Cross-Linkable Highly Fluorinated Poly(Arylene Ether Ketones/Sulfones) for Optical Waveguiding Applications

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Novel cross-linkable, highly fluorinated poly(arylene ether ketones/sulfones) have been prepared by copolycondensation reactions of perfluorinated aromatic ketone/sulfone with 4,4′-(hexafluoroisopropylidene)diphenol and a tetrafluorostyrol-containing bisphenol (i.e., 1,1-bis(4-hydroxyphenyl)ethyl-1-phenyl 2,3,5,6-tetrafluorostyrol ether). The reactions were conducted at low temperature in the presence of calcium hydride and cesium fluoride. The resulting polymers have number-average molecular weights in the range of 25 000−36 000, excellent solubilities in common organic solvents, high glass transition temperatures (T_g) in the region of 150−185 °C, and good thermal stabilities (T_d up to 480 °C). Tough, flexible, and transparent thin films of these polymers can be readily prepared by both solution casting and spin-coating. By adjusting the feed ratio of monomers, the refractive index and cross-linking density of the polymers can be readily controlled. Cross-linking of these polymers has been demonstrated by both thermal heating and UV irradiation. The cross-linked polymer thin films exhibit low optical loss (∼0.5 dB/cm) and low birefringence ($\sim 2 \times 10^{-3}$) at 1550 nm, demonstrating that they are promising candidates for optical waveguide materials.

Introduction

Photonics is rapidly emerging as a dominant technology for broadband processing and transmission of information. Key issues in the widespread implementation of optical networks based on wavelength division multiplexing (WDM) are reducing the cost and optimizing the performance of critical waveguide devices such as modulators, switches, optical interconnects, and splitters, which are predominantly based on inorganic materials (e.g., silica, lithium niobate, and III−V semiconductors). To address these issues, innovations are being actively pursued to achieve novel passive waveguide materials that are cost-effective, have excellent processability and optical performances (e.g., high optical transparency at telecommunication wavelengths, low birefringence, and good chemical and physical stability), and can be easily integrated with semiconductor circuitry.

Organic polymers appeared to be promising candidates for this application due to their easy processability, low cost fabrication potential, and structure−property tunability.[1] Various highly halogenated polymers, specifically fluorinated polymers containing the minimum amount of absorptive bonds such as C−H, O−H, and N−H have been developed and demonstrated their promising waveguiding properties.[2−5] However, for practical waveguide device applications, challenges still remain in developing polymers that have all the required properties as mentioned above. To meet these requirements, in addition to highly fluorinated structures for achieving low optical loss, polymers with relatively flexible main chain structures, high glass transition temperatures, and an ability to be cross-linked either thermally or photochemically are desired.

Poly(arylene ether ketone)s (PAEKs) and poly(arylene ether sulfone)s (PAESs), which are well-known high-performance polymers used in a wide range of demanding applications from aerospace to microelectronics, are characterized by their excellent thermal, mechanical, and environmental stabilities. In addition, due to the existence of the

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flexible ether linkages in the backbone, these polymers commonly have a lower birefringence compared with other high T_g polymers.[3e,5] Because of these attractive properties, attention has been drawn to the highly fluorinated PAEKs and PAESs as optical waveguide materials.[6,7] However, their application into photonic devices is limited. One of the reasons for this lack of utilization comes from the difficulties in obtaining structurally well-defined PAEKs or PAESs using the traditional polycondensation reaction between a highly active perfluorinated diphenyl monomer (i.e., decafluorobenzophenone or decafluorodiphenyl sulfone) and the bisphenol compounds.

To explore the potential of these types of polymers in waveguide applications, we recently established a new efficient synthetic method to prepare these highly fluorinated PAEKs and PAESs with high molecular weights and linear structures.[8,9] All the obtained polymers showed excellent processability, high glass transition temperatures, low optical losses at 1550 nm, and low birefringence. Encouraged by these results, we have developed a systematic approach to the preparation of highly fluorinated PAEKs and PAESs waveguide materials that involves the introduction of cross-linking functionality and the fine-tuning of refractive indices of the polymers by the use of cross-linkable tetrafluorostyrol groups as pendant groups. By varying the tetrafluorostyrol content in the polymers, polymer films with different cross-linking densities and controllable refractive indices have been prepared. The thermal cross-linking and photopatterning of these cross-linkable fluorinated PAEKs and PAESs have been investigated and optical properties of the cross-linked films such as optical loss and birefringence at telecommunication wavelengths have been characterized. Preliminary results regarding the fabrication and performance of waveguide devices based on these polymers are also presented.

Experimental Section

Materials. 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA) and decafluorobenzophenone were purified by recrystallization from toluene and 2-propanol, respectively. Decafluorodiphenyl sulfone was prepared according to the literature.[8] *N*,*N*-Dimethylacetamide (DMAc) was dried over calcium hydride and distilled under vacuum. All other chemicals were purchased from Sigma-Aldrich Chemicals and used as received.

