Synthesis of Crosslinkable Fluorinated Linear-Hyperbranched Copolyimides for Optical Waveguide Devices

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ABSTRACT: A series of novel crosslinkable fluorinated linear-hyperbranched copolyimides (co-FHBPIs) were prepared by condensation of 1,3,5-tris(2-trifluoromethy-4-aminopheoxy) benzene (TFAPOB), 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene (6FAPB), and 4,4'-(2-(3',5'-ditrifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (6FPDA) with different feed ratio, which followed by reaction with 3-ethynylaniline. Under this circumstance, as the TFAPOB/6FAPB ratio increases, the T_g of the polymers decreases gradually from 218 to 199°C, and the Young's moduli decreases from 2.14 to 1.64 GPa. Although, the refractive indices are adjustable in the ranges of 1.5755–1.5631, and the polymer birefringences decrease from 0.0122 to 0.0012 at wave length 650 nm. The polymer films were fabricated by spin-coating and crosslinked by thermal curing. The cured films have good resistance to common organic solvents such as acetone, tetrahydrofuran, N, N-dimethylformamide, dimethyl sulfoxide, and chloroform. The glass transition temperature of E-coFHBPI 50 (the TFAPOB/(6FAPB+ TFAPOB) ratio is 50%)changes from 200 to 243°C after curing, which shows higher thermal stability up to 582°C (5% weight loss). Rib-type optical waveguide device is fabricated by E-coFHBPI 50, which demonstrates an obvious near-field mode pattern of the waveguide. All the results indicated that the polymers are promising candidates for optical waveguide materials. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012
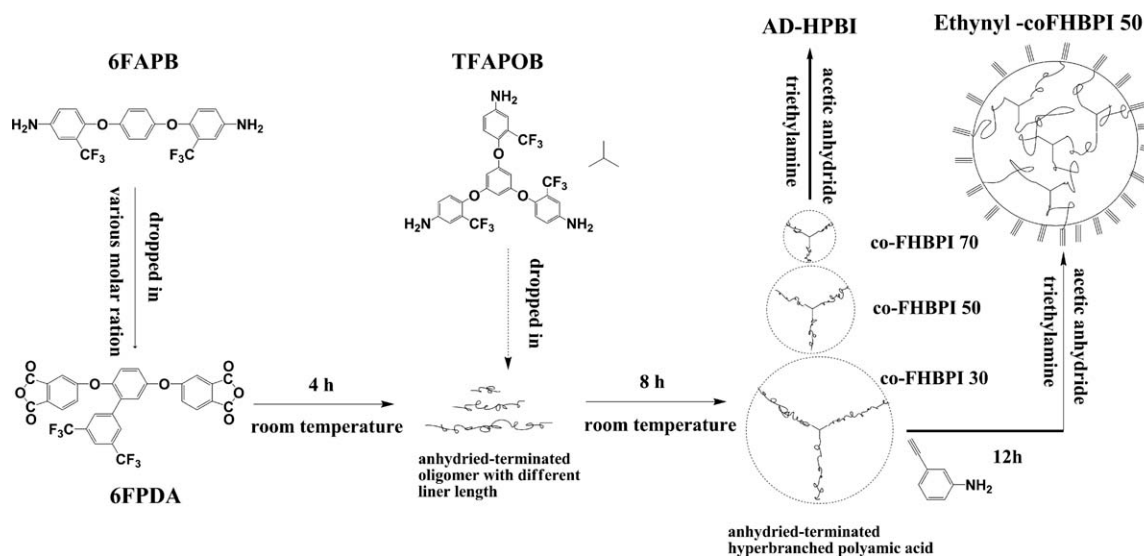
INTRODUCTION

Fluorinated polymer optical waveguides have attracted considerable attention for their possible application as optical components in interconnects and optical communication systems, due to their excellent optical, thermal, and environmental properties and easy, cost-effective, and large-scale device fabrication because of their potential ease of manufacture at low temperature, and the low cost of processing.[1–6] As a result, the development of fluorinated polymers for photonic applications has been the focus of significant research activities in the last decade.[7–11] It was reported that transmission losses in polymers are induced by the vibration absorption of the C—H bond. Many researchers could minimize the loss at 1.3 and 1.55 μm by substituting hydrogen with heavy atoms such as fluorine, deuterium, and chlorine. Meanwhile, thermal and chemical stability of fluorinated polymers are improved by the introduction of crosslinkable groups at the chain ends.[12,13]

Fluorinated polyimides are suitable candidates for real device application due to their excellent thermal and mechanical properties.[14–16] But polyimides need improvements to lower the birefringence due to their stiff backbone. Our laboratory explored several kinds of fluorinated hyperbranched polyimide (FHBPI) and linear fluorinated polyimide with pendant group for optical waveguide materials.[17–20] The monomer 1,3,5-tris(2-trifluoromethy-4-aminopheoxy) benzene (TFAPOB; see Scheme 1) had been designed to contain a trifluoromethyl group and a flexible ether group to reduce the refractive index and the birefringence of the FHBPIs. The obtained polymers had excellent thermal stabilities and show low optical absorption in the near infrared region.

