

Cross-linkable highly halogenated poly(arylene ether ketone/sulfone)s with tunable refractive index: Synthesis, characterization and optical properties

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Abstract

A series of novel cross-linkable, highly halogenated poly(arylene ether ketone)s (**HPAEKs**) and poly(arylene ether sulfone)s (**HPAESs**) with different bromine contents have been designed and prepared by polycondensation reactions for use as optical waveguide materials. The method used for their preparation involved reacting decafluorodiphenyl ketone/sulfone (DFPK/DFPS) with a mixture of 4,4'-isopropylidene bis(2,6-dibromophenol) (4Br-BPA), 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), and 1,1-bis(4-hydroxyphenyl)ethyl-1-phenyl-2,3,5,6-tetrafluorostyrol ether (BHPFS). The feed ratio of 4Br-BPA to the total bisphenols varied from 0 to 80 mol.%, while that of BHPFS remained at 20% for all polymers. The resulting polymers have excellent solubility in most common organic solvents such as tetrahydrofuran, cyclohexanone and *N,N*-dimethylacetamide (DMAc) and can be easily cast into optical-quality thin films. A high glass transition temperature in the range of 164–206 °C was found for these polymers, which could be further increased by about 20 °C upon thermal or photochemical cross-linking. Slab and channel waveguides have been prepared from these polymers. All of them exhibited low optical loss (0.4–0.6 dB/cm) at the telecommunication wavelength of 1550 nm. Due to the relatively higher polarizability of the C–Br bond than that of the C–H bond, an increase in the refractive index was observed as the bromine content in the polymers increased. Consequently, the refractive index of **HPAEKs** and **HPAESs** can be readily adjusted within a wide range from 1.51 to 1.57 by simply changing the ratio of the bromine-containing bisphenol in the feed. This variability, along with the excellent cross-linking capability, allows these polymers to be used as both the core and the cladding materials for the waveguide device fabrication and provides a greater flexibility in the design of device structures.

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1. Introduction

The use of organic polymers in optical waveguide devices, particularly for applications in optical networks based on wavelength division multiplexing (WDM) has been actively pursued in the past decade due to their ease of processing, low cost, and good compatibility for integration with semiconductor components [1,2]. Typically, these waveguide devices,

such as electro-optic modulators, variable optical attenuators, optical interconnects, splitters, and arrayed waveguide gratings (AWG), comprise a three-layer structure, in which the light propagates through a central core sandwiched between two cladding layers. In the past, core-layer material based on fluorinated polyimides [3], fluorinated polyacrylates [4], perfluorocyclobutyl aryl ethers [5], and Teflon AF has been intensely developed with high optical transparency at the telecommunication wavelengths (e.g., 1300 and 1550 nm). However, for the practical fabrication of optical devices, it is essential for both the core and the cladding materials to have excellent properties in terms of low optical loss, low

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birefringence, and high T_g . The core and the cladding materials should also be compatible to have controlled refractive indices, good interfacial adhesion, and similar thermal expansion coefficients. Good thin-film processability and cross-linking functionality of these materials are also highly desired for an easy construction of multilayer waveguide structures, where multilayer films are required. Cross-linking individual layers obviate problems inherent to solvent coating one polymer over another.

Towards meeting all these materials' requirements, various types of waveguide polymers have been developed and active materials' innovations are being carried out. Among them, fluorinated poly(arylene ether ketone/sulfone)s (PAEKs/PAESs) have recently drawn attention as a class of promising waveguide materials [6,7]. Non-fluorinated PAEKs/PAESs were traditionally studied as high-performance polymers and have been used in a wide range of demanding applications from aerospace to microelectronics, owing to their unique features such as high thermal, mechanical and environmental stabilities. Upon fluorination, these polymers exhibited low optical propagation losses at the telecommunication wavelength region. Due to the existence of flexible ether linkages in the polymer backbone, relatively low birefringence values in comparison with other high T_g polymers such as polyimides were also achieved [3]. In addition, it has been found that the method used in their preparation (i.e., through polycondensation reactions of two or more monomers in a stepwise way) offers a great deal of flexibility in controlling materials' properties such as the refractive index and birefringence.

In a previous study, we developed a novel type of cross-linkable fluorinated PAEKs/PAESs that showed very good waveguide properties (e.g., optical loss at 1550 nm was around 0.5 dB/cm) and excellent multilayer processability [8]. Our goal in this study was therefore to develop complementary materials that would allow the fabrication of multilayer waveguide structures. Ideally, we were seeking low-loss fluorinated PAEKs/PAESs with tunable refractive index, so that the same type of polymers can be used for both the core and the cladding layers. The inherent advantages of this design include a good interface adhesion and comparable thermal expansion coefficients between the core and the cladding layers. As a consequence, we have designed and synthesized a series of novel highly halogenated polymers (HPAEKs/HPAESs) by copolymerizations of a brominated bisphenol and fluorinated bisphenols with a perfluorinated biphenyl compound (DFPK or DFPS). The large polarizability and low overtone absorption associated with the C–Br bonds were found to contribute to a higher refractive index in the resulting polymers while retaining a low optical loss. As a result, by controlling the bromine content in the polymers, the refractive index of HPAEKs/HPAESs could be readily adjusted within a wide range of 1.51–1.57. This allows not only the use of the resulting polymers as both the core and the cladding materials in a waveguide device, but also a great flexibility in the device design. Multilayer waveguide devices based on these polymers, such as arrayed waveguide gratings and splitters, have been fabricated and characterized.