Measurements. Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity Inova spectrometer at a resonance frequency of 400 MHz for ^{1}H and 376 MHz for ^{19}F. The chemical shifts relative to tetramethylsilane for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR as internal reference are reported on the ppm scale. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector at a wavelength of 260 nm. Raman spectra were recorded on a Bruker FRA 106/S FT-Raman spectrometer. IR spectra were collected using a MIDAC FT-IR spectrometer (model M1200-SP3) with a resolution of 2 cm^{-1}. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA Instruments TGA 2950 and DSC 2920 respectively, at a heating rate of 10 °C/min under nitrogen (50 mL/min). EI mass spectroscopy was measured at the University of Ottawa, Regional Mass Spectrometry Center. Melting points were determined using a Mettler FP1 melting point apparatus. Photo cross-linking of polymer films was performed using a Hanovia analytic model UV lamp with a 310−400-nm filter. Scanning electron microscopy (SEM) was performed on JEOL JSM-840-A, JEOL 35 CF, and FEI QUANTA 600 scanning electron microscopes. The refractive indices of the polymer films at 1537 nm were determined using the prism coupling technique with an uncertainty of ±0.0004. Optical losses of the polymers were measured at 1550 nm on slab waveguide samples using the technique of high index liquid immersion.[7b,10] The propagation losses of straight waveguides at 1550 nm were measured using the cut-back method.

1,1-Bis(4-hydroxyphenyl)ethyl-1-phenyl 2,3,5,6-tetrafluorostyrol ether (BHPFS). To a 100-mL round-bottom flask charged with 1,1,1-tris(4-hydroxyphenyl)ethane (10.5 g, 0.034 mol), pentafluorostyrene (5.2 g, 0.027 mol), and DMAc (40 mL), were added calcium hydride (2.1 g, 0.05 mol) and cesium fluoride (0.20 g, 1.32 mmol). The mixture was heated to 80 °C with stirring under argon in the dark for 18 h. After the solution cooled to room temperature, it was filtered to remove the inorganic solids. This solution was then added to hydrochloric acid (300 mL, 0.5 N) and extracted with diethyl ether (150 mL) three times. The ether phases were combined and washed with distilled water until neutral, then dried over anhydrous magnesium sulfate, and rotaevaporated to give a white powdered crude product. Column chomotography (ethyl acetate/hexane, 1/3.5, v/v) through silica gel was then used to obtain the pure product (4.5 g, 35% yield). Mp 173 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.22 (2H, s), 7.09 (2H, m), 7.01 (2H, m), 6.90 (4H, m), 6.74 (5H, m), 6.09 (1H, d, $J = 18.4$ Hz), 5.80 (1H, d, $J = 12.00$ z), 2.09 (3H, s). ^{19}F NMR (376 MHz, acetone-d_6): δ −144.57 (2F, dd, $J = 9.1$, 20.6 Hz), −156.36 (2F, dd, $J = 9.0$, 20.6). MS (EI, *m/z*): 480 (M^+, 3.8%), 465 ($M - CH_3$, 100%).

Cross-Linkable Fluorinated PAEKs (FPAEK 1−3). A typical synthetic procedure for the preparation of **FPAEK 1** is as follows. To a solution of decafluorobenzophenone (1.1290 g, 3.118 mmol), 6F-BPA (0.9183 g, 2.731 mmol), and **BHPFS** (0.1858 g, 0.387 mmol) in anhydrous DMAc (18 mL) were added cesium fluoride (0.03 g, 0.20 mmol) and calcium hydride (0.30 g, 7.14 mmol). The mixture was stirred at 60 °C under argon in the dark for 3 h. After filtration to remove the insoluble inorganic salts, the solution was added dropwise to a mixture of methanol (200 mL) and hydrochloric acid (8 mL, 2 N). The resulting white precipitate was collected by filtration, washed thoroughly with methanol, and dried at room temperature under vacuum (0.1 mmHg) (1.80 g, 85% yield). IR (NaCl, cm^{-1}): 1690 (C=O). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.47 (28H, d, $J = 8.8$ Hz), 7.34 (28H, d, $J = 8.8$ Hz), 7.08 (12H, m), 6.73 (1H, dd, $J = 18.0$ Hz, 12.0 Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz). ^{19}F NMR (376 MHz, acetone-d_6):

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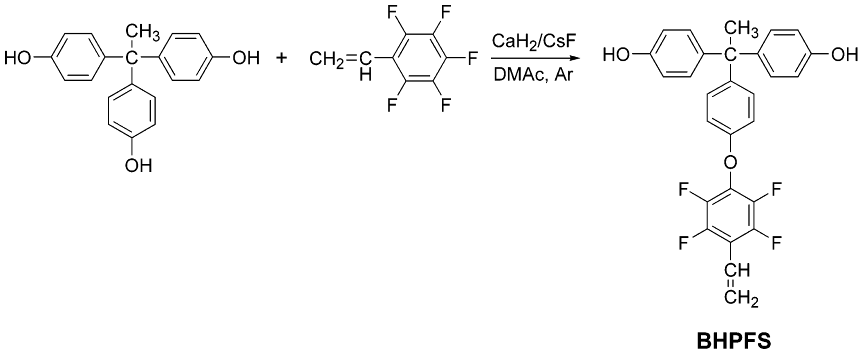
Scheme 1. Synthesis of Cross-Linkable Bisphenol (BHPFS)



δ −63.61 (42F, s), −142.34 (28F, m), −142.59 (4F, m), −144.63 (2F, m), −153.24 (28F, m), −153.58 (4F, m), −156.53 (2F, m).