Generally speaking, owing to the formation of globular macromolecules, highly branched polymers have poor mechanical properties, that is, referable the lack of chain entanglements.[21] In this work, we had synthesized a series of anhydride terminated fluorinated hyperbranched copolyimides and reacted the end group with 3-ethynylaniline. For comparison, we synthesized a linear polyimide and a hyperbranched polyimide with 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene (6FAPB)

Scheme 1. Synthetic procedures of the PIs.

and TFAPOB, respectively, which enhance the chain entanglement and improve the mechanical properties of FHBPIs. In addition, the introduction of bulky moieties into polyimide backbones would enhance solubility and reduce refractive index and birefringence. Their thermal properties, mechanical properties, and optical properties were investigated. Furthermore, the introduction of crosslinking group was used to increase thermal stability and chemical resistance and decrease the birefringence. Using crosslinkable E-coFHBPI 50, we fabricated rib-type optical waveguide device successfully by reactive ion etching (RIE) technique.

EXPERIMENTAL

Materials
Phloroglucinol (Aldrich), 3-ethynylaniline(Aldrich),3-trifluoromethyl-4-chloronitro-benzene(Aldrich) and 4-Nitrophthalodinitrile (TCI), and potassium carbonate (K_2CO_3) were used as received. (3,5-ditrifluoromethylphenyl)-1,4-hydroquinone was synthesized according to the literature.[22] N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc), acetic anhydride, and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. 6FAPB was synthesized in our laboratory according to the previously reported method.[23]

Characterization
IR spectra (KBr) were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer (Madison, Wisconsin). ^{1}H NMR spectra were recorded on a Bruker 510 NMR spectrometer (500 MHz) (Karlsruhe, Germany) with tetramethyl silane as a reference. Wide-angle X-ray diffraction (WAXD) measurements were made at room temperature using a Rigaku/max-rA diffractometer (Tokyo, Japan) equipped with a Cu Kα radiation source. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument (Milford, Massachusetts) with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min. Inherent viscosity was determined on an Ubbelohde viscometer in thermostatic container

with the polymer concentration of 0.5 g/dL in DMAc at 25°C. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821[e] instrument (Zurich, Switzerland) at a heating rate of 20°C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere under a heating rate of 10°C/min and polymers were contained within open aluminum pans on a PERKIN ELMER TGA-7 (Waltham, Massachusetts). The scanning electron microscope measurements were performed on a SHIMADZU SSX-550 microscope (Kyoto, Japan). Near infrared spectra were measured by a Jasco V-570 UV/VIS/near-infrared (NIR) spectrophotometer (Tokyo, Japan). The birefringence of the polymer films, at the 650 nm wavelength, were determined by coupling angles of transverse electric (TE) of transverse magnetic (TM) optical guided modes with a gadolinium gallium garnet prism. The mechanical tests in tension were carried out using a SHIMADZU AG-I at a constant crosshead speed of 10 mm/min.

Monomer Synthesis
Synthesis of TFAPOB. TFAPOB was synthesized according to a previously reported two-step reaction procedure.[25] First, phloroglucinol was reacted with 3-trifluoromethyl-4-chloronitrobenzene to yield the intermediate product, 1,3,5-tris(2-trifluoromethyl-4-nitropheoxy) benzene (TFNPOB). Subsequently, the TFNPOB was reduced to TFAPOB with hydrazine in ethanol. Yield: 70%, m.p. 180°C. IR (KBr, cm^{-1}): 3509, 3407, 3368, and 3222. ^{1}H NMR (500 MHz, dimethyl sulfoxide [DMSO]-d_6, δ, ppm): 5.49 (s, 6H, NH_2), 5.97 (s, 3H), 6.70 (t, 3H), 6.87 (t, 3H), 6.89 (s, 3H).

Synthesis of 4,4′-(2-(3′,5′-ditrifluoromethylphenyl)-1,4-phenylenedioxy)-diphthalic anhydride (6FPDA). As show in Scheme 1, anhydride was synthesized from the nitro-displacement reaction of TCI with (3,5-ditrifluoromethylphenyl)-1,4-hydroquinone in DMF in presence of potassium carbonate as the base, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile)s and cyclodehydration of the resulting bis(ether diacid)s.

The synthesis details were described in a previous article.[18,19] The characterization of the target bis(ether anhydrides)s were listed as follows. Yield: 83%, m.p. 157–159°C. IR (KBr, cm^{-1}): 1852 (asym. C=O), 1770 (sym. C=O), 1276 (C—O—C), 1120 (C—F). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.25 (s, 2H), 8.14 (d, J = 7.8 Hz, 1H), 8.09 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.68 (s, 2H), 7.60 (s, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.43 (s, 2H).