2. Experimental section

2.1. Materials

The synthesis of 1,1-bis(4-hydroxyphenyl)ethyl-1-phenyl-2,3,5,6-tetrafluorostyrol ether (BHPFS) has been reported previously [8]. 4,4'-(Hexafluoroisopropylidene)diphenol (6F-BPA, Sigma–Aldrich) and 4,4'-isopropylidene bis(2,6-dibromophenol) (4Br-BPA, Sigma–Aldrich) were purified by recrystallization from toluene. Decafluorodiphenyl ketone (DFPK, Sigma–Aldrich) was purified by recrystallization from isopropanol. Decafluorodiphenyl sulfone (DFPS) was prepared according to the method reported in the literature [9]. All other chemicals were purchased from Sigma–Aldrich and used as received.

2.2. Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity Inova spectrometer at a resonance frequency of 400 MHz for ^1H NMR, and 376 MHz for ^{19}F NMR. The chemical shifts relative to tetramethylsilane for ^1H NMR and CFCl_3 for ^{19}F NMR are reported on the parts per million scale. The molecular weights of the polymers were determined by size exclusion chromatography (SEC) 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 254 nm. A set of Microstyrigel columns (10^3 , 10^4 , and 10^5 Å) was calibrated using a set of polystyrene standards in THF. Raman and IR spectra were recorded on a Bruker FRA 106/S FT-Raman spectrometer and a MIDAC FT-IR spectrometer, respectively. Differential scanning calorimetric (DSC) measurements and thermogravimetric analyses (TGA) were performed on a TA Instruments DSC 2920 and on a TA Instruments TGA 2950, respectively, using a heating rate of 10 °C/min under nitrogen. The refractive indices of the polymer films were determined at 1537 nm using the prism coupling technique with an uncertainty of ± 0.0004 . Optical losses of the polymer films were measured at 1550 nm on slab waveguide samples using the technique of high-index liquid immersion [10]. The propagation losses of straight waveguides were measured at 1550 nm using a cut-back method [11].

2.3. Synthesis of cross-linkable highly halogenated polymers

The synthesis of the fluorinated poly(arylene ether ketone/sulfone), (HPAEK/S-0) without any bromine atoms in the polymer backbone was conducted by polymerizing DFPK or DFPS with 80 mol.% of 6F-BPA and 20 mol.% of BHPFS as reported previously [8].

2.3.1. Cross-linkable highly halogenated poly(arylene ether ketone)s (HPAEK-1–HPAEK-4)

The synthesis of the halogenated poly(ether ketone)s is illustrated as follows.

HPAEK-1: to a solution of 4Br-BPA (0.1997 g, 0.3672 mmol), 6F-BPA (0.2461 g, 0.7319 mmol), BHPFS (0.1302 g, 0.2710 mmol) and DFPK (0.4987 g, 1.3772 mmol) in 10 mL of anhydrous DMAc was added cesium fluoride (0.50 g, 3.30 mmol). The mixture was stirred at 55 °C under argon for 5 h. After filtration to remove insoluble inorganic salts, the viscous polymer solution was added dropwise to methanol (120 mL). The resulting polymer product was collected by filtration, washed thoroughly with distilled water and methanol, and dried at room temperature under vacuum (0.1 mmHg) (0.80 g, 80% yield). ^1H NMR (400 MHz, acetone- d_6): δ 7.70 (5.4H, s), 7.48 (11H, d, $J = 8.8$ Hz), 7.34 (11H, d, $J = 8.8$ Hz), 7.08 (12H, m), 6.73 (1H, dd, $J = 18.0, 12.0$ Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.82 (8H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.6 (16F, s), -142.5 (20F, m), -144.5 (2F, m), -153.2 (11F, m), -153.5 (4F, m), -156.5 (2F, m), -157.0 (5F, m). IR (NaCl, cm^{-1}): 1689, 1648, 1606.

The following polymers with different 4Br-BPA contents were prepared using the same procedure as outlined above and characterized as follows.

HPAEK-2: 81% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.70 (8H, s), 7.49 (8H, d, $J = 8.8$ Hz), 7.35 (8H, d, $J = 8.8$ Hz), 7.09 (12H, m), 6.74 (1H, dd, $J = 18.4, 12.0$ Hz), 6.08 (1H, d, $J = 18.4$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.81 (12H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.6 (12F, s), -142.5 (20F, m), -144.6 (2F, m), -153.2 (8F, m), -153.5 (4F, m), -156.4 (2F, m), -157.0 (8F, m). IR (NaCl, cm^{-1}): 1688, 1646, 1607.

HPAEK-3: 77% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.70 (11H, s), 7.48 (5.5H, d, $J = 8.8$ Hz), 7.34 (5.5H, d, $J = 8.8$ Hz), 7.10 (12H, m), 6.73 (1H, dd, $J = 18.0, 12.0$ Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.80 (16H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.4 (8F, s), -142.4 (20F, m), -144.6 (2F, m), -153.2 (5F, m), -153.5 (4F, m), -156.5 (2F, m), -157.0 (11F, m). IR (NaCl, cm^{-1}): 1688, 1646, 1607.

HPAEK-4: 75% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.68 (16H, s), 7.10 (12H, m), 6.72 (1H, dd, $J = 18.0, 12.0$ Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.81 (24H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -142.6 (20F, m), -144.6 (2F, m), -153.5 (4F, m), -156.5 (2F, m), -157.1 (16F, m). IR (NaCl, cm^{-1}): 1689, 1647, 1606.

