They also reduce the birefringence due to inefficient chain packing. In addition, introduction of the side phenyl group may make the polymer have a high T_g. The detailed relationships between the chemical structures and physical properties are discussed below.

Polymer properties

The solubilities of the PIs were summarized in Table II. All the polymers showed excellent solubility in aprotic polar solvent (NMP, DMAc and CHCl₃), and even in less polar solvents like acetone and THF. The excellent solubility of PIs could be attributed to the presence of flexible ether structure, CF₃ groups and the bulky CF₃/Cl-phenyl substitutes in the diamines, which appeared to force the two phenyl rings into adopting noncoplanar conformation. This, in turn, hindered dense chain packing, reduced chain-chain interactions and provided enhanced solubility.

The thermal behavior data of all the PIs were listed in Table I, including DSC and TGA results. T_g values of III-based PIs and IV-based PIs were in the ranges of 240–246°C and 236–244°C, respectively. In generally, T_g were correlated with the polymer structure, the molecular packing and chain conformation (chain rigidity and linearity) of polymer.[37] Depended on the chain flexibility degree of dianhydride component, T_g values of PIs obtained from HQDPA showed the lowest T_g and PIs derived from 6FDA had the highest T_g in all series. T_g values of III-based PIs were higher than IV-based PIs. All polymers had excellent thermal stability, and no obvious decomposition was observed below 500°C. Film samples of PIs underwent 5% weight losses at 530–590°C in

TABLE II
Solubility of Polyimides

Polymers	Solvents[a] NMP	DMAc	DMF	DMSO	THF	CHCl₃	Actone	Ethanol
IIIa	++	++	++	++	++	++	++	−
IIIb	++	++	++	++	++	++	+	−
IIIc	++	++	++	++	++	++	++	−
IVa	++	++	++	++	++	++	+	−
IVb	++	++	++	++	++	++	+	−
IVc	++	++	++	++	++	++	++	−

Qualitative solubility was determined with as 10 mg of polymer in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating.
[a] NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

TABLE III
Mechanical Properties and Optical Properties of Polyimides

Polymers	Film thickness (μm)	Tensile strength (MPa)	Elongation at break (%)	Youngs' modulus (GPa)	$\lambda_0{}^a$ (nm)	UV-Transmittance[b] (%)
IIIa	60	69	14	2.0	388	87
IIIb	65	75	16	2.0	386	89
IIIc	58	67	11	1.8	406	91
IVa	49	56	17	1.9	372	89
IVb	52	90	23	2.2	372	89
IVc	59	95	25	2.4	405	89

[a] Cutoff wavelength defined as the point at which the transmittance becomes less than 1%.
[b] UV-transmittance at 800 nm (%).

nitrogen. Their char yield at 800°C in nitrogen was in the ranged of 44–47 wt %.

All the films were transparent and flexible. Their mechanical properties were summarized in Table III. III-based PIs and IV-based PIs had tensile strength, elongation at break, and Young's modulus in the ranges of 56–95 MPa, 11–25% and 1.8–2.4 GPa, respectively. The WAXD results were shown in Figure 4 and proved that all the polymers were amorphous. The d-spacing results of all the polymers are similar and about 4.48 Å. The amorphous behavior of polymers was mainly due to the existence of bulky substituents (CF3 group and phenyl group), which disrupted the regularity of molecular chains and inhibited their close packing.

Optical properties

The films were measured for optical transparency with UV-visible spectroscopy and Figure 5 showed the results. The cutoff wavelength (absorption edge, λ_0) value and the percentage transmittance at 800 nm from these spectra were listed in Table III. All the PIs had shorter λ_0 than 410 nm and exhibited the high