FPAEK 2. 86% yield. IR (NaCl, cm^{-1}): 1690 (C═O). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.46 (16H, d, *J* = 8.8 Hz), 7.33 (16H, d, *J* = 8.8 Hz), 7.09 (12H, m), 6.72 (1H, dd, *J* = 18.0 Hz, 12.0 Hz), 6.08 (1H, d, *J* = 18.0 Hz), 5.79 (1H, d, *J* = 12.0 Hz). ^{19}F NMR (376 MHz, acetone-*d*$_6$): δ −63.61 (24F, s), −142.37 (16F, m), −142.66 (4F, m), −144.63 (2F, m), −153.26 (16F, m), −153.58 (4F, m), −156.54 (2F, m).

FPAEK 3. 85% yield. IR (NaCl, cm^{-1}): 1690 (C═O). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.48 (12H, d, *J* = 8.8 Hz), 7.34 (12H, d, *J* = 8.8 Hz), 7.09 (12H, m), 6.72 (1H, dd, *J* = 18.0 Hz, 12.0 Hz), 6.07 (1H, d, *J* = 18.0 Hz), 5.78 (1H, d, *J* = 12.0 Hz), 2.08 (3H, s). ^{19}F NMR (376 MHz, acetone-*d*$_6$): δ −63.60 (18F, s), −142.33 (12F, m), −142.56 (4F, m), −144.64 (2F, m), −153.24 (12F, m), −153.56 (4F, m), −156.53 (2F, m).

Cross-Linkable Fluorinated PAESs (FPAES 1−3). The following is a typical synthetic procedure for the preparation of **FPAES 1**. To a solution of decafluorodiphenyl sulfone (1.0260 g, 2.577 mmol), 6F-BPA (0.7593 g, 2.258 mmol), and **BHPFS** (0.1531 g, 0.319 mmol) in anhydrous DMAc (18 mL) were added cesium fluoride (0.03 g, 0.20 mmol) and calcium hydride (0.30 g, 7.14 mmol). The mixture was stirred under argon at 55 °C in the dark for 3 h. After filtration to remove the insoluble inorganic salts, the solution was added dropwise to a mixture of methanol (200 mL) and hydrochloric acid (8 mL, 2 N). The resulting white precipitate was collected by filtration, washed thoroughly with methanol, and dried at room temperature under vacuum (0.1 mmHg) (1.51 g, 82% yield). IR (NaCl, cm^{-1}): 1389, 1297 (O═S═O). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.47 (28H, d, *J* = 8.8 Hz), 7.34 (28H, d, *J* = 8.8 Hz), 7.08 (12H, m), 6.73 (1H, dd, *J* = 18.0 Hz, 12.0 Hz), 6.08 (1H, d, *J* = 18.0 Hz), 5.78 (1H, d, *J* = 12.0 Hz). ^{19}F NMR (376 MHz, acetone-*d*$_6$): δ −63.61 (42F, s), −137.18 (28F, m), −137.56 (4F, m), −144.53 (2F, m), −151.92 (28F, m), −152.31 (4F, m), −156.44 (2F, m).

FPAES 2. 82% yield. IR (NaCl, cm^{-1}): 1389, 1297 (O═S═O). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.46 (16H, d, *J* = 8.8 Hz), 7.33 (16H, d, *J* = 8.8 Hz), 7.08 (12H, m), 6.72 (1H, dd, *J* = 18.0 Hz, 12.0 Hz), 6.08 (1H, d, *J* = 18.0 Hz), 5.79 (1H, d, *J* = 12.0 Hz), 2.08 (3H, s). ^{19}F NMR (376 MHz, acetone-*d*$_6$): δ −63.62 (24F, s), −137.18 (16F, m), −137.56 (4F, m), −144.54 (2F, m), −151.94 (16F, m), −152.29 (4F, m), −156.46 (2F, m).

FPAES 3: 84% yield. IR (NaCl, cm^{-1}): 1389, 1297 (O═S═O). ^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.47 (12H, d, *J* = 8.8 Hz), 7.33 (12H, d, *J* = 8.8 Hz), 7.09 (12H, m), 6.73 (1H, dd, *J* = 17.7 Hz, 11.8 Hz), 6.08 (1H, d, *J* = 18.0 Hz), 5.78 (1H, d, *J* = 11.8 Hz), 2.09 (3H, s). ^{19}F NMR (376 MHz, acetone-*d*$_6$): δ −63.62 (18F, s), −137.18 (12F, m), −137.56 (4F, m), −144.53 (2F, m), −151.92 (12F, m), −152.29 (4F, m), −156.44 (2F, m).