Polymer Synthesis

Synthesis of Linear Polyimide. 6FPDA (1.8432 g, 3 mmol) was dissolved with 18 mL DMAc in a 50 mL thoroughly dried three-neck flask. To this dianhydride solution, 6FAPB (1.2850 g, 3 mmol) and an additional 13 mL of DMAc were added. The mixture was stirred in nitrogen at room temperature for 24 h to yield a viscous poly(amic acid) (PAA) solution with 10% solid content. Chemical imidization was carried out via the addition of 2 mL of an acetic anhydride/pyridine (5/4 v/v) mixture into the PAA solution. The mixture was stirred at 60°C for 6 h to yield a polyimide solution, which was poured into methanol to give a precipitate and collected by filtration. The polyimide was washed thoroughly with methanol, and dried at 80°C *in vacuo* for 24 h. IR (KBr, cm^{-1}): 1780 and 1726 (C=O stretching), 1375 (C—N—C stretching), 1246 (C—O—C stretching), 1137 (—CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.99 (s, 2H), 7.87 (d, 1H), 7.83 (s, 1H), 7.77 (s,1H), 7.73 (s, 1H), 7.54–7.49 (m, 4H), 7.35–7.26 (m, 6H), 7.15 (d, 4H), 7.05 (t, 2H)

Synthesis of Anhydride-Terminated Hyperbranched Polyimide. 2 mmol (1.2288 g) of dianhydride was dissolved in 20 mL of DMAc under N$_2$ flow in a 100 mL thoroughly dried three-neck flask. Then 1 mmol (0.6034 g) of TFAPOB in 10 mL DMAc was added dropwise to the dianhydride solution through a syringe over 3 h to yield a viscous PAA solution with 5% solid content. After TFAPOB solution was completely added, the reaction mixture was further stirred at room temperature for 24 h to afford an anhydride-terminated PAA solution. The PAA was subsequently converted to polyimide either chemical imidization process. Chemical imidization was carried out via the addition of 0.5 mL of triethylamine and 1.5 mL of acetic anhydride into the PAA solution at room temperature overnight. The resulting homogeneous polyimide solution was poured into methanol to give a white precipitate, which was collected by filtration, washed thoroughly with methanol and dried under vacuum at 80°C for 24 h. IR (KBr, cm^{-1}): 1781 and 1726 (C=O stretching), 1377 (C—N—C stretching), 1246 (C—O—C stretching), 1135 ([sdbond]CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.99 (s, 2H), 7.89–7.71 (m, 4H), 7.68–7.42 (m, 4H), 7.35–7.07 (m, 5H), 6.63 (s, 1H).

Synthesis of Anhydride-Terminated Copolyimides with Different Linear Length (co-FHBPI 30,50, and 70). For convenience, in this article, all the fluorinated hyperbranched copolyimide are denominated in shortened forms. For example, "co-FHBPI 50" means the fluorinated hyperbranched copolyimide made from amine monomer mixture which the ratio of TFAPOB/(6FAPB+ TFAPOB) is 50%. The names of the other copolyimides are similar to it.

A typical synthetic procedure for the preparation of co-FHBPI 50 is as follows. 1.5 mmol (0.9216 g) dianhydride was dissolved in 10 mL of DMAc under N$_2$ flow in a 100 mL thoroughly dried three-neck flask. Then 0.5 mmol (0.2142 g) of 6FAPB in 5 mL DMAc was added dropwise to the dianhydride solution. After 6FAPB solution was completely added, the reaction mixture was further stirred at room temperature for 6 h to obtain an anhydride-terminated oligomer solution. And then 0.5 mmol (0.3017 g) of TFAPOB in 13 mL DMAc was added dropwise to the oligomer solution and the reaction mixture was further stirred at room temperature for 6 h to get an anhydride-terminated hyperbranched polyamic acid with 5% solid content. The PAA was subsequently converted to polyimide by chemical imidization process. Chemical imidization was carried out via the addition of 0.75 mL of triethylamine and 1.5 mL of acetic anhydride into the PAA solution at room temperature overnight. The resulting homogeneous polyimide solution was poured into methanol to give a white precipitate, which was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 80°C for 24 h. Other co-FHBPIs were synthesized in an analogous procedure.

Co-FHBPI 30: IR (KBr, cm^{-1}): 1780 and 1726 (C=O stretching), 1377 (C—N—C stretching), 1246 (C—O—C stretching), 1135 (—CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.98 (s, 2H), 7.90–7.81 (s, 2H), 7.81–7.70 (s, 2H), 7.59–7.44 (m, 4H), 7.38–7.25 (m, 9H), 7.13 (d, 4H), 7.04 (t, 2H), 6.63 (s, 1H).

Co-FHBPI 50: IR (KBr, cm^{-1}): 1782 and 1725 (C=O stretching), 1377 (C—N—C stretching), 1246 (C—O—C stretching), 1135 (—CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.98 (s, 2H), 7.91–7.70 (m, 4H), 7.70–7.42 (m, 4H), 7.40–7.24 (m, 9H), 7.13 (d, 4H), 7.04 (t, 2H), 6.61 (s, 1H).

