ORIGINAL ARTICLE

Synthesis and characterization of fluorinated crosslinkable poly(phthalazinone ether)s bearing tetrafluorostyrene groups for optical waveguides

Guanghui Li^{1,2}, Jinyan Wang^{1,2,3}, Su Guixian^{1,2}, Xigao Jian^{1,2,3}, Linghua Wang⁴ and Mingshan Zhao⁴

A series of novel fluorinated crosslinkable poly(phthalazinone ether)s bearing tetrafluorostyrene groups (FSt-FPPEs) was prepared by polycondensation from 4-(4'-hydroxyphenyl)-phthalazin-1(2H)-one (DHPZ), decafluorobiphenyl, 4,4-(hexafluoroisopropylidene)diphenol (6F-BPA) and pentafluorostyrene (FSt) for optical waveguide applications. The obtained polymers exhibited good solubility in common organic solvents and could be easily cast into optical-quality thin films. The resulting polymers could be thermally crosslinked either at 160 °C in the presence of a free radical initiator dicumyl peroxide under vacuum or at 280 °C in the absence of any initiator under vacuum. The polymers had high glass transition temperatures in the range 164–269 °C, which could be further increased by about 10 °C on thermal crosslinking. The crosslinked polymers had good thermal stabilities (the temperatures of 1% mass loss after curing ranged from 478 to 490 °C) and high glass transition temperatures. The crosslinked polymer films also exhibited good optical properties. By adjusting the feed ratio of the reactants, the refractive indices of transverse electronic and transverse magnetic modes (at 1550 nm) could be controlled well in the range of 1.4952–1.5625 and 1.4924–1.5538, respectively. The optical losses of the crosslinked polymers were rather low, <0.3 dB cm⁻¹ at 1550 nm.

Polymer Journal (2010) 42, 880–886; doi:10.1038/pj.2010.85

Keywords: crosslinking; fluorinated poly(arylene ether); phthalazine; polymer optical waveguide

INTRODUCTION

In recent years, organic polymer materials have received considerable attention in the field of photonic devices^{1–3} because of their feasible processing, low-cost fabrication potential and structure–property tunability.^{4–7} The key requirements for their use as optical waveguides include a low optical loss in the infrared region, high thermal stability, easily controlled refractive index, low birefringence and good adhesion to the silicon substrate. However, most hydrocarbon-based polymers show a large transmission loss in the infrared region because of the vibrational overtone absorption of the vibration overtones of C–H, O–H and N–H bonds.^{8–10} The intrinsic absorption loss can be reduced by designing polymers in which the high absorption vibration overtones of C–H groups are replaced with low absorption loss fluorocarbon C–F groups.^{11,12} Among all fluorinated polymers, fluorinated poly(arylene ether)s have been shown to be one of the most promising classes of candidates for optical waveguide devices.^{13–16} Fluorinated poly(arylene ether)s not only have lower near-infrared region absorption but also show higher thermal stability and lower water absorption. However, it is difficult for fluorinated polymers to adhere to many substrates because of their inert natures and low surface energies.

Crosslinked polymer systems have been reported to have several advantages, such as increased thermal stability, improved chemical resistance and improved adhesion to the substrate.^{3,17} In previous research, we synthesized a series of fluorinated poly(phthalazinone ether)s¹⁸ and a crosslinked poly(phthalazinone ether ketone) bearing tetrafluorostyrene groups.¹⁹ We previously demonstrated that fluorinated poly(phthalazinone ether)s had inherently low optical losses and good refractive index controllability, whereas the crosslinked poly(phthalazinone ether ketone) had low birefringence and good adhesion with semiconductor substrates. Therefore, we aimed to synthesize a group of polymers (called as fluorinated crosslinkable poly(phthalazinone ether)s bearing tetrafluorostyrene group (Fst-FPPE) that combine the excellent properties of the above two classes of polymers. Thus, a series of Fst-FPPEs were synthesized. The chemical structures of the resulting polymers were confirmed by ¹H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) methods. The thermal crosslinking of the Fst-FPPE films and optical properties such as refractive indices, optical losses and birefringences of the crosslinked films were also investigated by differential scanning calorimetry (DSC), FT-IR and a Sairon SPA-4000 prism coupler (Sairontech, Gwangju, Korea).

¹State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, PR China; ²Department of Polymer Science and Materials, Dalian University of Technology, Dalian, PR China; ³Liaoning High Performance Resin Engineering Research Center, Dalian, PR China and ⁴School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian, PR China

Correspondence: Associate Professor J Wang and Professor X Jian, Department of Polymer Science and Materials, Dalian University of Technology, Dalian Zhongshang Road 158#, Dalian 116012, PR China.