Film Preparation for the Measurement of Refractive Index. The polymer solutions were prepared in cyclohexanone (∼20%, w/v), to which was added dicumyl peroxide as the thermal initiator (1 wt %, relative to polymer). The solutions were then filtered through a Teflon syringe filter with a pore size of 0.2 μm and spin-coated onto a SiO_2/Si substrate. The resulting films (3−7 μm in thickness) were baked at 130 °C for 30 min. Thermal curing of the films was then carried out by heating slowly to 160 °C and maintaining this temperature for 2 h under an inert atmosphere.

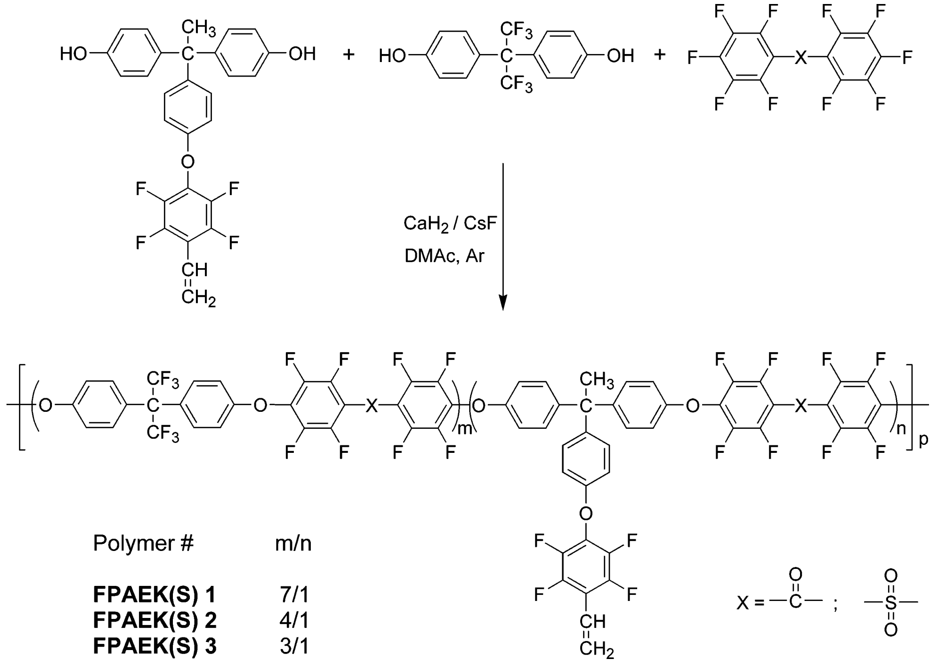
Photopatterning. The polymer solutions were prepared in cyclohexanone (∼10%, w/v), to which was added 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (photo acid generator, 5 wt % relative to the polymer). The solutions were then filtered through a Teflon syringe filter with a pore size of 0.2 μm and spin-coated onto a silicon wafer. The films (∼2 μm thick) were dried at 50 °C for 4 h and then at 70 °C under vacuum for 12 h. Photopatterning of the films was performed by exposing the films to the UV light through a mask for 20 min, followed by a postbaking at 140 °C for 1 min and developing with tetrahydrofuran (20 s) and acetone (20 s).

Results and Discussion

Synthesis of Cross-Linkable Bisphenol (BHPFS). It is known that replacement of C−H units by C−F units is an efficient way to increase the optical transparency of a polymeric material in the near-infrared telecommunication windows (1.3 and 1.55 μm).[3−5] Consequently, highly fluorinated polymers that have the minimal amount of C−H, O−H, and N−H bonds are eagerly being sought for their potential applications in waveguide devices. To ensure that the resulting materials have improved chemical and mechanical stabilities, many are being designed to contain either thermally or photochemically reactive groups that can undergo intermolecular reactions under external stimuli to form cross-linked polymer networks. In our study, to introduce cross-linking functionality into highly fluorinated PAEKs and PAESs, a fluorinated bisphenol monomer containing a tetrafluorostyrol unit (**BHPFS**) was designed and prepared via a nucleophilic mono-substitution of 1,1,1-tris(4-hydroxyphenyl)ethane with pentafluorostyrene (as shown in Scheme 1). Although the exclusion of some di-substitution and tri-substitution reactions was difficult, pure **BHPFS** could be easily separated from the product mixture by column chromatography in a yield of 35%.

It should be noted that the presence of the four fluorine atoms in **BHPFS** not only lowers the optical loss at the telecommunication wavelengths, but also decreases the nucleophilicity of the vinyl moiety significantly due to its strongly electronegative character.[5a] Accordingly, the **BHPFS**

Scheme 2. Synthesis of Cross-Linkable Polymers (FPAEK 1−3 and FPAES 1−3)



was found to be quite stable at high temperatures (e.g., <150 °C) and under visible light, which allows the synthesis and purification of **BHPFS** and polymers containing **BHPFS** to be carried out under normal reaction conditions. However, in the presence of a suitable initiator, **BHPFS**-based polymer films are sufficiently reactive to induce cross-linking of the tetrafluorostyrol units when exposed to heat or UV light.