2.3.2. Cross-linkable highly halogenated poly(arylene ether sulfone)s (HPAES-1–HPAES-4)

The preparation of these polymers is illustrated as follows.

HPAES-1: to a solution of 4Br-BPA (0.2351 g, 0.4322 mmol), 6F-BPA (0.2900 g, 0.8625 mmol), BHPFS (0.1561 g, 0.3249 mmol) and DFPS (0.6462 g, 1.6229 mmol) in anhydrous DMAc (11 mL) was added cesium fluoride (0.60 g, 3.90 mmol). The mixture was stirred under argon at 45 °C for 5 h. After filtration to remove the inorganic salts, the polymer solution was added dropwise to methanol (150 mL). The resulting polymer was collected by filtration, washed thoroughly with distilled water and methanol, and dried at room temperature under vacuum (0.1 mmHg) (1.00 g, 79%

yield). ^1H NMR (400 MHz, acetone- d_6): δ 7.68 (5.5H, s), 7.45 (11H, m), 7.32 (11H, m), 7.08 (12H, m), 6.72 (1H, dd, $J = 18.4, 12.0$ Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.81 (8H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.6 (16F, m), -137.4 (20F, m), -144.5 (2F, m), -151.8 (11F, m), -152.3 (4F, m), -155.9 (5.4F, m), -156.4 (2F, m). IR (NaCl, cm^{-1}): 1641, 1606, 1389, 1297.

The following polymers with different amounts of 4Br-BPA were prepared using the same procedure as outlined above and characterized as follows.

HPAES-2: 78% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.68 (8H, s), 7.45 (8H, m), 7.32 (8H, m), 7.08 (12H, m), 6.73 (1H, dd, $J = 17.6, 12.0$ Hz), 6.08 (1H, d, $J = 17.6$ Hz), 5.79 (1H, d, $J = 12.0$ Hz), 1.81 (12H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.6 (12F, m), -137.4 (20F, m), -144.5 (2F, m), -151.9 (8F, m), -152.4 (4F, m), -155.9 (8F, m), -156.4 (2F, m). IR (NaCl, cm^{-1}): 1642, 1604, 1393, 1299.

HPAES-3: 76% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.67 (11H, s), 7.45 (5.5H, m), 7.32 (5.5H, m), 7.09 (12H, m), 6.72 (1H, dd, $J = 18.4, 12.0$ Hz), 6.08 (1H, d, $J = 18.4$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.81 (16H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -63.6 (8F, m), -137.5 (20F, m), -144.5 (2F, m), -151.9 (5F, m), -152.3 (4F, m), -155.9 (11F, m), -156.4 (2F, m). IR (NaCl, cm^{-1}): 1637, 1604, 1389, 1297.

HPAES-4: 78% yield. ^1H NMR (400 MHz, acetone- d_6): δ 7.67 (16H, s), 7.07 (12H, m), 6.72 (1H, dd, $J = 18.0, 11.6$ Hz), 6.08 (1H, d, $J = 18.0$ Hz), 5.78 (1H, d, $J = 12.0$ Hz), 1.81 (24H, s). ^{19}F NMR (376 MHz, acetone- d_6): δ -137.4 (20F, m), -144.5 (2F, m), -152.3 (4F, m), -155.9 (16F, m), -156.4 (2F, m). IR (NaCl, cm^{-1}): 1637, 1604, 1389, 1297.

2.4. Film preparation for refractive index measurement following thermal cross-linking

A polymer solution was prepared by dissolving the polymer (~30% w/v) and a thermal cross-linking initiator (dicumyl peroxide, 1 wt.% relative to polymer) in cyclohexanone. The polymer solution was 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 dried at 60 °C (30 min) and 130 °C (30 min) to remove the residual solvent. Thermal curing was then achieved by heating the films slowly to 160 °C and maintaining at this temperature for 2 h under vacuum.