E-mails: wangjinyan1970@yahoo.com.cn or jian4616@dl.cn

Received 21 April 2010; revised and accepted 2 August 2010

EXPERIMENTAL PROCEDURE

Materials

4-(4'-Hydroxyphenyl)phthalazin-1(2H)-one (DHPZ) was a gift from Dalian Polymer New Material (Dalian, PR China) and was recrystallized in *N,N*-dimethyl acetamide (DMAc) and dried under vacuum at 120 °C for 24 h before use. 4,4'-(Hexafluoroisopropylidene)diphenol (6F-BPA), pentafluorostyrene (FSt) and decafluorobiphenyl (DFBP) were purchased from Sigma-Aldrich and used without any further treatment. Analytical grade DMAc (Tianjin Fuyu Fine Chemical Industry, Tianjin, PR China) was purified by reduced pressure distillation before use, and the middle fractions were subsequently collected and stored over molecular sieves (Type 4 Å). Analytical grade anhydrous dicumyl peroxide (DCP), potassium fluoride (KF), calcium hydride (CaH₂), tetrahydrofuran, chloroform (CHCl₃), *N*-methyl pyrrolidone, acetone, dimethyl sulfoxide, benzene and cyclohexanone were purchased from Tianjin Fuyu Fine Chemical Industry, and used without any further treatment.

Instruments

¹H NMR (400 MHz) was performed with a Varian Unity Inova 400 spectrometer (Varian, Palo Alto, CA, USA) at an operating temperature of 25 °C using CDCl₃ as a solvent, and the results were listed in parts per million downfield from tetramethylsilane. FT-IR spectra were recorded by the reflection method with a Thermo Nicolet Nexus 470 FT-IR spectrometer (Thermo Nicolet Nexus, Vernon Hills, IL, USA). Gel permeation chromatography (GPC) was carried out on a HP 1090 HPLC instrument (Agilent, Illinois, CA, USA) equipped with 5-μm Phenogel columns (linear, 4×500 Å) arranged in a series with chloroform as a solvent and a ultraviolet detector at 254 nm. The values were calibrated versus a polystyrene standard. Glass transition temperature (*T*_g) was determined with a Mettler DSC 822 differential scanning calorimeter (Mettler-Toledo, Zurich, Switzerland) under flowing nitrogen at a heating rate of 10 °C min⁻¹ from 50 to 400 °C. Thermogravimetric analysis of the polymers was performed on a

Mettler TGA/SDTA851 thermogravimetric analysis instrument under a nitrogen atmosphere at a heating rate of 20 °C min⁻¹ from 100 to 750 °C. Optical properties such as refractive index and optical loss were measured using a Sairon SPA-4000 prism coupler with a tolerance of ± 0.0002.

Synthesis of FPPE

Fluorinated poly(phthalazinone ether) was synthesized by a nucleophilic aromatic substitution (S_NAr) polycondensation reaction, as illustrated in Scheme 1. The typical preparation of these polymers was carried out as follows: KF (0.0581 g, 1.00 mmol) and CaH₂ (0.4210 g, 10.00 mmol) were added to a solution of DHPZ (1.1912 g, 5.00 mmol) and DFBP (1.7040 g, 5.10 mmol) in 30 ml anhydrous DMAc. Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 90 °C and kept at this temperature for 4 h. Small samples of the reaction solution (~0.2 ml) were removed at intervals during the reaction for GPC. The solutions were first filtered to remove insoluble salts and then dropped into an acidic water/methanol mixture (2:1 v:v) and agitated to precipitate the polymer. The resulting powder was washed twice with water and dried under vacuum overnight before GPC.