optical transparency of 87–91%. Normally, the PIs exhibited strong absorption in UV-visible spectra, because of their highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation. However, the fluorinated PIs which had flexible ether group and CF_3 group with bulky side groups in the diamine could reduce the intermolecular CTC between alternating electron-donor
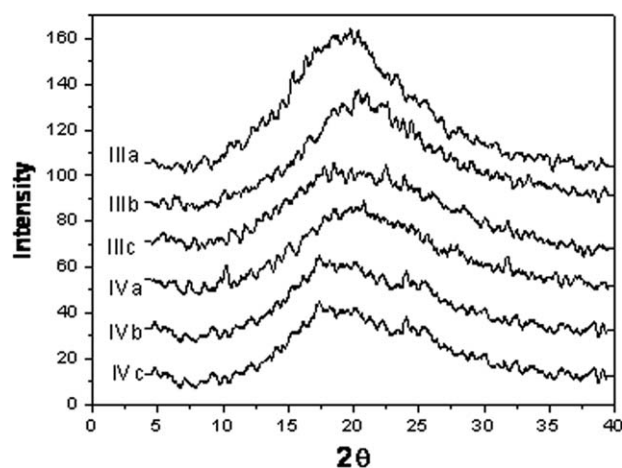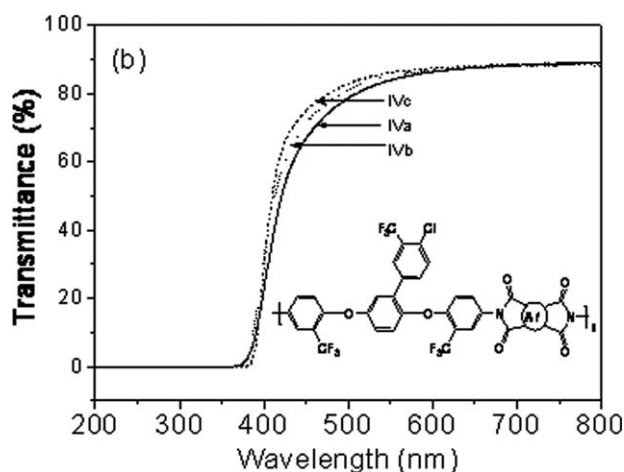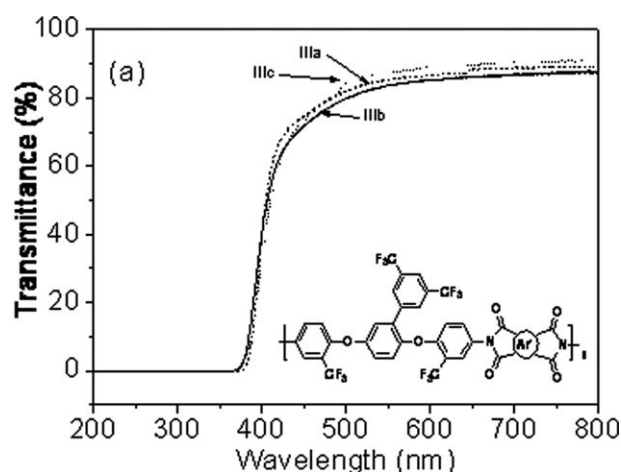
Figure 5 UV-visible spectra of polyimide films.

Figure 4 Wide-angle X-ray diffractograms of polyimides.

TABLE IV
Refractive Index and Birefingence of Polyimides

| Polymer | Refractive index[a] | | Birefringence[b] | | |
| | | | Refractive index at 650 nm | | |
	1310 nm	1550 nm	TE model (n_{xy})	TM mode (n_z)	n_{TE}-n_{TM}
IIIa	1.5628	1.5619	1.6289	1.6144	0.0145
IIIb	1.5504	1.5496	1.6165	1.6013	0.0152
IIIc	1.5382	1.5378	1.5982	1.5825	0.0157
IVa	1.5991	1.5990	1.6486	1.6358	0.0128
IVb	1.5782	1.5782	1.6384	1.6251	0.0133
IVc	1.5506	1.5500	1.6149	1.5997	0.0152

[a] The refractive indices of the polymer films were obtained using a spectroscopic ellipsometer.
[b] The birefringence of the polymer films were measured by the method of coupling angles of TE or TM optical modes with a prism at 650 nm.

(diamine) and electron-acceptor (dianhydride) moieties.[20,38] The bulky and electron-withdrawing CF_3-phenyl group was effective in reducing the CTC formation between polymer chains through steric hindrance and the inductive effect and weakening chain-to-chain cohesive force due to lower polarizability of the C-F bond.

Low birefringence is important requirement in application of a wavelength division multiplex system, because the optical components having the high birefringence show a high polarization dependent loss (PDL) that causes a degradation of the transmission quality or a failure of the optical system.[39] It was well known that the birefringence was caused by the orientation of the polymer chain in the direction parallel to the substrate during the spin-coating procedure. However, there were the flexible ether linkages in the backbone and the bulky pendant in the molecular structure, and they probably reduced the orientation and decreased the birefringence of PIs. The birefringence at 650 nm was measured by the prism-coupling method, as shown in Table IV. All the PIs (III-based PIs and IV-based PIs) had the low birefringence (0.0133–0.0157), and the data were lower than those of rigid PIs.[40] These results supported the reverse relationship between the birefringence and the T_g. Usually there is a trade-off between the birefringence and T_g, because high-T_g polymers generally contain rigid aromatic groups, which tend to be oriented during chemical and/or physical processes.[41] However, it was difficult to explain that the III-based PIs with larger bulky pendant had the higher birefringence than IV-based PIs. The results of DSC and birefringence could not agree with our knowledge. Here, we propose a hypothesis to explain these phenomena. III-based PIs and IV-based PIs have the difference of geometrical conformation, and the IV-based PIs should have the

longer pendant groups than III-based PIs. Perhaps, the factor can affect the polymer chain packing.

