Highly Fluorinated Aromatic−Aliphatic Copolyethers

Jianfu Ding,*,† Jia Jiang,‡ Chantal Blanchetière,‡ and Claire L. Callender‡

Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6, and Communications Research Centre Canada, Ottawa, Ontario, Canada K2H 8S2

Received August 6, 2007; Revised Manuscript Received November 21, 2007

ABSTRACT: A series of novel highly fluorinated aromatic−aliphatic copolyethers have been prepared by copolycondensation reactions of decafluorodiphenylsulfone (DFPSO) with hexafluorobisphenol-A (6F-BPA) and a highly fluorinated linear or branched diol (6C_F-diol or 7$_b$$C_F$-diol) at different feed ratios of [diol]/[6F-BPA]. The reactions can be completed in 2−5 h in the presence of CsF in DMAc at room temperature to produce polymers with number average molecular weight (M_n) up to 45 000 Da. ^{1}H and ^{19}F NMR studies show that the composition of the resultant polymers agrees well with the feed ratio of the monomers in the reaction. This feature leads to a feasible tune of glass transition temperatures (T_g) and refractive indexes of the produced polymers by a simple control of the feed ratio. As the [diol]/[6F-BPA] ratio increases, the T_g of the copolymers decreases gradually from 185 to 87 °C and 94 °C, and the refractive index decreases from 1.5120(n_{TE})/1.5089(n_{TM}) to 1.4643(n_{TE})/1.4629(n_{TM}) and 1.4487(n_{TE})/1.4471(n_{TM}) for the copolymers from 6C_F-diol and 7$_b$$C_F$-diol, respectively. Meanwhile, the increase of the [diol]/[6F-BPA] ratio also effectively reduces the birefringence of the polymer films from 3.1×10^{-3} to 1.4×10^{-3} for the polymers from 6C_F-diol and to 1.6×10^{-3} for the polymers from 7$_b$$C_F$-diol. Well-developed waveguide structures with smooth ridge walls from these polymers have also been demonstrated using a cost-effective soft lithography technique.

Introduction

Polymeric materials are good candidates for photonic applications due to their excellent optical, thermal, and environmental properties and easy, cost-effective, and large scale device fabrication.[1,2] However, the high overtone absorptions of the C−H, O−H, and N−H bonds of hydrocarbon polymers can cause drastic optical loss in the optical communication wavelength regions around 1.33 and 1.55 μm. Using fluorine to replace hydrogen in polymers can theoretically reduce the intrinsic optical loss by about 5 orders of magnitude.[2] As a result, the development of fluorinated polymers for photonic applications has been the focus of significant research activities in the past decade.[2−5] Among them, fluorinated poly(arylene ether)s have demonstrated many advantages, including easy proccessability, high chemical and thermal stability, low optical loss and low birefringence. This series of polymers also demonstrated a high potential to tune the physical and optical properties through simple chemical structure modifications and copolymerization.[6−22] Although the fluorine content of this type of the polymers is higher than most other easily processable fluorinated polymers, it is still limited because of the use of non-fluorinated or partially fluorinated bisphenols for polymer preparation. Fully fluorinated bisphenols are not available and thus the fluorine content of bisphenols is always low. This limitation hampers the potential to further reduce the intrinsic optical loss at communications wavelength of this series of polymers. Recently we have developed a simple method to successfully prepare highly fluorinated poly(arylene alkylene ether)s, where highly fluorinated diols instead of bisphenols are polymerized with decafluorodiphenyl compounds.[20] The resulting polymers have higher fluorine contents than their fully aromatic analogues. However, because of the highly symmetrical chain structures and high flexibility of the fluorinated alkylene segments in the polymers, most of the synthesized materials exhibit a high tendency to crystallize. The crystalline morphology of polymer materials will increase the heterogeneity of their optical properties and lead to a significant optical loss due to light scattering and thus should be avoided in optical waveguide applications. Fortunately, the crystallization capability of these polymers can be suppressed by introducing branched diol into the polymers[20] and by copolymerizing with a bisphenol co-monomer. The latter will be discussed in this paper.