Synthesis of FSt-FPPEs

FSt-FPPEs were synthesized by a two-step nucleophilic aromatic substitution (S_NAr) polycondensation reaction, as illustrated in Scheme 2. The typical preparation of these polymers (FSt-FPPE-2) was carried out as follows: KF (0.2324 g, 4.00 mmol) and CaH₂ (1.6838 g, 40.00 mmol) were added to a solution of 6F-BPA (0.8406 g, 2.50 mmol) and DHPZ (1.7868 g, 7.50 mmol) in 10 ml anhydrous DMAc. After nitrogen was purged through the reaction mixture with stirring for 10 min, FSt (0.1745 g, 0.90 mmol) was added to the reaction mixture. The mixture was then slowly heated to 90 °C and kept at this temperature for 1 h in darkness. After cooling to room temperature, DFBP (3.1908 g, 9.55 mmol) in 30 ml anhydrous DMAc was added to the reaction mixture. After that, the mixture was slowly heated to 90 °C and kept at this temperature for 3 h in darkness. After cooling, the viscous solution was slowly poured into a sufficient amount of ethanol containing a few drops of hydrochloric acid. The crude polymer was rinsed six times with hot distilled water to remove inorganic salts. The dried polymer was purified by dissolving it in DMAc, filtering the solution through a 0.45-μm Teflon microfilter before pouring it into ethanol and subsequently rinsing it six times with hot deionized water. The purified polymer was dried at 60 °C under vacuum for 24 h. The total yield of FSt-FPPE-2 was 85%. ¹H-NMR (400 MHz, CDCl₃, p.p.m.) δ: 5.75 (d, *J*=12 Hz), 6.14 (d, *J*=18 Hz), 6.70 (dd, *J*=18 Hz, 12 Hz), 7.07 (d, *J*=8 Hz, 2 H), 7.24 (d, *J*=8.0 Hz, 3 H), 7.42 (d, *J*=8 Hz, 2 H), 7.69 (d, *J*=8 Hz, 3 H), 7.80–8.00 (4.5 H, m), 8.63 (1.5 H, m). ¹⁹F-NMR (376 MHz, CDCl₃, p.p.m.) δ: -64.07(s), -136.66(m), -137.43(m), -143.27(m), -152.40(m).

FSt-FPPE-1: 82% yield. ¹H-NMR (400 MHz, CDCl₃, p.p.m.) δ: 5.75 (d, *J*=12 Hz), 6.13 (d, *J*=18 Hz), 6.70 (dd, *J*=18 Hz, 12 Hz), 7.25 (d, *J*=8 Hz, 2 H),

Scheme 1 Synthesis of FPPE.

Scheme 2 Synthesis of FSt-FPPEs.

7.69 (d, $J=8$ Hz, 2 H), 7.75–8.00 (3 H, m), 8.63 (1 H, m). ^{19}F -NMR (376 MHz, CDCl_3 , p.p.m.) δ : -136.67(m), -137.41(m), -143.24(m), -152.46(m).

FSt-FPPE-3: 84% yield. ^1H -NMR (400 MHz, CDCl_3 , p.p.m.) δ : 5.74 (d, $J=12$ Hz), 6.13 (d, $J=18$ Hz), 6.69 (dd, $J=18$ Hz, 12 Hz), 7.06 (d, $J=8$ Hz, 4 H), 7.25 (d, $J=8$ Hz, 2 H), 7.42 (d, $J=8$ Hz, 4 H), 7.69 (d, $J=8$ Hz, 2 H), 7.75–8.00 (3 H, m), 8.62 (1 H, m). ^{19}F -NMR (376 MHz, CDCl_3 , p.p.m.) δ : -64.07(s), -136.66(m), -137.41(m), -143.26 (m), -152.44(m).

FSt-FPPE-4: 86% yield. ^1H -NMR (400 MHz, CDCl_3 , p.p.m.) δ : 5.74 (d, $J=12$ Hz), 6.12 (d, $J=18$ Hz), 6.70 (dd, $J=18$ Hz, 12 Hz), 7.06 (d, $J=8.5$ Hz, 12 H), 7.24 (d, $J=9.9$ Hz, 2 H), 7.42 (d, $J=8.3$ Hz, 12 H), 7.68 (d, $J=8.1$ Hz, 2 H), 7.80–8.00 (3 H, m), 8.63 (1 H, m). ^{19}F -NMR (376 MHz, CDCl_3 , p.p.m.) δ : -64.07(s), -136.66(m), -137.43(m), -143.27(m), -152.40(m).

FSt-FPPE-5: 86% yield. ^1H -NMR (400 MHz, CDCl_3 , p.p.m.) δ : 5.74 (d, $J=12$ Hz), 6.13 (d, $J=18$ Hz), 6.69 (dd, $J=18$ Hz, 12 Hz), 7.06 (d, $J=8$ Hz, 4 H), 7.42 (d, $J=8$ Hz, 4 H). ^{19}F -NMR (376 MHz, CDCl_3 , p.p.m.) δ : -64.09(s), -137.45(m), -152.37(m).

Thermal crosslinking of FSt-FPPEs

To study the thermal crosslinking of FSt-FPPEs, the polymers were first dissolved in chloroform at a concentration of 30% (w/v). The films were then cast from the solutions and dried at room temperature. The thermal crosslinking behaviors of the films were then determined by heating the polymer films either at 160 °C in the presence of a free-radical initiator DCP (1 wt% relative to the polymer) for 4 h under vacuum or at 280 °C in the absence of any initiator for 20 min under vacuum. The effect of thermal crosslinking on T_g was then determined by DSC.