The optical waveguide application also needs the low optical loss in the near IR region, especially in the communication windows. The propagation losses of the PIs were measured by the near-infrared (NIR) absorption spectra, and the results normalized by the film thickness were shown in the Figure 6. All the films showed the low absorption loss in the communication windows and the high contents of CF_3/Cl in PIs were the key role. The carbon-hydrogen (C—H) and oxygen-hydrogen (O—H) bonds influence strongly on the absorption in the near-infrared region. It was reported that the absorption due to C—H bonds could be reduced by the replacement of hydrogen in the C—H bonds to heavy atoms such as fluorine and chlorine.[13,14] Three C—H bond vibrational absorption peaks also could be observed in the near IR region, although all the PIs had the optical loss: (1) the C—H first stretching overtone band ($\nu_{C—H}$) around 1650 nm; (2) the weaker
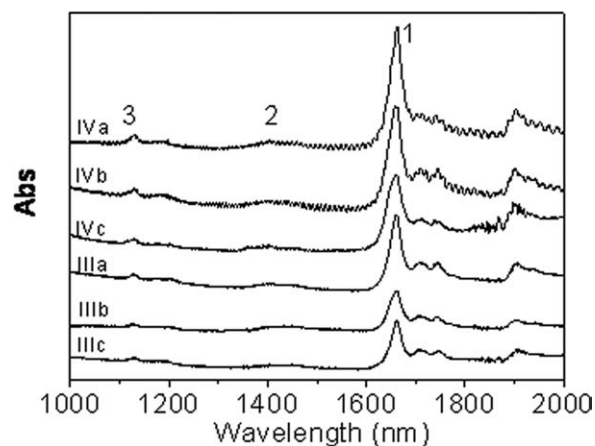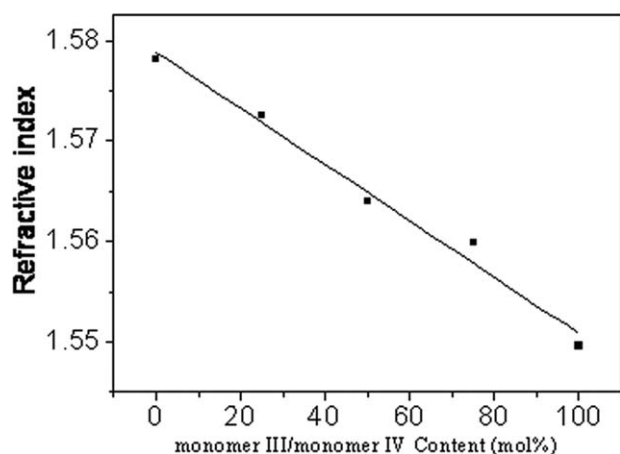

Figure 6 Near-IR spectra of polyimide.

Figure 7 Refractive indices of fluorinated and chloro-fluorinated copolyimides at 1550 nm.

combination band of the C—H stretching and deformation ($2\nu_{C-H} + \delta_{C-H}$) around 1400 nm; (3) the C—H stretching second overtone band ($2\nu_{C-H}$); around 1100 nm. However, three C—H bond vibrational absorption peaks were not in the communication windows, and at telecommunication wavelength of 1310 and 1550 nm, all the polymer films exhibited low light absorption that would satisfy the demand of the optical materials. For the different dianhydride monomers in the polymers, the absorption peak intensity of C—H stretching increased in the order of a-based PIs > b-based PIs > c-based PIs. It was attributed to the different content of C—H bonds that affected on the NIR absorption. For the different diamine monomers, the absorption peak intensity of III-based PIs was lower than that of IV-based PIs, because the electron-withdrawing intensity of —CF3 groups and -Cl groups was different.

The refractive indices of all the PIs were summarized in Table IV, and the refractive indices of IV-based PIs were higher that those of III-based PIs. Comparison to two series of PIs (III and IV), they had the similar physical and optical properties, except for their refractive indices. Here, we may capitalize this advantage to challenge to use two series of PIs or their copolymers as the core and cladding materials. On the basis of the device design and waveguide geometry, the precisely control of refractive index is exceedingly important for optical waveguide materials. The core polymers for waveguide device need the higher refractive index than that of the cladding material. If the nonfluorinated materials with the higher refractive index are selected, they will enhance the optical absorption. Here, the IV-based PIs containing —Cl had the high refractive index and low optical absorption at the same time. The appropriate index difference between core and cladding for either a single-mode or a multi-mode waveguide is strongly dependent on the dimension of waveguide and

wavelength of the light source.[23] It was obvious that two homo-polymers could not satisfy the requirement about appropriate index difference, and the copolymerization was a very effective method. The copolymerization of different fluorine content-containing monomers provided good methodology to control the refractive indices of polymers for waveguide applications.[42] The copolymers were prepared by the appropriate molar ratio of diamine III and IV with OPDA and the refractive indices (1550 nm) of copolymers were shown in Figure 7. It was very fantastic that the refractive indices increased linearly with increasing content of monomer IV. The refractive indices of the polymers varied from 1.5496 to 1.5782 on changing the feed ratio of the diamine monomers. The data proved that the refractive indices of the copolymers could be easily and precisely controlled by combination of III and IV content in the polymers. Meanwhile, the copolymers with the good control of the refractive index would not cause further optical loss at communication windows.