The refractive index is also a very important property of materials for photonic applications. Current optical communication networks are based on silica optical fiber and devices. In order to integrate with these devices and materials and to reduce the optical loss associated with index mismatch, polymer materials with refractive index values close to that of the silica materials (1.46) are desired.[2−5] However, only very few fluorinated polymers have refractive indices close to this region.[23] For example, the widely used fluorinated polyimides usually have refractive indexes higher than 1.50.[23−27] Fluorinated poly(arylene ether)s generally also have a value around 1.50, and this value can be tuned up easily by introducing polar groups as in poly(arylene ether ketone) and poly(arylene ether sulfone) and copolymerizing with co-monomers containing heavier atoms such as bromine.[17,18] However, it appears difficult to lower the refractive index. A possible approach is to introduce fluorinated aliphatic segments into the polymers.[8,19] Our recently developed highly fluorinated poly(arlylene alkylene ether)s display much lower refractive indices than their aromatic analogues, with values close to that of silica optical fiber. In this paper, we will report an approach to continuously tune the refractive index of the polymers by copolymerization of a decafluorodiphenyl compound with a fluorinated diol and a bisphenol at controlled feed ratios.

---

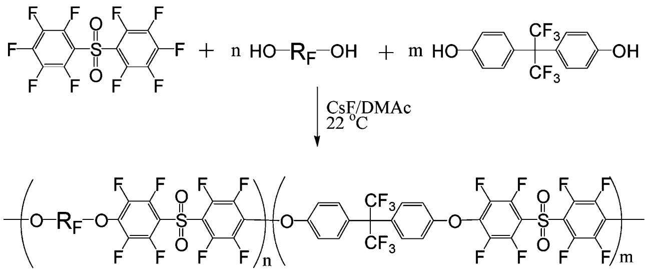
* Corresponding author. E-mail: jianfu.ding@nrc-cnrc.gc.ca. Phone: (+613) 993-4456.

† National Research Council of Canada.

‡ Communications Research Centre Canada.

10.1021/ma071766n CCC: $40.75

Scheme 1. Copolymers Prepared from Polycondensation of DFPSO with 6F-BPA and $6C_F$-Diol or 7_bC_F-Diol in the Presence of CsF in DMAc at 22 °C with the Reaction Times Listed in Table 1



R_F	Diol	Polymer
$-CH_2CF_2CF_2CF_2CF_2CH_2-$	$6C_F$	P($6C_F$-BPA)SO-n/m
$-CH_2CFCH_2-$ $CF_2CF_2CF_2CF_3$	7_bC_F	P(7_bC_F-BPA)SO-n/m

n/m = 0/100, 25/75, 50/50, 75/25, 100/0

Table 1. The Preparation and Characterization of the Polymers

polymer	*n*/*m*	time[a] (h)	M_n[b] (kDa)	PDI[b]	T_g[c] (°C)	$T_d^{5\%}$ (°C)[e]
P($6C_F$)SO	100/0	3.0	30.6	3.1	87.0[d]	412.3
P($6C_F$-BPA)SO-75/25	75/25	2.0	45.4	4.2	114.5	416.1
P($6C_F$-BPA)SO-50/50	50/50	2.5	27.8	2.9	138.0	423.2
P($6C_F$-BPA)SO-25/75	25/75	3.5	25.4	2.8	163.7	442.2
P(7_bC_F)SO	100/0	3.5	22.5	2.5	94.7	386.7
P(7_bC_F -BPA)SO-75/25	75/25	2.1	45.4	3.8	121.3	406.6
P(7_bC_F-BPA)SO-50/50	50/50	5.2	20.4	3.3	145.5	413.2
P(7_bC_F-BPA)SO-25/75	25/75	5.2	28.5	2.9	167.6	437.8
P(BPA)SO	0/100	1.5	32.3	3.3	185.2	458.0

[a] The polycondensations were conducted in DMAc in the presence of CsF at 22 °C. [b] M_n and PDI values were obtained from SEC measurement. [c] T_g was measured from the second heating scan for which the sample was freely cooled from 250 °C. [d] A broad melting peak was found in the as-prepared sample at ~172 °C. [e] $T_d^{5\%}$ was detected using TGA under the protection of nitrogen.