Film preparation and measurement of optical properties

These experiments used highly polished Si or SiO_2 wafers as substrates. Organic residues on the Si or SiO_2 substrates were removed by successive ultrasonic cleaning with acetone, alcohol and ion-free pure water. The polymer solutions were prepared by dissolving FSt-FPPEs (30% v/v) with 1 wt% DCP in cyclohexanone. The solutions were then filtered through a 0.22- μm Teflon microfilter and spin coated on Si or SiO_2 substrates. The spin-coating speeds ranged from 1000 to 4000 r.p.m. To guarantee the quality of the spin-coated films, the entire spin-coating procedure was carried out in a 1000-class ultraclean room. The resulting films were dried at 60 °C (30 min) and 120 °C (30 h) to remove the residual solvent under vacuum. Thermal crosslinking was then performed by heating the films slowly to 160 °C and holding them at this temperature for 4 h under vacuum. The refractive indices of the polymer films were measured by the prism-coupling method at wavelengths of 1310 and 1550 nm with a tolerance of ± 0.0002 . The optical losses of the polymer films were measured on slab waveguide samples using the high-index liquid immersion technique.²⁰ In this technique, light was coupled to a slab waveguide by prism coupling. After propagating for a certain distance, the light was out-coupled from the waveguide by immersing it into a high-index liquid. The propagation loss was calculated, with the out-coupled optical power described as a function of the propagation distance.

RESULTS AND DISCUSSION

Synthesis of FPPE

The polycondensation of DHPZ with DFBP has been modified by suspending CaH_2 and a trace amount of KF in the reaction medium.²¹ The GPC results obtained under these conditions are shown in Figure 1. Note that the specimens used to obtain these data were recovered by dropping the reaction solution into a mixture of acidic water/methanol (2:1 v/v) so that both the polymer and low molecular weight cyclic oligomers were collected.²² The presence of cyclic oligomers can be clearly seen as a small peak at 17 min in the low molecular weight region of the GPC curves.

When the DFBP is in a 51:50 excess over DHPZ, as the molecular weight increases with the reaction time, the GPC curves show a very similar pattern until the reaction reaches completion. No peak is observed in the high molecular weight region of the GPC associated with the branched polymers. With excess DHPZ (51:50 mol), the GPC peaks show a similar pattern as observed for excess DFBP before the reaction reaches

Figure 1 Gel permeation chromatography (GPC) curves of the samples taken at different reaction times from the synthesis of FPPE catalyzed by potassium fluoride (KF) and calcium hydride (CaH_2) in *N,N*-dimethyl acetamide (DMAc) at 90 °C. The molar ratio of 4-(4'-hydroxyphenyl)-phthalazin-1(2H)-one (DHPZ)/decafluorobiphenyl (DFBP) is (a, b) 50:51 and (c, d) 51:50. ^aGPC curves of the samples taken 3 h after FPPE synthesis catalyzed by KF and CaH_2 with a feed ratio of (DHPZ)/(DFBP)=50:51 at 90 °C. ^bGPC curves of the samples taken 2 h after FPPE synthesis catalyzed by KF and CaH_2 with a feed ratio of (DHPZ)/(DFBP)=50:51 at 90 °C. ^cGPC curves of the samples taken 3 h after FPPE synthesis catalyzed by KF and CaH_2 with a feed ratio of (DHPZ)/(DFBP)=51:50 at 90 °C. ^dGPC curves of the samples taken 2 h after FPPE synthesis catalyzed by KF and CaH_2 with a feed ratio of (DHPZ)/(DFBP)=51:50 at 90 °C.

completion. However, when the reaction comes close to completion, the excess -O-H and -N-H have no choice but to react with the *ortho*-fluorines because almost all the *para*-fluorines have been consumed. Figure 1 also shows that the curve of c shows a shoulder peak associated with the polymer branching. This result provides evidence that, under these conditions, it is difficult to synthesize hydroxy-terminated polymers.

Synthesis of FSt-FPPEs

As the reactivity of DFBP is higher than that of FSt and it is difficult to synthesize hydroxyl-terminated polymers, the latter and bisphenol-like DHPZ were first reacted by the catalysis of the complex KF/CaH_2 through feeding together and then reacted with DFBP to yield the crosslinkable FSt-FPPEs with tetrafluorostyrene at the chain end (see Scheme 2). To avoid unexpected FSt polymerization, the synthesis of FSt-FPPEs was conducted in the dark to keep out the ultraviolet rays present in sunlight. Note that the end group tetrafluorostyrene was expected to significantly decrease the nucleophilicity of the vinyl moiety because of its strongly electronegative character. Accordingly, the obtained FSt-FPPE polymers were found to be quite stable at high temperatures (for example, <120 °C) and under visible light, which allows the optical films to be fabricated under normal reaction conditions. However, in the presence of a suitable initiator, FSt-FPPE films are sufficiently reactive to induce crosslinking of the tetrafluorostyrol units when exposed to heat or ultraviolet light.