3. Results and discussion

3.1. Polymer synthesis

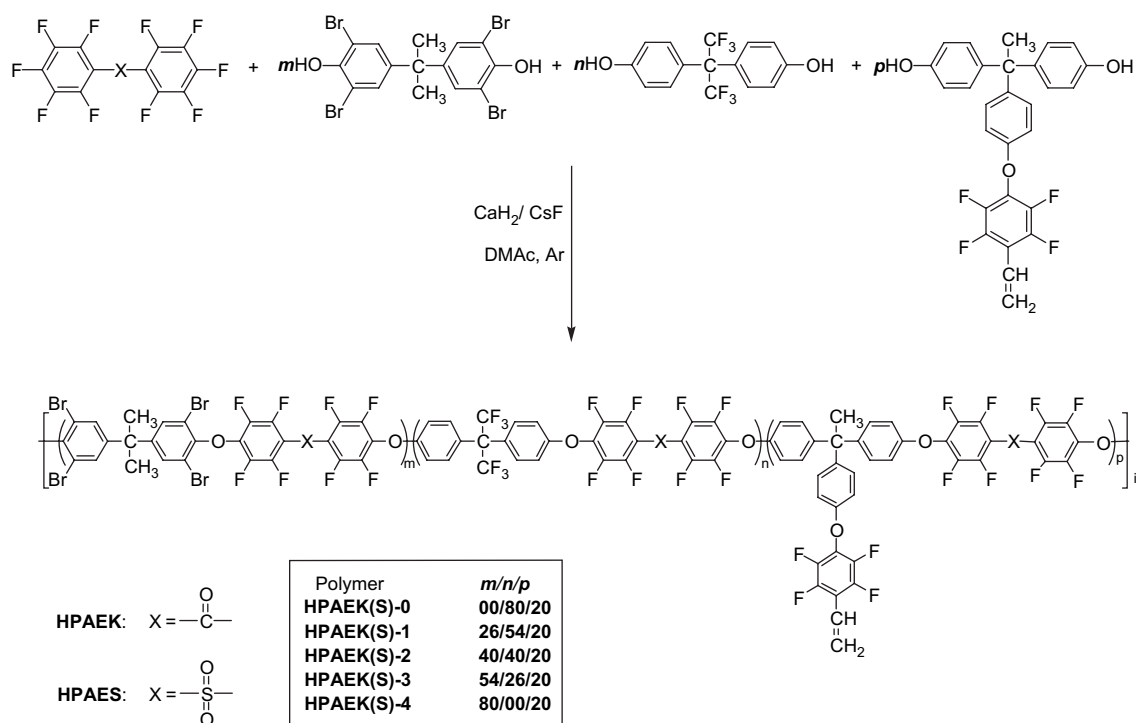
Studies have shown that the overtone absorptions associated with the C–X bonds (X = F, Br and Cl) at the infrared telecommunication wavelengths of 1300 and 1550 nm are five orders of magnitude less than those associated with the C–H bonds, whose overtone absorptions have been known as the main cause for optical attenuations of organic materials

[12]. Therefore, to minimize the optical absorption of the resultant polymers, perfluorinated monomers, decafluorodiphenyl ketone or sulfone (DFPK or DFPS) and halogenated bisphenols, which are 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA), 4,4'-isopropylidene bis(2,6-dibromophenol) (4Br-BPA), and 1,1-bis(4-hydroxyphenyl)ethyl-1-phenyl-2,3,5,6-tetrafluorostyrol ether (BHPFS), were employed as monomers for the synthesis of the waveguide polymers. The purpose of the copolymerization of 4Br-BPA together with 6F-BPA in this study is twofold. (1) Due to the larger polarizability of C–Br bonds than C–H bonds and C–F bonds, introduction of the species containing C–Br bonds into the polymer structures in a controlled way may lead to a fine tuning of the refractive index of the resulting polymers. Consequently, a waveguide structure with both the core and the cladding materials using the same type of highly halogenated poly(arylene ether ketone/sulfone)s can be fabricated. This is highly desirable in practical device fabrications since both improvement of the interface adhesion and decrease in the difference of thermal expansion coefficients can be achieved when the same type of materials is used for the core and the cladding layers. (2) Good optical transparency of the resulting polymers at the telecommunication wavelengths is also ensured due to the small overtone absorptions associated with the C–Br bond at 1300 and 1550 nm.

Traditionally, the synthesis of poly(ether ketone/sulfone)s is carried out at high temperatures (e.g., 160 °C) in polar aprotic solvents, such as dimethylsulfoxide and *N,N*-dimethylacetamide (DMAc), and in the presence of potassium carbonate as the base. However, due to the strong activation effect of electron-withdrawing fluorine atoms, DFPK and DFPS

exhibited high reactivity at both the *para* and the *ortho* positions (relative to the carbonyl and sulfone groups). Consequently, when the traditional reaction conditions were used for these perfluorinated monomers, highly branched and cross-linking structures were obtained. To overcome this problem and take advantage of the high reactivity associated with DFPK and DFPS, a new synthetic methodology has been developed by using cesium fluoride instead of potassium carbonate [13]. Under the new polycondensation reaction condition, cesium fluoride acts as catalyst to convert the phenol group to the phenoxide ion. In addition, it also acts as a base, neutralizing the HF produced during the reaction to form a CsHF₂ complex, thereby promoting the polymerization reaction. Using this approach, the polymerizations of DFPK and PFPS with various bisphenols can be accomplished at a very low temperature to afford a satisfactory molecular weight (e.g., >20,000) and side reactions at *ortho* position can be significantly suppressed.

In this study, both the highly halogenated poly(ether ketone)s (HPAEKs) and poly(ether sulfone)s (HPAESs) have been prepared using this modified nucleophilic polycondensation reaction at low temperature (55 °C for HPAEKs and 45 °C for HPAESs as in Scheme 1). During these polymerization reactions, the feed ratio of 4Br-BPA to the total bisphenol monomers was varied from 0 to 80 mol.% to allow for a wide-range tuning of the refractive index (Table 1). In addition, a tetrafluorostyrol-containing bisphenol, BHPFS, was also introduced into all polymer structures at a constant feed ratio of 20 mol.% (relative to the total bisphenols) to enable the formation of cross-linking networks. In our previous studies, we have found the tetrafluorostyrol group to be stable to heat



Scheme 1. Synthesis of HPAEKs and HPAESs.