Results and Discussion

Polymer Preparation. Generally, all the copolymers were prepared by the copolymerization of decafluorodiphenyl sulfone (DFPSO) with hexafluorobisphenol-A (6F-BPA) and a highly fluorinated linear or branched diol (1*H*,1*H*,6*H*,6*H*-perfluoro-1,6-hexanediol, $6C_F$-diol, or 2-fluoro-2-perfluorobutyl-1,3-propanediol, 7_bC_F-diol). As shown in Scheme 1, P($6C_F$-BPA)SO-*n*/*m* and P(7_bC_F-BPA)SO-*n*/*m* were used to represent the polymers prepared from $6C_F$-diol and 7_bC_F-diol, respectively, where *n*/*m* is the feed ratio of [diol]/[6F-BPA]. The polymerizations were conducted in *N*,*N*-dimethylacetamide (DMAc) in the presence of CsF at 22 °C with reaction times listed in Table 1. In this reaction, the feed ratio of DFPSO over the sum of the bisphenol and diol was kept at 2.01/2.00 in order to produce polymers with high molecular weight, and the *n*/*m* ratio was controlled as shown in Table 1 for tuning the properties of the resultant polymers. CsF has been shown to effectively activate bisphenols,[17−22] as well as fluorinated alkylene diols for the reaction with DFPSO.[20] The copolymerizations of DFPSO with 6F-BPA and $6C_F$-diol or 7_bC_F-diol at different *n*/*m* ratios displayed similar reaction behaviors and were completed in 2−5 h to produce copolymers with number average molecular weights (M_n) up to 45 000 Da.

The chemical composition of the copolymers was elucidated from ^{1}H and ^{19}F NMR data. Only three different types of protons exist in both P($6C_F$-BPA)SO and P(7_bC_F-BPA)SO copolymers. These two series of the polymers displayed very simple ^{1}H NMR spectra with similar characteristics, showing two peaks in the aromatic region at 7.45 and 7.32 ppm and one peak in the aliphatic region at around 5.22 ppm. The two aromatic peaks are ascribed to the ortho and meta protons in the 6F-BPA units, and their chemical shifts do not change with the *n*/*m* ratios and the type of diols, while the aliphatic proton peak which is attributed to the proton in the diol units is at a slightly different position for P($6C_F$-BPA)SO (5.20 ppm) and for P(7_bC_F-BPA)SO (5.23 ppm). The integral intensity ratio of the aromatic peaks over the aliphatic peak agrees very well with the *n*/*m* ratio. This result indicates that both the diol and bisphenol are completely incorporated into the copolymers. The ^{19}F NMR of both series of copolymers display complicated patterns, but the position of the peaks do not significantly change with the *n*/*m* ratios in the different samples. The spectra of P(7_bC_F-BPA)SO copolymers are displayed in Figure 1 as an example for discussion. All the peaks of the spectra are assigned using the structure shown in the same figure. The relative peak intensities correlate well with the *n*/*m* ratios. It is interesting that the resonance of the ortho fluorine atoms of the DFPSO unit split into four peaks at −138.6, −138.9, −139.6, and −139.9 ppm due to the different combinations of two possible adjacent units (7_bC_F or 6F-BPA) at either side. Using A to represent for the 7_bC_F unit and B for the 6F-BPA unit, four possible combinations can be found for these triads with the DFPSO unit in the center: AB, BA, AA, and BB. Therefore these four peaks can be easily assigned to these different triads as indicated in Figure 1. The relative intensities of these peaks depend on the *n*/*m* ratios and the relative reactivity of 7_bC_F-diol and 6F-BPA in the copolymerization. Under the assumption that these two monomers have the same reactivity, statistically random copolymers will be obtained. In this case, the relative content of the triads of AB, BA, AA, and BB will be $(n \times m)/(n + m)$, $(m \times n)/(n + m)$, $(n \times n)/(n + m)$, and $(m \times m)/(n + m)$, respectively. In the

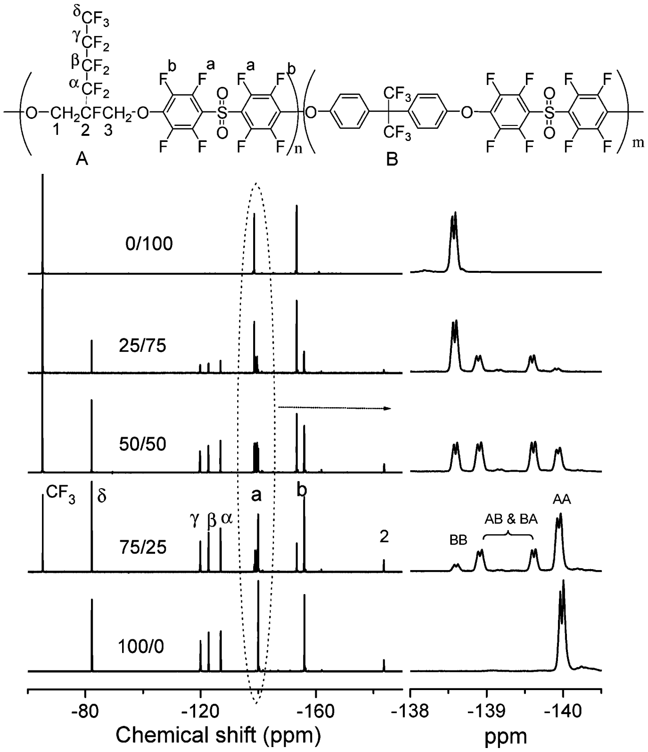


Figure 1. ^{19}F NMR spectra of P(7_bC_F-BPA)SO with different [7_bC_F]/[6F-BPA] ratios.