Fabrication and characterization of Rib-Type waveguides

In view of the good optical properties and the excellent processability of these fluorinated PIs, they were promising candidates for both core and cladding materials in photonic device applications. A single mode waveguide was fabricated using the IVa by reactive ion etching (RIE) technique. Figure 8 showed the top view SEM images of the straight waveguide. The brighter areas represented the ridge of the waveguide. The silica layer of the darker substrate was identified as the bottom layer. A 1550 nm light from the tunable semiconductor laser was coupling into the waveguides with the tapered fiber. The output signal was collected and was shown by a monitor. A typical near-field pattern of the straight waveguide at the wavelength of
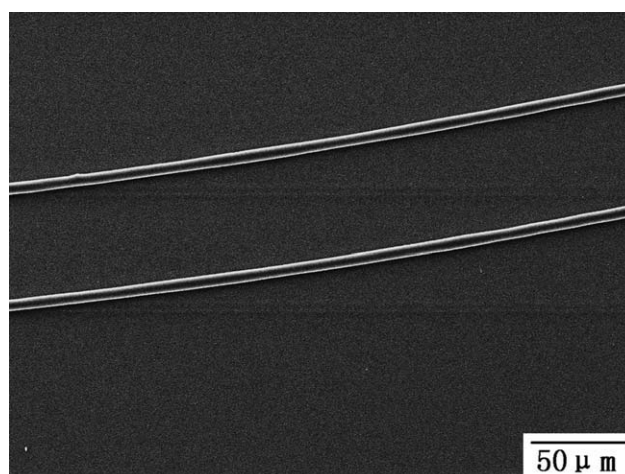

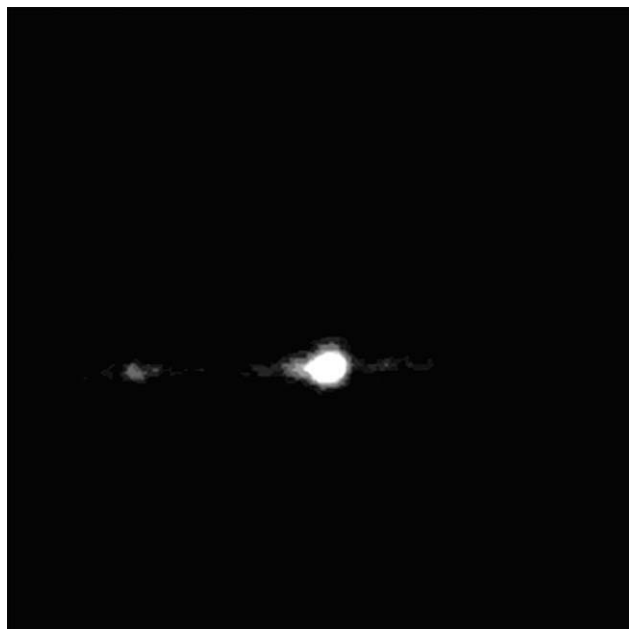**Figure 8** SEM photo of waveguide device.

Figure 9 Near-field pattern of waveguide mode at 1550 nm.

1550 nm was illustrated in Figure 9. This pattern indicated that a single mode optical waveguide device could availably propagate the light wave.

CONCLUSIONS

Two series of fluorinated and chlorofluorinated PIs with ether linkages and bulk side groups in the backbone had been successfully synthesized from two novel diamine monomers with CF_3 or Cl units. The obtained PIs hold on the advantage of fluorinated polyimide materials, including excellent solubility, high thermal stability and good mechanical property. It was more fantastic that they also had excellent optical property, including the high optical transparency, small birefringence, and low NIR absorptions loss at the communication windows. Based on advantage that the two series of PIs (III-based PIs and IV-based PIs) have the similar physical and optical properties except for refractive index, the refractive indices could be controlled precisely by the copolymerization. This method can avoid effectively the higher optical loss which come from the material with the higher refractive indices in the core. Waveguides devices were fabricated from fluorinated and chlorofluorinated PIs. All the characterizations proved that the resulting PIs were potential candidates for a real device application at a telecommunications wavelength.

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