Table 1
Synthesis and properties of **HPAEKs** and **HPAESs**

Polymers	4Br-BPA content ^a (%)	BHPFS content ^b (%)	M_n^c ($\times 10^3$)	M_w/M_n	T_g^d (°C)	T_d^e (°C)
HPAEK-1	26.6	20.0	24.0	2.5	164.0	473.8
HPAEK-2	40.0	20.0	19.7	2.2	166.6	469.5
HPAEK-3	53.3	20.0	17.6	2.6	170.2	462.4
HPAEK-4	80.0	20.0	21.0	3.0	177.6	452.2
HPAES-1	26.6	20.0	22.9	2.9	194.5	465.6
HPAES-2	40.0	20.0	17.2	2.3	195.8	458.4
HPAES-3	53.3	20.0	22.5	2.1	197.9	453.7
HPAES-4	80.0	20.0	18.5	2.7	205.6	449.6

^a Feed molar ratio of 4Br-BPA relative to the total bisphenols.

^b Feed molar ratio of BHPFS relative to the total bisphenols.

^c Number average molecular weight determined by SEC.

^d Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen.

^e Temperature for 5% weight loss measured by TGA with a heating rate of 10 °C/min in nitrogen.

and visible light as well as the reaction conditions employed in the polycondensation reactions. However, in the presence of a suitable initiator such as a peroxide or a photoacid, the tetrafluorostyrol groups in polymers readily undergo thermal or photochemical intermolecular reactions to produce a densely cross-linked polymer [8]. SEC analysis revealed that the resulting polymers have molecular weights around 20,000 and polydispersity in the range of 2.1–3.0. ¹H and ¹⁹F NMR spectra confirmed that the desired polymer structures were obtained based upon the feed ratios of the monomers.

3.2. Polymer characterizations

The ¹H NMR analysis of all the halogenated polymers revealed the presence of three resonances at 6.73, 6.08 and 5.78, which correspond to the three protons on the vinyl group of the BHPFS units. Meanwhile the ¹⁹F NMR analysis indicates three peaks (peaks 2, 4 and 6 in Fig. 1) attributable to the fluorine atoms at the *meta* position with respect to sulfone groups in the DFPS units which are adjacent to the 4Br-BPA, 6F-BPA and BHPFS units, respectively. The integration of these peaks allows for an estimation of the compositions of each bisphenol moiety in the polymers, which was found to be consistent with designed polymer structures based upon the monomer feed ratios used in the reactions. Since no peak attributable to branched structures was discernible in the ¹⁹F NMR spectra, it suggests that linear structures were obtained for **HPAEKs** and **HPAESs**. These results indicate that a good control of composition of the resulting polymers could be easily achieved by varying the feed ratio of bisphenols. This factor is important for the application of the resulting polymers in waveguide devices since 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.

Further information of the polymer structures can be inferred from glass transition temperature (T_g) measurements (Table 1). The DSC heating scans in nitrogen at a heating rate of 10 °C/min revealed only one distinct T_g in the range of 164–206 °C for the resulting polymers. According to Fox

equation, the T_g of a random copolymer, such as **HPAEKs** and **HPAESs**, can be predicted based on the feed ratio of the monomers as presented in Fig. 2 using Eq. (1):

$$\frac{1}{T_g} = \frac{wt_1}{T_{g1}} + \frac{wt_2}{T_{g2}} \quad (1)$$

where T_g is the glass transition temperature of the copolymer, wt_1 is the weight fraction of 4Br-BPA relative to the total bisphenol, wt_2 is the sum of the weight fractions of 6F-BPA and BHPFS, T_{g1} and T_{g2} are the glass transition temperatures of the ‘homopolymers’ derived from 4Br-BPA with DFPK or DFPS (e.g., $T_g = 185$ °C for the ketone polymer) and from 6F-BPA and BHPFS with DFPK or DFPS (e.g., $T_g = 153$ °C for the ketone polymer), respectively. Herein, 6F-BPA and BHPFS were treated as an integral because copolymers derived from a mixture of these two bisphenols with different feed ratios exhibited basically the same T_g [8]. Fig. 2 displays the measured T_g and the predicted trend line according to the Fox equation. A good agreement of the T_g of the resulting copolymers with values predicted by the Fox equation according to the feed ratios is observed. Thus, it can be concluded that the three bisphenol comonomers, i.e., 4Br-BPA, 6F-BPA and BHPFS, have been randomly incorporated into the polymers. The random chain structure of the polymers is important for the waveguide applications. It ensures a homogeneous morphological structure with minimized fluctuations of density and refractive index in the film, so that the optical loss aroused from light scattering was minimized.

In the DSC curves of **HPAEKs** and **HPAESs**, besides the T_g transitions in the range of 164–206 °C, an exothermic transition peak around 250 °C was observed for all the polymers in the heating scan, which is attributable to the thermal cross-linking reaction of the tetrafluorostyrol groups. TGA indicated that all the polymers had good thermal stability in nitrogen, with the decomposition temperatures (5% weight loss) above 450 °C. However, as the 4Br-BPA content in the polymers was increased, a slight drop in the thermal stability was observed, which may be associated with the less thermally stable C–Br bonds in these polymers [14].