Co-FHBPI 70: IR (KBr, cm^{-1}): 1781 and 1726 (C=O stretching), 1377 (C—N—C stretching), 1246 (C—O—C stretching), 1135 (—CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.98 (s, 2H), 7.90–7.70 (m, 4H), 7.71–7.42 (m, 4H), 7.35–7.22 (m, 9H), 7.13 (d, 4H), 7.04 (t, 2H), 6.63 (s, 1H).

Synthesis of Ethynyl-Terminated Copolyimides. The 3-ethynylaniline was added into a solution of co-FHBPI 50 based poly(amic acid) precursors which were prepared by the same procedures as mentioned above. The reaction mixtures were stirred for 6 h. A mixture of 0.5 mL of triethylamine and 1 mL of acetic anhydride was then added stirred at 60°C for anther 8 h. After cooling to room temperature, the mixture was precipitated from ethanol (300 mL). The polymers were collected by filtration and dried under vacuum at 80°C for 24 h. IR (KBr, cm^{-1}): 3305 (C[tbond]C stretching) 1781 and 1729 (C=O stretching), 1378 (C—N—C stretching), 1245 (C—O—C stretching), 1136 (—CF$_3$ stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.98 (s, 2H), 7.88–7.71 (m, 4H), 7.66–7.36 (m, 4H), 7.35–7.26 (m, 9H), 7.13 (d, 4H), 7.04 (t, 2H), 6.62 (s, 1H), 3.11 (s, 1H).

Preparation of PI Membranes and Thermal Curing. Ethynyl-terminated copolyimides were dissolved in DMAC at concentrations 10–30 wt %. The solutions were filtered with a syringe through a 0.2 um Teflon membrane filter. The solutions cast

Table I. Inherent Viscosity, GPC Data and Thermal Properties of PIs

Polymer	Inherent viscosity η_{inh}(dL/g)[a]	GPC data		DSC	TGA	
		$M_w{}^b \times 10^4$	$M_w/M_n{}^b$	$T_g{}^c$ (°C)	$T^d{}_{5\%}$ (°C)	$T^d{}_{10\%}$ (°C)
Linear polyimide	0.75	6.1	1.5	218	576	598
co-FHBPI 30	0.61	4.8	2.8	214	571	595
co-FHBPI 50	0.50	3.5	3.0	209	566	594
co-FHBPI 70	0.38	3.2	3.9	203	556	580
FHBPI	0.23	3.7	3.5	199	566	602
E-coFHBPI 50	0.58	4.5	3.8	200	581	606
Cured E-coFHBPI 50	–	–	–	243	–	–

[a] Determined with 0.5% solution in a solvent (DMAc) at 25°C, [b] Relative to polystyrene standard, using DMF as the eluent, [c] Baseline shift in the second heating DSC traces, with a heating rate of 20°C/min in nitrogen, [d] Temperature at 5% and 10% weight loss were recorded by TGA at a heating at 10°C/min in nitrogen.

onto a flat glass plate with a programmed procedure (80°C, 1 h; 150°C, 1 h; 180°C, 1 h) in a ventilated oven to remove the solvents. Then the plate was put into a vacuum oven, treated at 270°C for 2 h to prepare insoluble films.

RESULTS AND DISCUSSION

Synthesis and Characterizations of Polymer

co-FHBPIs. A series of co-FHBPI were synthesized successfully by a two-stage one pot method: the linear oligomer was prepared with desired length at first, then the dendritic monomer TFAPOB were added to the first reactive flask to form co-FHBPI-based polyamic acid precursors. Then 3-ethynylaniline was added into these co-FHBPI-based polyamic acid precursors prepared by the same procedures as mentioned above. The an-

hydride-terminated and ethynyl-terminated ones were chemically converted into polyimides in the presence of acetic anhydride and triethylamine at 40°C.

As shown in Table I, the weight-average molecular weights and polydispersities range of the co-FHBPIs are 32,000–48,000 and 2.8–3.9 respectively, relative to the polystyrene standards. The intrinsic viscosities are evaluated in DMAc at 25°C with an Ubbelohde viscometer, and the results fall within the range of 0.23–0.75 dL/g. The structures of the co-FHBPIs have been confirmed by fourier transform infrared spectroscopy (FTIR) and ^{1}H NMR spectra.