The inorganic salts in the reaction system should be completely eliminated during the purification process to avoid undesirable optical loss. The purification of the resulting FSt-FPPEs involved filtering their DMAc solutions through a 0.45- μm Teflon microfilter before precipitating them into a sufficient amount of ethanol containing a

few drops of concentrated hydrochloric acid and then boiling them in pure water, followed by filtration and thorough washing with pure water and methanol.

GPC analysis indicated that the number-average molecular weight of the obtained polymers ranged from 0.84 to 1.24×10^4 , and the molecular weight distribution of the polymers ranged from 2.20 to 2.63, as shown in Table 1.

The obtained FSt-FPPE polymers were characterized by $^1\text{H-NMR}$, and the spectra are shown in Figure 2. On a detailed examination of the $^1\text{H-NMR}$ spectra, all the polymers exhibited three protons at 6.71,

6.14 and 5.79 p.p.m. on the vinyl group of the FSt units, which indicates that the FSt units were attached to the polymers and remained stable during the synthesis procedure. Except for FSt-FPPE-5, the polymers had the typical signal of a phthalazinone segment around 8.6 p.p.m., which increased with the feed ratio of DHPZ. The aromatic peaks at 7.5–8.0 p.p.m. and around 7.24 p.p.m. were due to the phthalazinone unit, and the peaks around 7.06 and 7.42 p.p.m. were attributed to the 6F-BPA unit. Because the peaks of the FSt, DHPZ and 6F-BPA units can be easily distinguished in the $^1\text{H-NMR}$ spectra of FSt-FPPEs, the content of FSt units in the copolymer chain can be determined using the following equation:

$$\text{FSt content\%} = \frac{(I_{H_a} + I_{H_b} + I_{H_c})I_{H_8}/3}{I_{H_8} + (I_{H_1} + I_{H_2})/8} \times 100\% \quad (1)$$

where the FSt content is the molar ratio of the FSt unit relative to the total bisphenol content; I_{H_a} , I_{H_b} and I_{H_c} are the intensities of the H_a signal, H_b signal and H_c signal, respectively; and I_{H_8} , I_{H_1} and I_{H_2} are the intensities of the H_8 signal, H_1 signal and H_2 signal, respectively. The calculated results are summarized in Table 1. All the results given above indicate that the polymers have been successfully synthesized as designed.

The ^{19}F NMR spectra shown in Figure 3 further confirm the structure of the resulting polymers. In the asymmetric monomer DHPZ, the peak F1 adjacent to $-\text{N}-$ of lactam and the peak F4 adjacent to $-\text{O}-$ appeared at -143.2 and -152.4 p.p.m., respectively. The intensities of the two peaks at -137.5 and -152.4 p.p.m. arising from the F6, 7 and F5, 8 of the bisphenol 6F-BPA, respectively, decreased in proportion to the decreasing feed ratio of 6F-BPA. No obvious signal that was related to branching of the polymer chains was observed from the $^{19}\text{F-NMR}$ spectra.

Table 1 Results of polymerization of FSt-FPPEs

Polymers	6F-BPA content (mol%) ^a	DHPZ content (mol%) ^b	FSt content (mol%) ^c	FSt content from $^1\text{H-NMR}$, (mol%) ^d	M_n ($\times 10^4$) ^e	η^f
FSt-FPPE-1	0	100	9.0	8.78	0.84	2.20
FSt-FPPE-2	25	75	9.0	8.92	1.03	2.24
FSt-FPPE-3	50	50	9.0	8.84	1.21	2.53
FSt-FPPE-4	75	25	9.0	8.86	1.18	2.31
FSt-FPPE-5	100	0	9.0	8.86	1.24	2.63

^aFeed molar ratio of 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA) relative to the total bisphenols.

^bFeed molar ratio of 4-(4'-Hydroxyphenyl)phthalazin-1(2H)-one (DHPZ) relative to the total bisphenols.

^cFeed molar ratio of pentafluorostyrene (FSt) relative to the total bisphenols.

^dFeed molar ratio of FSt relative to the total bisphenols.

^e M_n , M_w values were determined by gel permeation chromatography (GPC) in CH_2Cl_2 with polystyrene (PS) as standard.