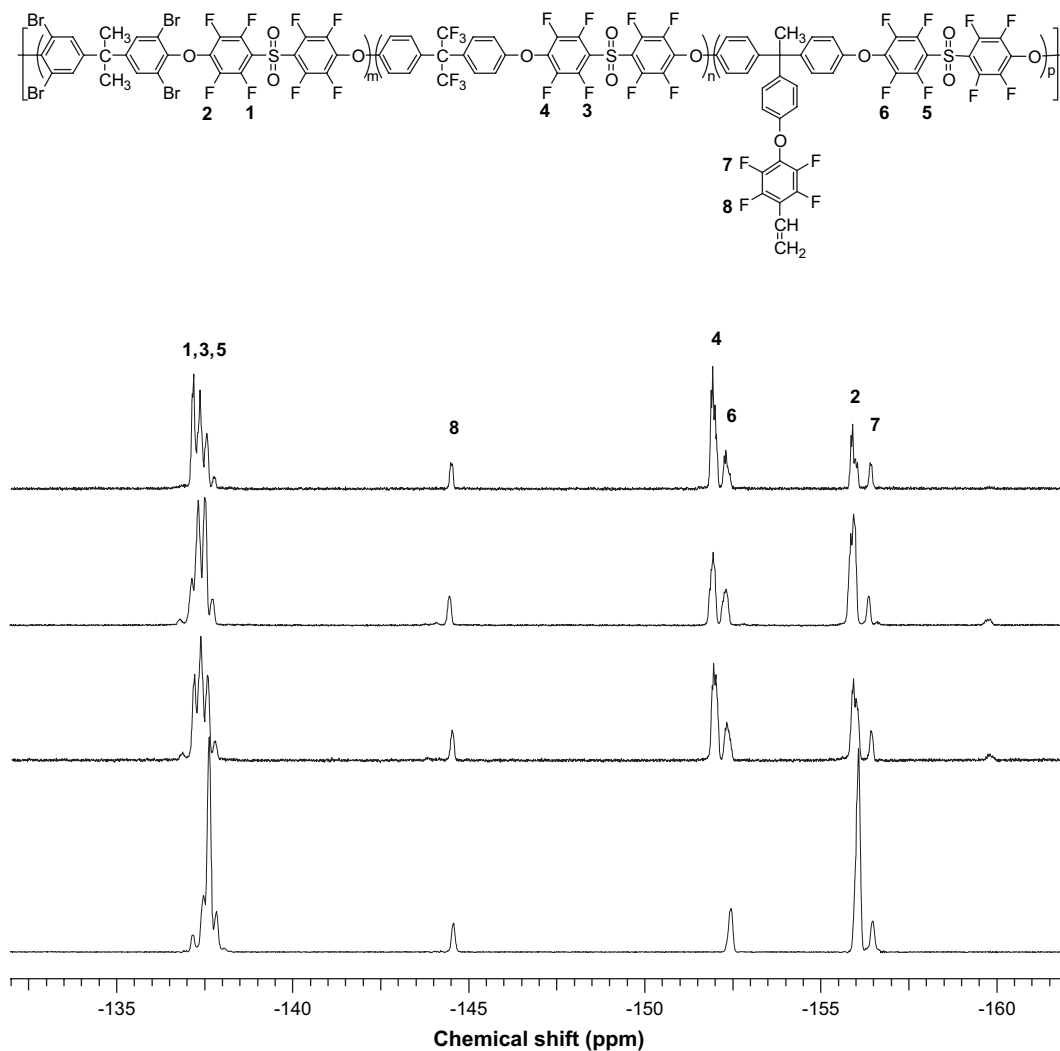


Fig. 1. ^{19}F NMR spectra of **HPAES-1**–**HPAES-4** (from top to bottom). For comparison, the spectra were normalized to the peak of tetrafluorostyrol unit (peak 8).

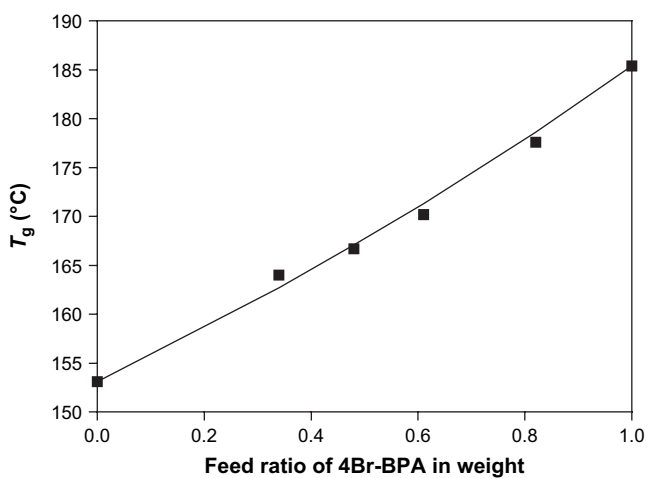


Fig. 2. Correlation between the glass transition temperature of **HPAEKs** and the feed ratio of 4Br-BPA (weight ratio relative to the total bisphenols). (■) Experimentally determined T_g values from DSC. The solid line represents the calculated values according to the Fox equation.

All the resulting **HPAEKs** and **HPAESs** showed excellent solubility in common organic solvents such as acetone, tetrahydrofuran (THF), DMAC and cyclohexanone. Transparent and flexible thin films of these polymers can be readily prepared by spin-coating or casting the polymer solutions onto a variety of substrates such as silica wafers and ITO glasses.