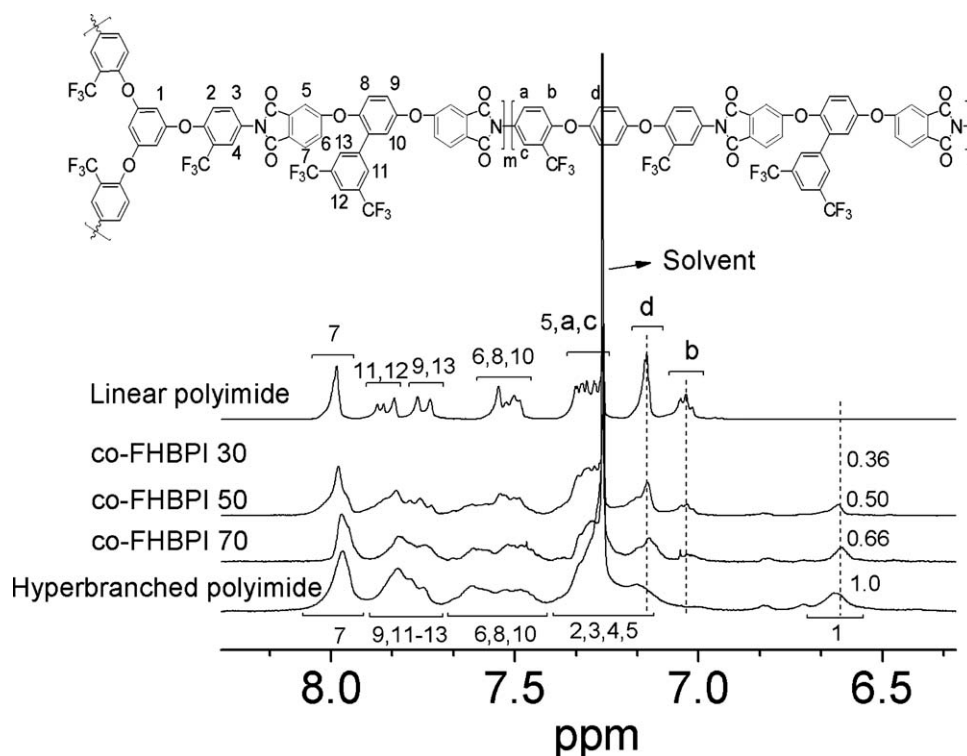The bands at 1781 (C=O asymmetrical stretching), and 1730 (C=O symmetrical stretching), and 1376 cm^{-1} (C—N

Figure 1. ^{1}H NMR spectra of the PIs in CDCl$_3$.

Table II. Mechanical Properties of PIs

Polymers	Film thickness (µm)	Tensile strength (MPa)	Elongation at break (%)	Youngs' modulus (GPa)
Linear polyimide	95	92	20	2.14
co-FHBPI 30	100	97	12	1.88
co-FHBPI 50	95	93	9	1.75
co-FHBPI 70	90	89	7	1.64

stretching) are the characteristic absorption bands of polyimides, together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C—O and C—F stretchings. No characteristic band of polyamic acid (around 1680 cm^{-1}) is found in IR spectra, indicating that the polyimides have been fully imidized.

As shown in Figure 1, the molecular structures of all co-FHBPIs were characterized by ^{1}H NMR in CDCl$_3$. The integration of these peaks was allowed for an estimation of the compositions of each amine moiety in the polymers, which was found to be consistent with designed polymer structures based upon the monomer feed ratios used in the reactions. All protons resonate in the region of 6.5–8.1 ppm and have been well assigned. The protons H$_1$ shifted to the high field because of the electron-donating property of aromatic ether group. The signals of H$_7$ close to the imide ring appear at the farthest downfield region of the spectrum. The intensity of H$_1$ signal increases with the feed ratio of TFAPOB. These results indicate that a good control of composition of the resulting polymers could be easily achieved by varying the feed ratio of TFAPOB/6FAPB. This significantly affects the resulting polymer in waveguide devices as a good structural control and reproducibility of optical properties such as refractive index of the resulting materials are critical issues for device design and successful device fabrications.

WAXD experiments were conducted in an attempt to evaluate the morphological structure of our synthesized polyimides. All the co-FHBPIs are broad and without obvious peak features, indicating their amorphous structure. The amorphous structure endows the obtained polyimides with good solubility.
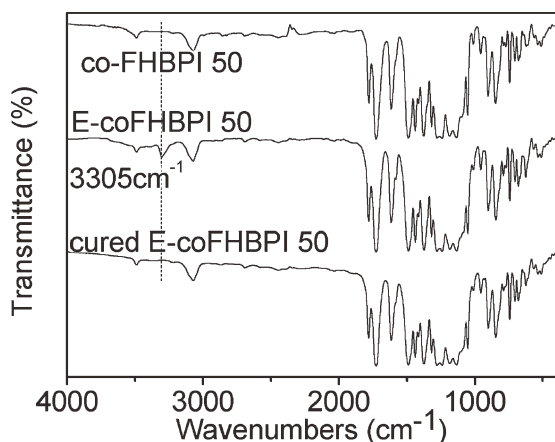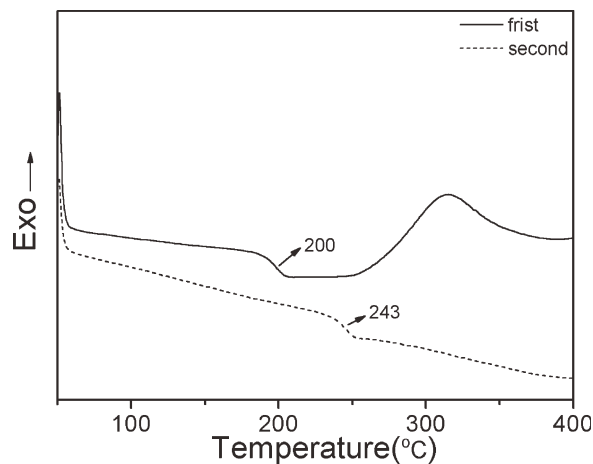

Figure 3. Typical DSC curves of E-coHBPI 50.