^f M_w/M_n were determined by GPC in CH_2Cl_2 with PS as standard.

Figure 2 ^1H -nuclear magnetic resonance of FSt-FPPEs.

Figure 3 ^{19}F -nuclear magnetic resonance of FSt-FPPEs.

Table 2 The solubility of the FSt-FPPEs

Polymers	CHCl_3	THF	Acetone	DMSO	NMP	DMAc	Benzene	DMF
FSt-FPPE-1	+	+	+	—	+	+	+	+
FSt-FPPE-2	+	+	+	—	+	+	+	+
FSt-FPPE-3	+	+	+	—	+	+	+	+
FSt-FPPE-4	+	+	+	—	+	+	+	+
FSt-FPPE-5	+	+	+	—	+	+	+	+

Abbreviations: DMAc, *N,N*-dimethyl acetamide; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl pyrrolidone; THF, tetrahydrofuran.

“+” soluble in room temperature; “—”, insoluble.

Solubility and thermal properties of FSt-FPPEs

As these polymers have a high fluorine content, non-coplanar phalazinone moieties and flexible ether linkages, they exhibited good solubility in common organic solvents such as tetrahydrofuran, CHCl_3 , cyclohexanone, DMAc, dimethyl formamide, *N*-methyl pyrrolidone and ethyl acetate at room temperature, as shown in Table 2, which facilitates film preparation and device fabrication.

The tetrafluorostyrene (FSt) units were found to be able to undergo crosslinking reactions by both thermal heating and ultraviolet irradiation.^{15,19} In this work, the thermal crosslinkings of FSt-FPPEs were studied by heating the polymer films at 280 °C without any radical initiator for 20 min under vacuum or at 160 °C with the DCP initiator for 4 h under vacuum.

Because the vinyl group has a specific FT-IR absorption signature, the thermal crosslinking reaction was monitored by FT-IR spectroscopy. The FT-IR spectrum of FSt-FPPE-1 showed a characteristic peak near 936 cm^{-1} after polymerization (stretching vibration of the vinyl double bond in the FSt group; Figure 4a). This peak disappeared after curing at 160 °C with initiator for 4 h under vacuum (Figure 4b),

Figure 4 Fourier transform infrared spectra of FSt-FPPE-1 (a) before thermal curing and (b) after thermal curing at 160 °C for 4 h with a 1 wt% initiator content.

which indicates that the tetrafluorostyrene units can undergo crosslinking reactions by thermal heating in the presence of the initiator DCP. As the FT-IR of Figure 4 shows, other FT-IR peaks are not affected after curing, indicating the high stability of this polymer at this temperature.

DSC analysis was also performed to study the effect of curing on the glass transition temperature (T_g) and the curing properties of the polymers without initiator. The results for the polymer FSt-FPPE-5 are shown in Figure 5. The exothermic peak attributed to the reaction

Figure 5 Differential scanning calorimetry traces of FSt-FPPE-5: (a) first scan, (b) second scan and (c) third scan.

of the styrol group in Figure 5a disappeared in Figures 5b and c. In addition, as the DSC scan number increased, the T_g of FSt-FPPE-5 was also increased from 164 to 177 °C, clearly indicating the occurrence of crosslinking reactions. After curing, the glass transition temperatures of the polymers increased by 10–15 °C.

The thermal stability of cured polymers was investigated by thermogravimetric analysis at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. The onset temperatures of 1% weight loss were over 463 °C (Table 3), indicating the excellent thermal stability of these polymers.

Optical properties

On the basis of the device design and waveguide geometry, the polymer used as the core material in a waveguide must have a higher refractive index than that of the cladding material. Thus, fine-tuning of the refractive index is exceedingly important for optical waveguide applications. Generally, the refractive index depends on molecular refraction and molecular volume and decreases with increasing fluorine content. In this study, the refractive indices of the polymers were controlled by changing the mole fraction of fluorine in the polymer. The refractive indices of the transverse electronic and transverse magnetic modes, n_{TE} and n_{TM} , of the crosslinked polymer thin films were determined using the prism coupling technique at 1550 nm. Table 3 shows the refractive indices of FSt-FPPEs at 1550 nm. The refractive index can be controlled using the copolymerization of various monomers, as shown in Figure 6. By adjusting the 6F-BPA content from 0 to 100 mol% (relative to the total bisphenols), the refractive indices of the transverse electronic and transverse magnetic modes decreased from 1.5625 to 1.4952 and from 1.5538 to 1.4924, respectively.