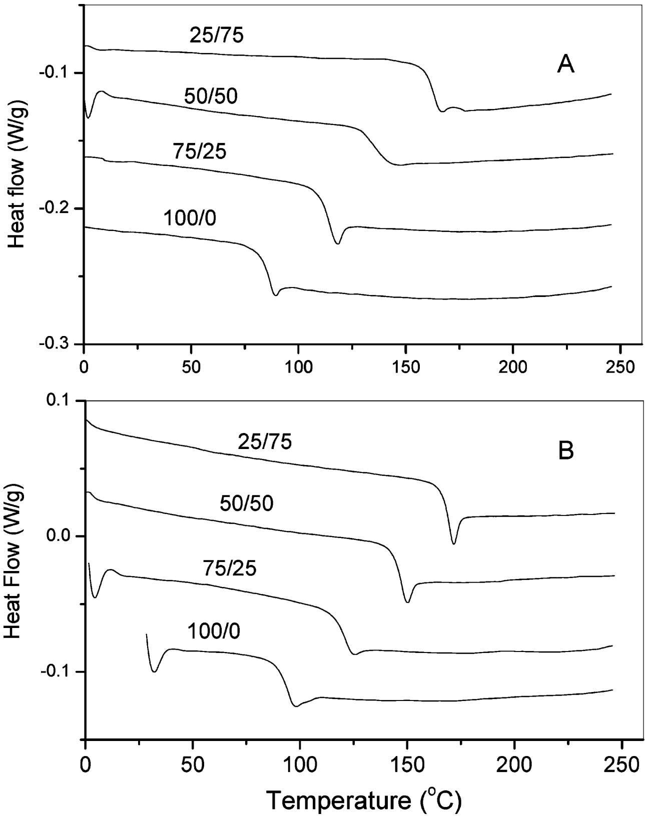


Figure 2. DSC curves of the second heating scan after the sample was freely cooled from 250 °C in the DSC cell: (A) P(6C$_F$-BPA)SO; (B) P(7$_b$C$_F$-BPA)SO.

NMR measurement, the triads AB and BA are identical and should produce only one peak for the same fluorine atom. However, the ortho fluorine atoms on either side of the sulfone group in these triads have different environments, one is close to the A unit and the other is close to the B unit and thus produce two different peaks as indicated in Figure 1. Therefore, under this circumstance, the resonance of the ortho fluorine atoms in these statistically random copolymers will produce four peaks with a relative intensities of 9/3/3/1 for 25/75, 1/1/1/1 for 50/50, and 1/3/3/9 for 75/25. The measured values of this ratio from the spectra in Figure 1 are 9.0/3.0/3.0/0.7 for 25/75, 1.0/1.0/1.0/0.9 for 50/50, and 1.0/3.0/3.0/8.8 for 75/25. Apparently, the intensity of the AA peak is slightly less than the prediction, indicating that the 7$_b$C$_F$-diol has a slightly lower reaction rate than 6F-BPA and produces a lower AA triad content in the polymers. This result agrees with the data reported in our previous work on the homopolymerization of DFPSO with 6F-BPA or 7$_b$C$_F$-diol.[19,20]