The solubility of polyimides was tested in various organic solvents. These polymers demonstrated good solubility in organic solvents such as DMSO, DMAc, DMF, N-methyl-2-pyrrolidone, and THF at room temperature, due to the poor intermolecular packing resulted from their pendant group and hyperbranched structures. Most of them can be even soluble in acetone and chloroform at room temperature. The good solubility of these copolyimides in common organic solvents can facilitate their film fabrications for optical waveguide devices. As shown in Table II, All of the linear and copolyimides have excellent mechanical properties.

E-coFHBPI. The molecular structure of ethynyl-terminated co-FHBPI 50 was characterized by ^{1}H NMR in CDCl$_3$. The aromatic protons resonate in the region of 6.6–8.1 ppm. The ethynyl moiety appears in 3.1 ppm.

As shown in Figure 2, the crosslinking reaction of ethynyl end group was monitored by IR spectroscopy as illustrated by E-coFHBPI 50. The ethynyl end polymer shows absorption of the hydrogen–carbon stretch of the carbon–carbon triple bond at 3305 cm^{-1} after end capping reaction, and the peak disappears after curing, whereas other FTIR peaks are not affected. This indicates that the polymer is very stable at high temperature
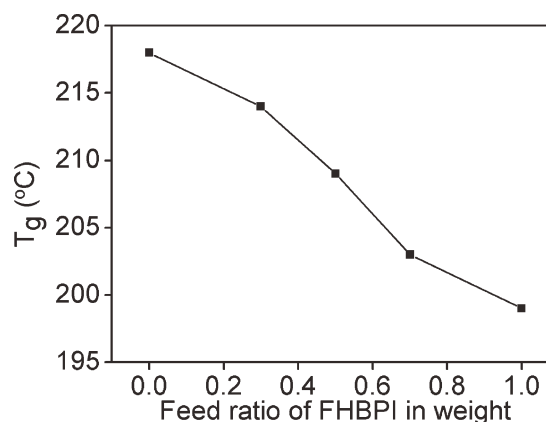

Figure 2. FTIR spectra of co-FHBPI 50, E-coFHBPI 50 and cured E-coFHBPI 50.

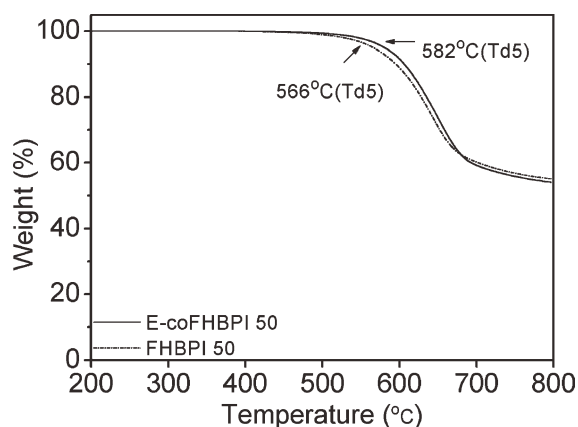**Figure 4.** Composition dependence of the T_g of TFAPOB and 6FAPB.

Figure 5. Typical TGA curves of co-FHBPI 50 and E-coHBPI 50.

(270°C) for 2 h. The crosslinking reactions are monitored by DSC measurements. (See Figure 3) The cured polymer film has good solvent resistance due to formation of a highly crosslinked network and it can not cause intermixing by solvents between layers by spin-coating.