Synthesis of Cross-Linkable Fluorinated Polymers. The cross-linkable fluorinated polymers (**FPAEK 1−3** and **FPAES 1−3**) were prepared by copolymerization of the perfluorinated monomers (i.e., decafluorobenzophenone or decafluorodiphenyl sulfone) with 6F-BPA and **BHPFS** (Scheme 2). Due to the activation effect of the strong electron-withdrawing ketone and sulfone groups, both the *para*- and *ortho*-fluorines in the perfluorinated monomers have high reactivities with bisphenols under traditional high-temperature polycondensation reaction conditions. To avoid serious branching or cross-linking side reactions that have been observed in several polymer syntheses under traditional polymerization conditions, the polymerizations were therefore carried out using a very mild reaction condition established in our group.[9] This reaction involves the use of cesium fluoride and calcium hydride as the catalyst and base, respectively, which have been found to facilitate the formation of the phenolates, and enables the polymerization to be performed at a temperature as low as 55 °C, rather than the higher polymerization temperature such as 150 °C employed when potassium carbonate is used as the base in conventional reaction conditions. Since no water was generated under our polymerization conditions, azeotropic distillation is not required.

The polymerization reactions were monitored by GPC and were found to be complete in 3 h, producing reasonably high molecular weight materials with low polydispersities. Table 1 illustrates the chemical structures and properties of **FPAEK 1−3** and **FPAES 1−3** with different amounts of the cross-linkable **BHPFS** unit (from 12.4 to 25 mol % relative to the total bisphenols in polymers). Typical number average molecular weights and polydispersities ranged from 25 000 to 36 000 and 2.6 to 4.6, respectively. The polymer structures were confirmed by ^{1}H NMR and ^{19}F NMR and were found in good agreement with the designed structures. On detailed examination of the ^{19}F NMR spectra, it was observed that, besides the six major peaks that were assigned as shown in Figure 1, three other small peaks were present. On the basis of previous study,[8,9] these peaks can be assigned to the three fluorine atoms associated with the phenyl sulfone end groups. No obvious signal related to branching of the polymer chains was observable from the ^{19}F NMR spectra. In the ^{1}H NMR spectra, three resonances at 6.73, 6.08, and 5.78 ppm were observed, attributable to the protons on the vinyl moiety of tetrafluorostyrol groups. No other aliphatic resonances could be found, indicating that the tetrafluorostyrol units were introduced successfully into fluorinated polymers and were stable to the polymerization conditions employed.

Table 1. Characterization of the Fluorinated Polymers Containing Tetrafluorostyrol Units

polymer	content of **BHPFS** (mol %)[a]	M_n[b]	M_w/M_n	T_g (°C)[c]	T_d (°C)[d]
FPAEK 1	12.4	35 400	4.6	154.0	485.0
FPAEK 2	20.0	29 100	3.8	153.8	485.5
FPAEK 3	25.0	25 900	3.6	153.6	481.5
FPAES 1	12.4	25 200	2.6	185.8	474.2
FPAES 2	20.0	29 000	4.3	186.7	466.9
FPAES 3	25.0	26 300	3.0	183.7	466.3

[a] Molar ratio of **BHPFS** relative to the total bisphenols. [b] Number average molecular weight determined by GPC. [c] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen. [d] Onset temperature for 5% weight loss measured by TGA with a heating rate of 10 °C/min in nitrogen.

All the polymers were determined to be amorphous by wide-angle X-ray crystallography and DSC. The TGA measurements indicated that the polymers have very high thermal stabilities as assessed by 5% weight loss temperatures (e.g., up to 480 °C in nitrogen). The polymers also had high

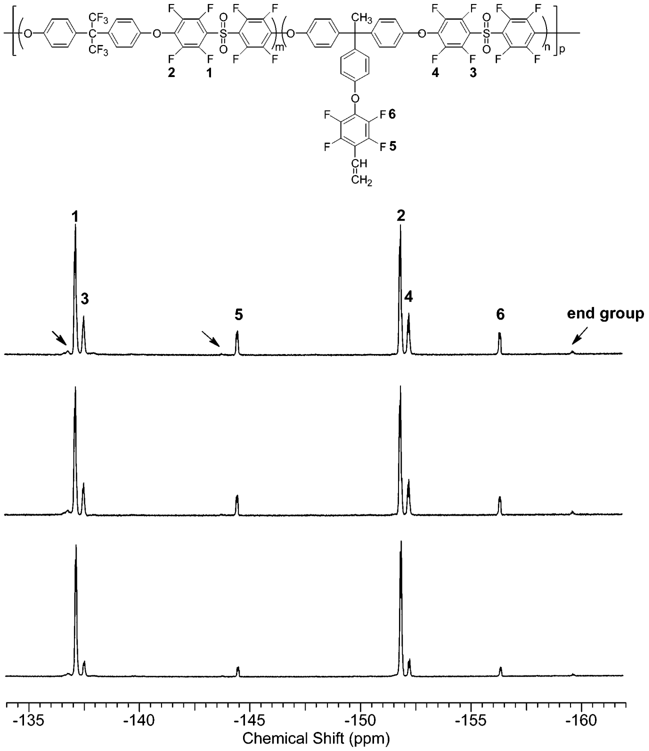


Figure 1. ^{19}F NMR spectra of **FPAES 1−3** (from bottom to top).