Birefringence is also an important issue for optical waveguides, and this property is proportional to the anisotropic ratio for the copolymer system.²³ On the one hand, the crank and twisted non-coplanar phthalazinone structure increases the chain-packing distances, reduces the intermolecular interactions of macromolecular chains and the regularity of the main chain, encumbers close chain packing and hinders the movement of the main chain. Compared with the 6F-BPA units in the polymer chains, the phthalazinone structure of DHPZ has more rigid units that can lead to large birefringence values. Table 3 shows that the birefringence of FSt-FPPEs increased from 0.0028 to 0.0087, with increasing DHPZ content from 0 to 100 mol% compared

Table 3 Optical and thermal properties of FSt-FPPEs

Polymers ^a	n_{TE} ^b	n_{TM} ^b	$\geq n^c$	Optical loss (dB/cm) ^d	T_g (°C) ^e	T_g (°C) ^f	$T_d^{1\%}$ (°C) ^h
FSt-FPPE-1	1.5625	1.5538	0.0087	0.207	269	283	490
FSt-FPPE-2	1.5448	1.5382	0.0066	—	248	261	481
FSt-FPPE-3	1.5272	1.5231	0.0041	0.197	207	218	473
FSt-FPPE-4	1.5097	1.5062	0.0035	—	188	199	463
FSt-FPPE-5	1.4952	1.4924	0.0028	0.145	164	171	478

^aThe sample codes were the same as shown in Table 1.

^bRefractive index of the transverse electronic mode or transverse magnetic mode at 1550 nm.

^c $\geq n = n_{TE} - n_{TM}$.

^dMeasured on slab waveguide samples using the high-index liquid immersion technique at 1550 nm.

^eMeasured after the sample curing.

^fGlass transition temperature measured by differential scanning calorimetry (DSC) with a heating rate of 10 °C min⁻¹ in nitrogen before curing.

^gGlass transition temperature measured by DSC with a heating rate of 10 °C min⁻¹ in nitrogen in the second scan.

^hThermal decomposition temperature, defined as the temperature of 1% weight loss, at a heating rate of 20 °C min⁻¹ in nitrogen after polymer curing.

Figure 6 Dependence between refractive index and 6F-BPA content (mol%) at 1550 nm.

Figure 7 Optical losses of the cured waveguide film along the waveguide length (FSt-FPPE-3).

with total bisphenol. All the birefringence values of our polymers are suitable for non-polarization devices.

The optical losses of FSt-FPPEs were evaluated from the slab waveguide losses using the high-index liquid immersion method, and the results are summarized in Table 3. The cured FSt-FPPEs show a low optical loss in the propagation region, and Figure 7 also shows the FSt-FPPE-3 optical insertion loss versus the waveguide length, which was obtained by the cutback method. The insertion loss shows a linear relationship with the waveguide length. These results demonstrate that the obtained polymers could be useful for optical waveguide applications.

CONCLUSION

A series of crosslinkable fluorinated poly(phthalazinone ether)s bearing tetrafluorostyrene groups were successfully synthesized by a two-step nucleophilic displacement polycondensation reaction starting from DHPZ, DFBP, FSt and 6F-BPA. The reactive tetrafluorostyrene units attached at the chain end of the polymer improve the thermal stability by thermal crosslinking reaction. By adjusting the feed ratio of the reactants, the refractive indices could be controlled well over a wide range from 1.50 to 1.55. The optical losses of the FSt-FPPEs exhibited relatively low values ($<0.3 \text{ dB cm}^{-1}$ at 1550 nm). Our group is now working to use these polymers to fabricate a passive optical waveguide.

ACKNOWLEDGEMENTS

This study was performed with support from the National Natural Science Foundation of China (Grant nos. 50143014, 60577014 and 60807015).