Thermal Properties

According to DSC and TGA, thermal analysis of the polyimides was performed. As shown in Table I, the T_g of the polyimides are in the range of 199–218°C, which increase in the order of linear polyimide > co-FHBPI 30 > co-FHBPI 50 > co-FHBPI 70 > FHBPI. It was attributed to the special hyperbranched structure in the center of triamine, which brought about less efficient chain packing and an increased free volume. DSC analysis was also performed to research the effect of curing on the glass transition temperature of the ethynyl terminated copolyimide (E-coFHBPI 50). These results are shown in Figure 4. A higher glass transition temperature is observed in the second heating run as a result of ethynyl crosslinking. The copolyimide exhibited an exothermic transition around 314°C on DSC heating associates with the thermal crosslinking reactions of the ethynyl group. The T_g of the resultant crosslinked copolyimide is about 43°C higher than that of the original copolyimide.
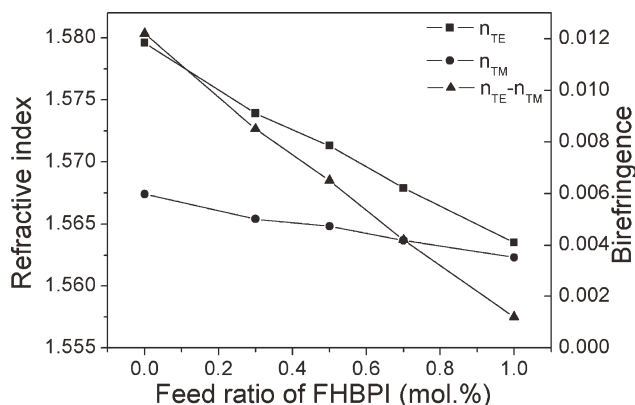
Table III. Refractive Indices and Birefringences of PIs

Polymer	n_{TE}[a]	n_{TM}[b]	n_{AV}[c]	Δn[d]
Linear polyimide	1.5796	1.5674	1.5755	0.0122
co-FHBPI 30	1.5739	1.5654	1.5711	0.0085
co-FHBPI 50	1.5713	1.5648	1.5691	0.0065
co-FHBPI 70	1.5679	1.5637	1.5665	0.0042
FHBPI	1.5635	1.5623	1.5631	0.0012
E-coFHBPI 50[e]	1.5724	1.5700	1.5716	0.0024

[a] In-plane refractive index at 650 nm: n_{TE}, [b] Out-of-plane refractive index at 650 nm: n_{TM}, [c] Average refractive index: $n_{AV} = (2n_{TE}+n_{TM})/3$, [d] Birefringence $\Delta n = n_{TE}-n_{TM}$, [e] E-coFHBPI 50 has been crosslinked.

TGA curves of obtained polymers show 5% and 10% weight loss in the range of 556–576°C and 580–602°C, respectively, indicating their high thermal stability. The FHBPI 50 has a high thermal stability with 5% weight loss of 566°C, and the 5% weight loss of E-coFHBPI 50 is 581°C. As a comparison, the T_d of copolyimide increases about 16°C for FHBPI and E-coFHBPI, the results are shown in Figure 5. Because the crosslinking reaction of the E-coFHBPI 50 carried out with increasing temperature. So the improvement of E-coFHBPI's thermal stability could be verified by the comparison of FHBPI and E-coFHBPI [24]. The thermal stability of E-co-FHBPI 50 was more excellent than other FHBPIs, which were reported previously.[25,26]

Optical Properties

The refractive indices of the polyimides were studied through the prism coupling technique at 650 nm on thin films and the values were in the range of 1.5755–1.5623. In fact, a good linear relationship (both n_{TE} and n_{TM}), between the refractive index of the polymer and the feed ratio of TFAPOB was observed as shown in Figure 6. When the feed ratio of TFAPOB increased from 0 to 100 mol %, the refractive index (n_{TE} and n_{TM}) decreased from 1.5796 to 1.5635 and 1.5674 to 1.5623, respectively. As the design and fabrication of waveguide structures depend on the difference in the refractive index between the core and the cladding materials, this linearity of refractive index over such a large range provides tremendous flexibility in the fabrication of waveguide devices using these fluorinated
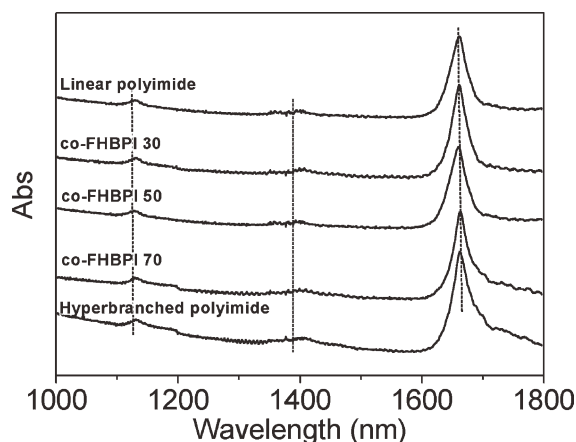

Figure 6. Composition dependence of the refractive index and birefringence of TFAPOB and 6FAPB.

Figure 7. Near-IR spectra of the PIs.

polyimides. It was attributed to the various structure and fluorinated content of the amine monomer. At the same time, when the feed ratio of TFAPOB increased from 0 to 100 mol %, the birefringences ($n_{TE}-n_{TM}$) of the copolyimides decreased from 0.0122 to 0.0012. The birefringence of FHBPIs which were reported previously[25,26] is in the range of 0.0021–0.0098. In contrast, the birefringence of E-coFHBPI 50 which we synthesized is 0.0024. From this, we thought that the optical properties of our polymer did not decrease after copolymeration and end capping. The fact is that the birefringence of polymers can be affected by chain flexibility and geometry of the repeat units. For FHBPIs, the "core" molecule, that is, the triamine structure which is expected to define the configuration of the repeat unit is nonplanar and asymmetric in geometry. Therefore, it can reduce the orientation of the bond involved in the polymer backbone and thus greatly reduces the birefringence. Based on this point, the higher content of TFAPOB led to a decrease in birefringence. After crosslinking, the refractive index increased and the birefringence decreased. This is because crosslinking led to a decrease in free-volume of the main chain and disordered chain packing of the polymers. The data of refractive indices and birefringences of polyimides (PIs) are shown in Table III.