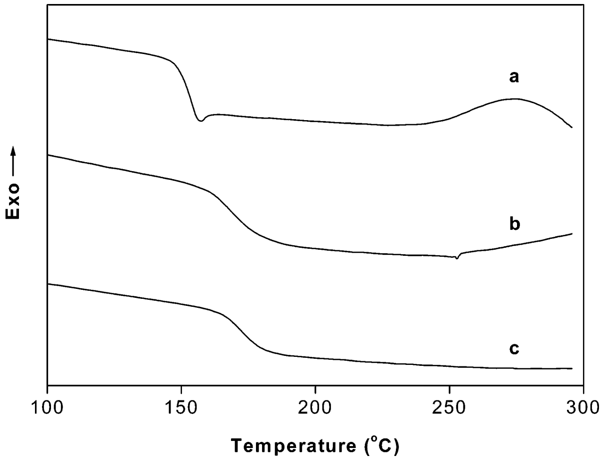


Figure 2. DSC curves of **FPAEK 2** (a) before cross-linking; (b) after photo cross-linking for 20 min with the presence of 5 wt % MSTA as photo initiator; and (c) after thermal cross-linking at 160 °C for 1 h with the presence of 1 wt % dicumyl peroxide.

glass transition temperatures as detected by DSC. In the case of the cross-linkable **FPAEK**s, the T_g values were around 153 °C, while the **FPAES**s showed T_g of around 186 °C. All the polymers exhibited an exothermic transition around 275 °C on DSC heating associated with the thermal cross-linking reactions of the styrol group (Figure 2a). The concentration of **BHPFS** in the polymers appeared to have no effect on the measured T_g and thermal stabilities. All the polymers had very good solubilities in common organic solvents such as acetone, THF, DMAc, and dichloromethane and were able to form tough, flexible, and transparent films using both casting and spin-coating techniques.

Thermal and Photo Cross-Linking. The tetrafluorostyrol units in the fluorinated polymers can undergo cross-linking reactions by both thermal heating and UV irradiation. The thermal cross-linking of **FPAEK 1−3** and **FPAES 1−3** was studied by heating the polymer films at either 160 °C in the presence of a free-radical initiator, dicumyl peroxide (1 wt % relative to the polymers), or at 260 °C in the absence of any initiator. After thermal curing for 1 h, all the polymers showed an increase in T_g of over 20 °C (Figure 2c). Since the vinyl double bond has a strong stretching vibration absorption in Raman spectra, the cross-linking reaction was monitored by FT-Raman spectroscopy. The absorption at 1430 cm^{-1} assigned to the stretching vibration of the vinyl double bond in the tetrafluorostyrol group was used for this purpose. Figure 3 compares the FT-Raman spectra of **BHPFS** and **FPAEK 2** in the presence of dicumyl peroxide before and after thermal cross-linking. From this figure it can be clearly seen that the band at 1430 cm^{-1} disappears on heating for 1 h, which suggests the completeness of cross-linking reaction. Soaking the cured polymer films in acetone for 3 days resulted in weight losses less than 1%, confirming the formation of a highly cross-linked network with good solvent resistance.

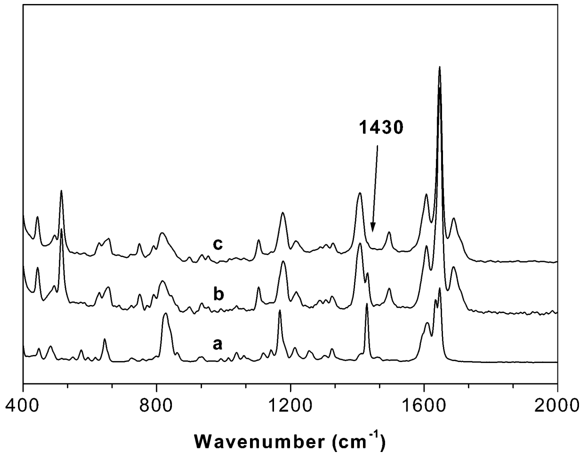


Figure 3. FT-Raman spectra of **BHPFS** (a); and **FPAEK 2** before thermal cross-linking (b); and after thermal cross-linking (c) at 160 °C for 1 h with the presence of 1 wt % of dicumyl peroxide.

The photo cross-linking of **FPAEK 1−3** and **FPAES 1−3** was realized by exposing the photo acid generator (PAG) containing polymer films to UV light in the range of 310−400 nm. This spectral region of UV light for the photo irradiation was chosen because of the strong absorption of the polymers at wavelengths below 300 nm. In our study, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MSTA) was employed as the photo acid generator, whose maximum absorption occurs at 379 nm. Such absorption is sufficiently detached from that of the absorption region of polymers, and therefore efficient acid generation was possible upon exposure to UV light. A typical DSC curve of the photo cross-linked **FPAEK 2** film containing 5 wt % MSTA is shown in Figure 2b, and demonstrates that the T_g increases about 13 °C upon UV irradiation for 20 min, indicating the occurrence of the photo cross-linking reaction. However, this increase in the T_g is less than that observed in the cases of the thermally cross-linked polymers (∼20 °C). This might be attributed to a lower efficiency of the cross-linking reaction due to a lower mobility of the polymer chains at the temperatures used for the photo cross-linking reaction.