- Fischbeck, G., Moosburger, R., Kostrzewa, C., Achen, A. & Petermann, K. Singlemode optical waveguides using a high temperature stable polymer with low losses in the 1.55 μm range. *Electron. Lett.* **33**, 518–519 (1997).
- Matsuura, T., Ando, S., Sasaki, S. & Yamamoto, F. Polyimides derived from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl. 4. Optical properties of fluorinated polyimides for optoelectronic components. *Macromolecules*. **27**, 6665–6670 (1994).
- Lee, H.-J., Lee, M.-H., Oh, M.-C., Ahn, J.-H. & Han, S. G. Crosslinkable polymers for optical waveguide devices. II. Fluorinated ether ketone oligomers bearing ethynyl group at the chain end. *J. Polym. Sci., Part A: Polym. Chem.* **37**, 2355–2361 (1999).
- Goodwin, A. A., Mercer, F. W. & McKenzie, M. T. Thermal behavior of fluorinated aromatic polyethers and poly(ether ketone)s. *Macromolecules*. **30**, 2767–2774 (1997).
- Blythe, A. R. & Vinson, J. Polymeric materials for devices in optical fibre systems. *Polym. Adv. Technol.* **11**, 601–611 (2000).
- Ma, H., Jen, A. K.-Y. & Dalton, L. R. Polymer-based optical waveguides: materials, processing, and devices. *Adv. Mater.* **14**, 1339–1365 (2002).
- Zhou, M. Low-loss polymeric materials for passive waveguide components in fiber optical telecommunication. *Opt. Eng.* **41**, 1631–1643 (2002).
- Groh, W. Overtone absorption in macromolecules for polymer optical fibers. *Macromol. Chem.* **189**, 2861–2874 (1988).
- Groh, W., Lupo, D. & Sixl, H. Polymer optical fibers and nonlinear optical device principles. *Adv. Mater.* **11**, 366–377 (1989).
- Takezawa, Y., Taketani, N., Tanno, S. & Ohara, S. Light absorption due to higher harmonics of molecular vibrations in transparent amorphous polymers for plastic optical fibers. *J. Polym. Sci., Part B: Polym. Phys.* **30**, 879–885 (1992).
- Yeniay, A., Gao, R., Takayama, K., Gao, R. & Garito, A. F. Ultra-low-loss polymer waveguides. *J. Lightwave Technol.* **22**, 154–158 (2004).
- Kaino, T. & Katayama, Y. Polymers for optoelectronics. *Polym. Eng. Sci.* **29**, 1209–1214 (1989).
- Kang, J.-W., Kim, J.-P., Lee, J.-S. & Kim, J.-J. Structure-property relationship of fluorinated co-poly(arylene ether sulfide)s and co-poly(arylene ether sulfone)s for low-loss and low-birefringence waveguide devices. *J. Lightwave Technol.* **23**, 364–373 (2005).
- Jiang, J., Callender, C. L., Blanchetiere, C., Jacob, S., Noad, J. P., Ding, J., Qi, Y. H. & Day, M. Optimizing fluorinated poly(arylene ether)s for optical waveguide applications. *Opt. Mater.* **28**, 189–194 (2006).
- Qi, Y., Ding, J., Day, M., Jiang, J. & Callender, C. L. Cross-linkable highly halogenated poly(arylene ether ketone/sulfone)s with tunable refractive index: synthesis, characterization and optical properties. *Polymer*. **47**, 8263–8271 (2006).
- Ding, J. & Qi, Y. The preparation and characterization of highly fluorinated poly(arylene alkylene ether)s. *Macromolecules*. **41**, 751–757 (2008).
- Ma, X., Lv, Z., Wang, D., Guan, S., Chen, C., Wang, G., Zhang, D. & Jiang, Z. Crosslinkable fluorinated poly(aryl ether ketone)s containing pendent phenylethynyl moieties for optical waveguide devices. *J. Photochem. Photobiol. A: Chem.* **188**, 43–50 (2007).
- Song, Y., Wang, J., Li, G., Sun, Q., Jian, X., Teng, J. & Zhang, H. Synthesis, characterization and optical properties of fluorinated poly(aryl ether)s containing phthalazinone moieties. *Polymer*. **49**, 4995–5001 (2008).
- Song, Y., Wang, J., Li, G., Sun, Q., Jian, X., Teng, J. & Zhang, H. Synthesis, characterization and optical properties of cross-linkable poly(phthalazinone ether ketone sulfone). *Polymer*. **49**, 724–731 (2008).
- Teng, C. Precision measurements of the optical attenuation profile along the propagation path in thin-film waveguides. *Appl. Opt.* **32**, 1051–1054 (1993).
- Ding, J., Day, M., Robertson, G. P. & Roovers, J. Highly fluorinated poly(arylene ether ketone) prepared by a CaH_2 -mediated polycondensation reaction. *Macromol. Chem. Phys.* **205**, 1070–1079 (2004).
- Liu, F., Ding, J., Li, M., Day, M., Robertson, G. & Zhou, M. Preparation of highly fluorinated poly(ether sulfone)s under mild polycondensation conditions using molecular sieves. *Macromol. Rapid Commun.* **23**, 844–848 (2002).
- Kang, J.-W., Kim, J.-P., Lee, J.-S. & Kim, J.-J. Structure-property relationship of fluorinated co-poly(arylene ether sulfide)s and co-poly(arylene ether sulfone)s for low-loss and low-birefringence waveguide devices. *J. Lightwave Technol.* **23**, 364–373 (2005).