As known, the replacement of C—H bonds with C—F bonds gives the polymeric material high optical transparency in the NIR telecommunication region.[27] As shown in the Figure 7, there is little light absorption at telecommunication wavelength of 1310 and 1550 nm due to their high fluorine contents. Therefore, co-FHBPIs are expected to be applicable to optoelectronic materials.

Fabrication and Characterization of Rib-Type Waveguides

In view of the good optical properties and the excellent processability of E-coHBPI 50, it is a good candidate material in photonic device applications. Single mode waveguides were fabricated using the E-coHBPI 50 by RIE technique. Figure 8 shows the top view of the core structure of straight waveguides. The core width is 10 μm. The spectral-transmission characteristics of waveguide device were measured by tunable laser with a center wavelength at 1550
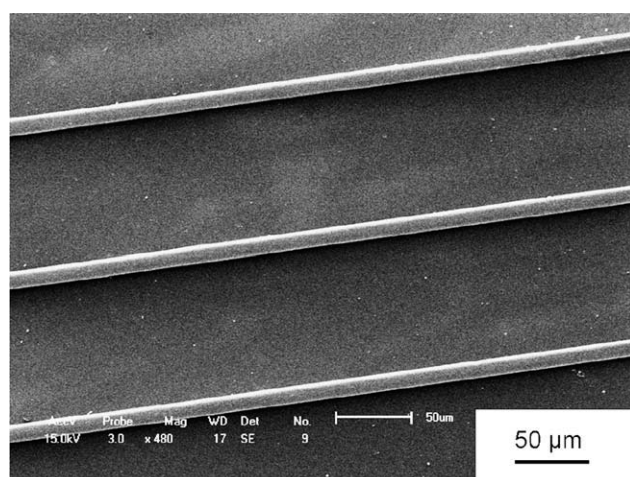

Figure 8. SEM photograph of straight waveguide fabricated with E-coFHBPI 50.
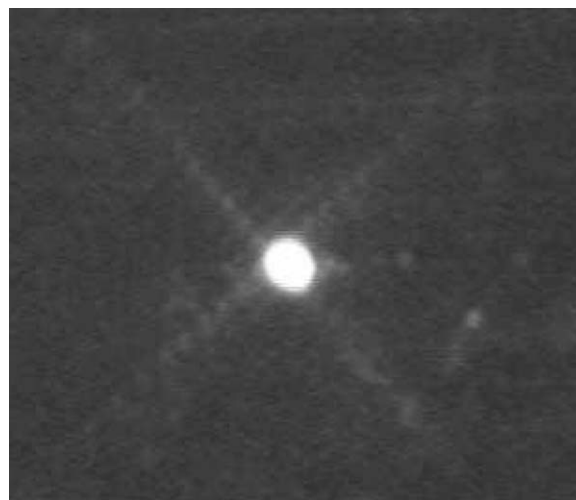

Figure 9. Near-field pattern of waveguide mode at 1550 nm.

nm and a spectrum analyzer. Light from a tunable semiconductor laser was coupled into the input waveguide through a fiber. The near-field mode pattern at the out channels (Figure 9) was observed with an infrared vidicon after being magnified by an objective lens. This pattern indicates that the optical waveguide operates successfully in a single mode. It is likely that the further introduction of additional crosslinkable groups at the end of the polymer should be helpful for the fabrication of multilayered optical waveguides. This result indicated that the E-coHBPI 50 is a good candidate for the optical waveguide device.

CONCLUSIONS

Novel crosslinkable fluorinated linear-hyperbranched copolyimides (co-FHBPI) for polymeric optical waveguide devices were synthesized successfully. The obtained polymers have high thermal stability and good solubility in organic solvents. The T_g, refractive index, birefringence, and Young's moduli regularly changed by combination of TFAPOB and 6FAPB content in the copolymer. These amorphous polymers easily provided transparent thin films by spin-coating or casting. The thermally crosslinked films of E-coFHBPI 50 showed higher T_g which changed from 200 to 243°C and better thermal stability up to 582°C (5% weight loss under nitrogen atmosphere). After crosslinking, the films were insoluble in common organic solvents, such as acetone, THF, methylene chloride, chloroform, DMF, and DMSO. Rib-type polymeric waveguide device was successfully prepared using E-coFHBPI 50, which showed an obvious near-field mode pattern of the waveguide, demonstrating that it is promising candidate for optical waveguide material.

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