The direct patterning of the core structures from these polymers has been explored using photolithography. In this

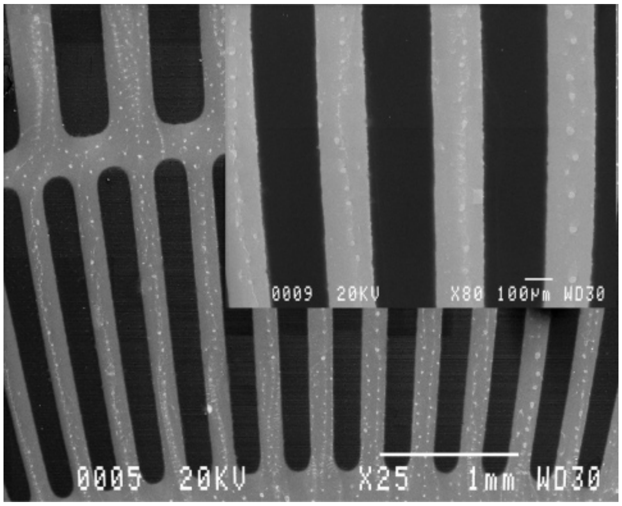


Figure 4. SEM images obtained with **FPAEK 3** thin film after UV irridiation for 20 min.

Table 2. Optical Properties of Cross-Linked Fluorinated Polymers

polymer	n_{TE}[a]	n_{TM}[a]	$n_{\mathrm{TE}} - n_{\mathrm{TM}}$ ($\times 10^{-3}$)	optical loss[b] (dB/cm)
FPAEK 1	1.5097	1.5074	2.3	0.35
FPAEK 2	1.5137	1.5117	2.0	
FPAEK 3	1.5168	1.5143	2.5	0.40
FPAES 1	1.5131	1.5110	2.1	0.55
FPAES 2	1.5175	1.5151	2.4	
FPAES 3	1.5204	1.5179	2.5	0.50

[a] Refractive index at 1537 nm. [b] Slab loss at 1550 nm.

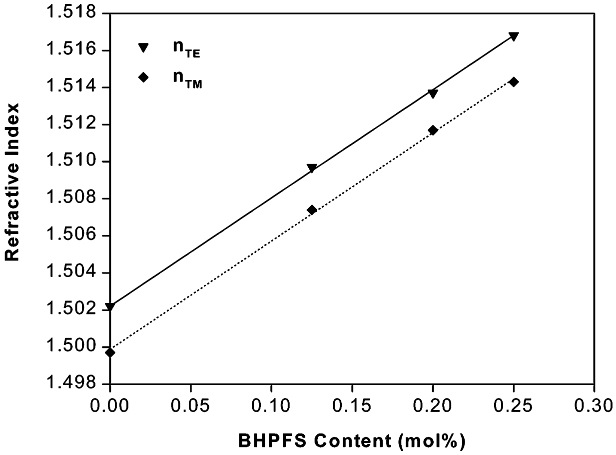


Figure 5. Dependence of refractive index of **FPAEK**s on **BHPFS** content.

study, the polymer films were UV irradiated through a mask. Figure 4 shows the top view SEM photograghs of a photopatterned **FPAEK 3** thin film containing MSTA. The dark areas represents the covered areas of the polymer. After UV irridiation for 20 min, the exposed areas of the film were cross-linked and showed a well-defined pattern. Although the side-walls of the polymer film are not as smooth as desired, these preliminary results are very promising and improvements can be expected by optimizing the photo cross-linking conditions such as photo initiator type and concentration, irradiation time, baking temperature and time, and developing methodology.[11] More detailed studies on the photopatterning of these polymers are under way in order to improve the resolution.

Optical Properties. Control of the refractive index (RI) of both the tansverse electric (TE) and transverse magnetic (TM) modes is exceedingly important for optical waveguide materials. The refractive indices of the cross-linked **FPAEK 1−3** and **FPAES 1−3** were measured by the prism coupling method at 1537 nm on thin films. For comparison, all polymer films were processed using the same procedure of thermal curing as described in the Experimental Section. These polymers showed relatively low refractive indices (Table 2) due to their high fluorine content. A linear relationship was observed between the refractive index (both n_{TE} and n_{TM}) of the polymers and the **BHPFS** content (Figure 5). By varying the **BHPFS** content from 0 to 25 mol % (relative to the total bisphenols), the refractive index of the TE mode increased linearly from 1.5022 to 1.5168 for the **FPAEK**s and from 1.5051 to 1.5204 for the **FPAES**s. This linear relationship represents an opportunity for the fine-tuning of the refractive index by changing the feed ratio of bisphenols. Comparison of the **FPAES**s to the **FPAEK**s reveals that the presence of the more polar sulfone linkages results in higher refractive index materials when the same amount of **BHPFS** is employed. For example, a difference of 0.003 in the refractive index (n_{TE}) was found between **FPAEK 1** (1.5097) and **FPAES 1** (1.5131). The birefringence of **FPAEK**s and **FPAES**s, as characterized by the difference between the n_{TE} and the n_{TM}, were found to be in the range of 2.0×10^{-3} to 2.5×10^{-3}. These values appeared to be unaffected by the content of the cross-linkable unit (**BHPFS**) and are comparable to those reported for several other fluorinated polyarylene ethers.[3e,5,6]

The optical losses of the polymers **FPAEKs 1** and **3** at 1550 nm were evaluated from the slab losses using a high index liquid immersion method. These polymers were observed to have very low optical losses at 1550 nm. For **FPAEK 1** and **FPAEK 3**, the optical losses were 0.35 and 0.40 dB/cm, respectively, whereas those for **FPAES 1** and **FPAES 3** were 0.55 and 0.50 dB/cm, respectively.