3.3. Polymer cross-linking

Although the tetrafluorostyrol units in the polymers have been found to be stable at low temperatures (e.g., $<160\text{ }^\circ\text{C}$) and to ambient light, they can undergo rapid intermolecular reactions under mild conditions in the presence of a suitable initiator. Consequently, the polymers can be readily cross-linked either by thermal heating or by UV irradiation [8]. In our study, the thermal cross-linking of **HPAEKs** and **HPAESs** was readily accomplished by heating the polymer thin films at $160\text{ }^\circ\text{C}$ for 2 h in the presence of a small amount of a thermal initiator, dicumyl peroxide (1 wt.% relative to the polymer). The T_g 's of the resultant cross-linked polymers were about

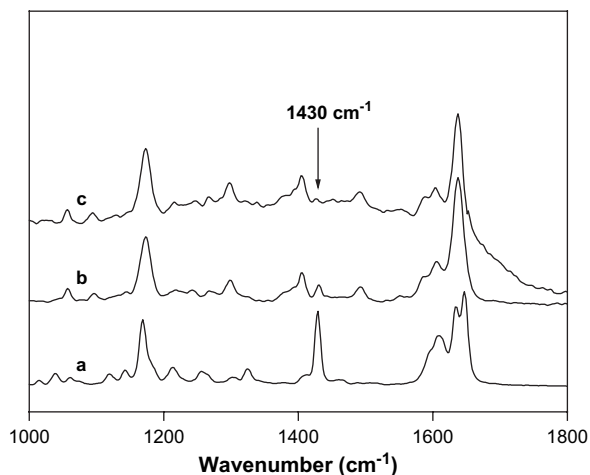


Fig. 3. The FT-Raman spectra of (a) BHPFS. (b) HPAES-2 before thermal cross-linking; (c) HPAES-2 after thermal cross-linking at 160 °C for 2 h in the presence of 1 wt.% of dicumyl peroxide.

20 °C higher than the original polymers and the polymers were no longer soluble in common organic solvents. The thermal cross-linking reaction of HPAES-2 was monitored using FT-Raman spectroscopy (Fig. 3). The vinyl absorption band of the BHPFS at 1430 cm⁻¹ disappeared as the polymer film was heated at 160 °C for 2 h, indicating the completeness of cross-linking reactions.

Direct photopatterning is a fast, convenient and economic approach for the fabrication of polymeric photonic devices. Compared with a conventional photolithography/reactive ion etching (RIE) process, UV photopatterning requires less process steps and shortens the manufacturing time, thereby offers a tremendous cost-effective advantage. Previous studies in our laboratory have shown that the tetrafluorostyrol group in BHPFS unit is an excellent photosensitive group [8]. In order to enable the fabrication of waveguide devices through direct photopatterning, several approaches have been carried out to optimize photocross-linking conditions of BHPFS-containing polymers. The results of these studies suggest that use of a cationic initiator, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (1 wt.% relative to the polymer), and exposure to UV light at 365 nm (10.4 mW/cm²) for 10 min followed by a post-baking at 150 °C for about 10 min and development in THF and acetone are very effective approaches. Using this methodology, high quality photopatterns were obtained with very well defined profiles. Similar to the case in thermal cross-linking, polymer films that were photochemically cross-linked showed an increased T_g and insolubility in common organic solvents. This approach has been used to fabricate a couple of waveguide devices such as straight waveguides and directional couplers with the BHPFS-containing polymers. Optical characterization indicates that the waveguide devices fabricated by direct photopatterning and a wet-etch process are comparable to that of waveguides fabricated by RIE process. The detailed results on direct photopatterning of waveguide devices using BHPFS-containing halogenated polymers were reported elsewhere [15].

3.4. Optical properties

The refractive indices of the halogenated polymers were studied using the prism coupling technique at 1537 nm on thermally cross-linked polymer thin films and values are in the range of 1.5117–1.5665 and 1.5151–1.5696 for HPAEKs and HPAESs, respectively (Table 2). As expected, an increase in the bromine content of the polymers resulted in an increase in the refractive index in both the TE and the TM modes. In fact, a good linear relationship, between the refractive index of the polymers and the feed ratio of 4Br-BPA was observed as shown in Fig. 4. Taking HPAEK as the example, when the feed ratio of 4Br-BPA was increased from 0 to 80 mol.%, the refractive index (n_{TE}) increased from 1.5137 to 1.5665. Since 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 halogenated polymers.

Table 2
Refractive indices of the HPAEKs and the HPAESs

Polymers	n_{TE}^a	n_{TM}^b	$n_{TE} - n_{TM}^c (\times 10^{-3})$
HPAEK-0	1.5137	1.5117	2.0
HPAEK-1	1.5318	1.5295	2.3
HPAEK-2	1.5408	1.5381	2.7
HPAEK-3	1.5486	1.5467	1.9
HPAEK-4	1.5665	1.5644	2.1
HPAES-0	1.5175	1.5151	2.4
HPAES-1	1.5347	1.5318	2.9
HPAES-2	1.5425	1.5398	2.7
HPAES-3	1.5516	1.5493	2.3
HPAES-4	1.5696	1.5670	2.6

^a Refractive index of the TE mode at 1537 nm.

^b Refractive index of the TM mode at 1537 nm.

^c Birefringence at 1537 nm.

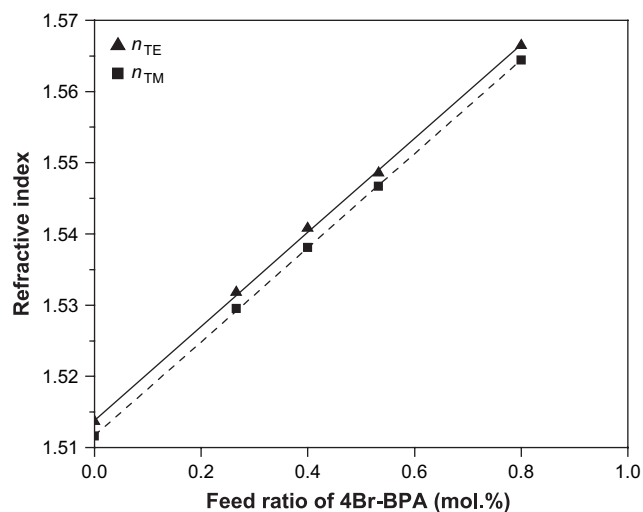


Fig. 4. The linear dependence of the refractive index of HPAEKs on the feed molar ratio of 4Br-BPA relative to the total bisphenols.