Thermal Properties. The thermal properties of these polymers have been analyzed by DSC and TGA, and the results are summarized in Table 1. The DSC data were obtained from the second heating scan as shown in Figure 2, where the sample was freely cooled from 250 °C in the DSC cell. It can be seen that all the copolymers display only a typical glass transition in the testing temperature range from 0 to 250 °C. No other transition was found either in this sample or in the as-prepared and annealed samples. This result indicates that all copolymers are completely amorphous. It should be noted that the polymer from 100% 6C$_F$-diol can crystallize and a broad melting peak is observed at 172 °C from the as-prepared and annealed samples.[20] Its crystallization rate in the solid is low, and the sample did not form any crystal when freely cooled from 250 °C in the DSC cell as indicated in Figure 2. Introducing 6F-BPA into this polymer to partially or completely replace 6C$_F$-diol suppresses the crystallization completely. All of the polymers from the branched diol 7$_b$C$_F$-diol are completely amorphous. This characteristic is very important for the materials to be used for optical waveguides. A stable and completely amorphous structure will ensure a highly homogeneous matrix with high optical transparency. Figure 3 shows that the T_g values for both series of copolymers decrease with increasing soft content in a nearly linear manner, changing from 185 to 87 °C for P(6C$_F$-BPA)SO copolymers and to 95 °C for P(7$_b$C$_F$-BPA)SO copolymers, where the soft content is defined as a weight percentage of 6C$_F$-DFPSO segments or 7$_b$C$_F$-DFPSO segments in the polymers. This result indicates that the flexibility of the polymer is significantly improved by the introduction of the fluorinated alkylene segments. This effect is beneficial to reduce the birefringence of the polymer film. Though the T_g for some of these polymers are too close to the operating temperature of many regular waveguide devices, which may lead to an unstable device performance, the use of such material as a cladding layer in the device may reduce the internal stress and therefore further reduce the birefringence of the device. TGA measurements showed that both series of polymers have a satisfactory thermal stability. The decomposition temperatures are about 400 °C.

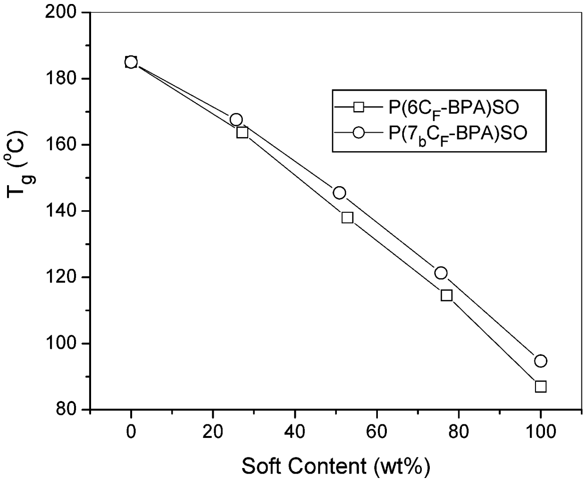


Figure 3. Composition dependence of T_g's of P(6C$_F$-BPA)SO and P(7$_b$C$_F$-BPA)SO.

Optical Properties. The refractive indices of thin films of these two series of copolymers were measured for TE and TM polarizations (designated n_{TE} and n_{TM}, respectively) by the prism coupling technique at 633 and 1537 nm. The results are shown in Figure 4. The polymer films were prepared by spin-coating 30% polymer solutions in cyclohexanone onto silicon wafers and baking under vacuum at 130 °C for 2 h. The refractive indices decrease with increasing content of aliphatic segments in the copolymers (Figure 4). A nearly linear relationship is found between the refractive index of the film and the content of soft segments. By variation of the content of soft segments from 0 to 100 wt %, the refractive index changes from 1.5120 to 1.4643 (TE polarization) and from 1.5089 to 1.4629 (TM polarization) at 1537 nm for P(6C$_F$-BPA)SO copolymers. The P(7$_b$C$_F$-BPA)SO copolymers displayed a higher sensitivity of the refractive indices to the content of the soft segments; as the n/m ratio is changed from 0/100 to 75/25, the refractive indices decrease from 1.5120 to 1.4650 (TE) and from 1.5089 to 1.4630 (TM) at 1537 nm. The extrapolation of this linear relation to 100 wt % of the soft segment results in 1.4487 for n_{TE} and 1.4471 for n_{TM}. The total refractive index change is 0.063. Such