Fabrication of Polymer Waveguide Devices. In view of the good optical properties and the excellent processability of these cross-linkable **FPAEK**s and **FPAES**s, they are promising candidates for both core and cladding materials in photonic device applications. As a result various waveguide devices such as straight waveguides and splitters (Figure 6) were fabricated using these cross-linkable **FPAEK**s and **FPAES**s by reactive ion etching (RIE) technique. The ridge widths and heights of the waveguides are typically in the range of 3− 7 μm with the side-walls that are very smooth and vertically sharp. Figure 6A shows the core structure of straight waveguides fabricated with the fluorinated polymers, **FPAEK 3**. These waveguides were fabricated by first depositing **FPAEK 3** onto a 15-μm silica layer coated silicon substrate (with a refractive index of 1.4452). The polymer film was then thermally cross-linked and a standard negative photoresist lift-off method was used to pattern a nickel mask on the polymer layer. Ridge waveguides were then formed using an O_2/CHF_3 RIE process. Finally, a 10-μm thick

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(11) (a) Macdonald, S. A.; Willson, C. G.; Freshet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151. (b) Gan, J.; Tian, H.; Chen, K. *Polym. Adv. Technol.* **2002**, *13*, 584. (c) Okamura, H.; Toda, S.; Tsunooka, M.; Shirai, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3055.

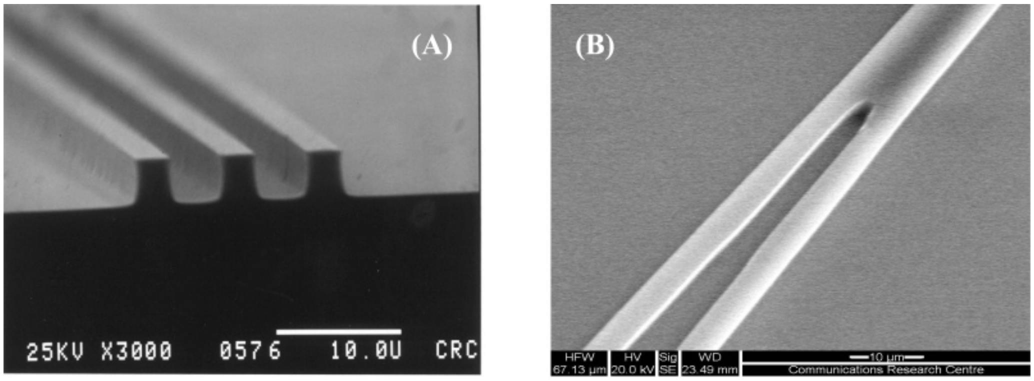

Figure 6. SEM pictures of the core structures of straight waveguides (A) and a 1 × 2 power splitter (B) fabricated with **FPAEK 3**. The core size for the straight waveguides is 3 × 3.5 μm.

cladding layer of a fluorinated polyether ketone reported previously[9d] with a refractive index 0.01 smaller than **FPAEK 3** was applied on the top after the removal of the metal mask. The propagation loss of the device was estimated by a cut-back method which measures the transmitted optical power in successively shorter lengths of waveguide. Light from a diode laser at 1550 nm was butt-coupled into a waveguide via a single mode fiber (SMF-28 8/125) and the transmitted power was collected by an objective lens and monitored using an optical power meter. With carefully cleaved samples, the coupling losses between the fiber and the waveguide endface are very repeatable, and the propagation loss in the waveguides can be calculated from the slope of the total loss versus length curves. The obtained data demonstrated very low propagation losses at 1550 nm of these devices. For example, a 5 × 5 μm straight waveguide had a propagation loss of around 0.7 dB/cm as determined by the cut-back method.

Conclusion

A series of cross-linkable fluorinated PAEKs and PAESs with good solubilities, good film-forming capabilities, high glass transition temperatures, low birefringence values, and good optical transparency at 1550 nm have been designed and prepared. The polymers can be cross-linked both thermally and photochemically, yielding materials with good chemical resistance and increased glass transition temperatures. Well-defined photopatterning of the polymers has been achieved in the presence of an appropriate photo acid generator and shown promising for direct photopatterning of waveguide structures. These polymers also showed a linear dependency of their refractive indices on the **BHPFS** content, thereby allowing the fine-tuning of the refractive indices of the polymers. Prototype waveguide devices have been processed by RIE from these materials and exhibited low propagation losses at 1550 nm.

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