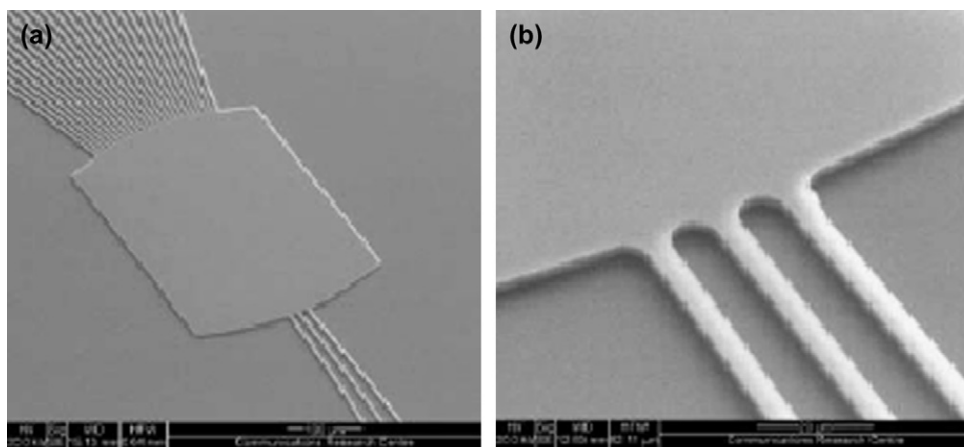


Fig. 5. SEM images of a three channel AWG device fabricated with a **HPAEK** ($n_{TE} = 1.5300$) as the core. (a) Top view; (b) input waveguides.

The birefringence of the resulting halogenated polymers was also evaluated and found to be around 2.0×10^{-3} . Although these values are still a bit high for some applications in WDM devices, it is anticipated to improve upon further structural modifications such as inserting fluorinated aliphatic spacer into the polymers. The preparation and application of these polymers are currently under way and will be published elsewhere. A physical doping technique is also reported to reduce the birefringence of polymers [16], in which an inorganic birefringent rod-shaped crystalline material with an opposite birefringence was doped. Both the polymer chains and the crystals were oriented so that the birefringence of the polymer is compensated by the opposing birefringence of the crystal. Comparison of the birefringence of polymers with different monomer feed ratios indicated that the different bromine contents in the polymers have a negligible effect on the birefringence values.

The optical loss of slab waveguides (5×40 mm) prepared using the thermally cross-linked halogenated polymers was measured at 1550 nm by the high-index liquid immersion technique. The values were found to be in the range of 0.4–0.5 dB/cm for **HPAEKs** and 0.5–0.6 dB/cm for **HPAESs**, indicating a high transparency of these polymers at the telecommunication wavelengths.

Given the excellent properties of these halogenated polymers for waveguide applications and the ability to control the refractive index over a wide range, multilayer waveguide devices with both the core and the cladding materials using the obtained polymers were fabricated using RIE technique. For example, a cross-linkable fluorinated poly(ether ketone) which has a refractive index of 1.5090 (n_{TE}) was chosen as the lower and upper cladding material, and an **HPAEK** (22 mol.% feed ratio of 4Br-BPA), which was specially designed to have a matched refractive index with the cladding (0.02 higher) was used as the core material. The straight waveguides with core ridge of 4×3 μm produced using this approach showed a low propagation loss in the order of 0.7 dB/cm. Fig. 5 shows SEM pictures of a three channel AWG with a channel spacing of 20 nm and the central wavelength at 1550 nm, fabricated using the halogenated polymers

described above. It can be seen that a well-defined waveguide structure with smooth sidewalls was obtained. In addition, the measured channel spacing and central wavelength were in good agreement with designed values. This AWG demultiplexer also exhibits a low insertion loss of 7 dB and a good thermal stability, with a central wavelength shift of less than 0.06 nm/ $^{\circ}\text{C}$. Details regarding the design, fabrication and characterization of a series of AWG devices using these cross-linkable halogenated polymers were reported in Ref. [17].

4. Conclusions

A series of cross-linkable, highly halogenated poly(arylene ether ketone/sulfone)s have been designed and synthesized by the copolymerization of 4Br-BPA, 6F-BPA and BHPFS with DFPK/DFPS. A precise control of the bromine content in the polymers could be easily accomplished by simply varying the feed ratio of 4Br-BPA to other monomers during the polymerization. This feature was utilized to produce a range of polymers with tunable refractive indices over a wide range from 1.51 to 1.57. The presence of the reactive tetrafluorostyrol units in the polymer structures facilitated thermal and photochemical cross-linking with the presence of a suitable initiator. Optical characterization of these materials indicated that they had very good transparency at 1550 nm and a linear dependency of the refractive indices on the bromine content. Consequently, multilayer waveguide devices with both the core and the cladding materials using these highly halogenated polymers were fabricated.

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