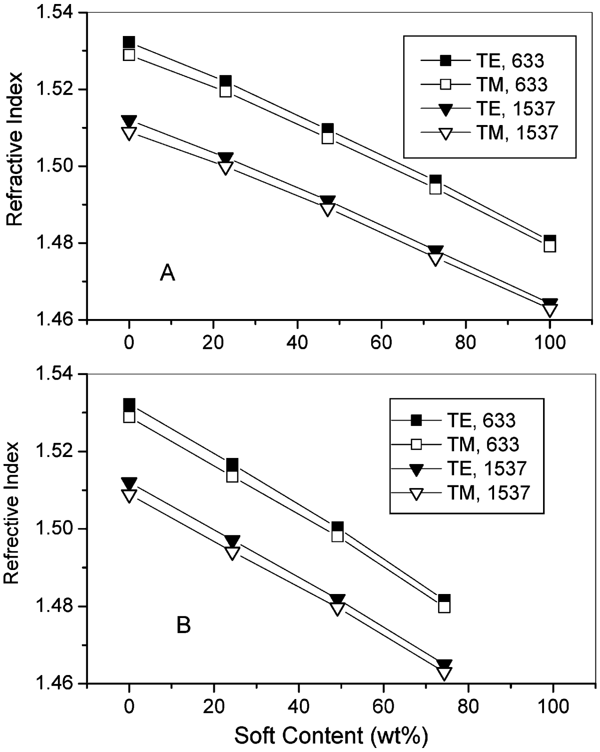


Figure 4. Composition dependence of the refractive index of (A) P(6C$_F$-BPA)SO and (B) P(7$_b$C$_F$-BPA)SO.

a wide tuning range of the refractive index at around the value of the silica optical fiber, obtained by simply controlling the alkylene diol content in the feed, provides valuable flexibility in optical waveguide device design and fabrication. In addition, as predicted, the introduction of soft alkylene units into the polymers also reduced the birefringence of the spin-coated films from 3.1×10^{-3} to 1.4×10^{-3} for P(6C$_F$-BPA)SO and to 1.6×10^{-3} for P(7$_b$C$_F$-BPA)SO.

Because of the excellent solubility and appropriate glass transition temperatures, the resultant polymers could be ideal candidates for waveguide fabrication using soft lithography.[28] It is a fast, convenient, and economic approach to the fabrication of polymeric electronic and photonic devices. Compared with the conventional photolithography/reactive ion etching and UV photo patterning processes, soft lithography requires less process steps and shortens the manufacturing time and thereby offers a tremendous cost-effective advantage. The scanning electron microscope images of the typical ridge structures from P(7$_b$C$_F$-BPA)SO-50/50 in Figure 5 indicates that well-defined waveguide structures with very smooth ridge walls are easily prepared using this technique. However, preliminary estimates of the optical loss are high, indicating some imperfections in the waveguide structures. Further optimization of the film quality, the fabrication process, and multilayer structures is underway.

Experimental Section

Materials. 1*H*,1*H*,6*H*,6*H*-perfluoro-1,6-hexanediol (6C$_F$-diol) and 2-fluoro-2-perfluorobutyl-1,3-propanediol (7$_b$C$_F$-diol) were purchased from Oakwood Products Inc. and used as received. Decafluorodiphenyl sulfone (DFPSO) was prepared according to a reported method.[13] The other chemicals were purchased from Sigma-Aldrich and used as received.

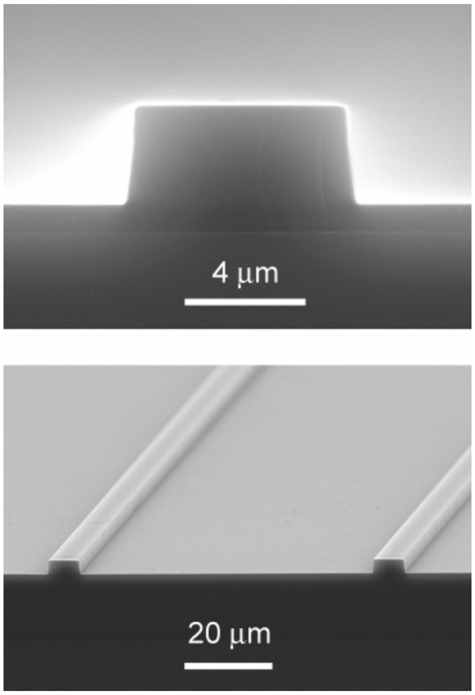


Figure 5. SEM photograph of the waveguides based on P(7$_b$C$_F$-BPA)-SO-50/50 fabricated with the soft-lithography method.

Characterizations. Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity Inova spectrometer at a resonance frequency of 400 MHz for ^{1}H NMR and 376 MHz for ^{19}F NMR in acetone-d_6. The chemical shifts relative to tetramethylsilane for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR are reported on the ppm scale. The molecular weights of the polymers were determined by size exclusion chromatography (SEC) using a Viscotek SEC system, which consists of a Viscotek VE1122 HPLC pump coupled with a Viscotek TDA triple detector and a Viscotek 2501 UV detector operated at 260 nm. A set of ViscoGEL columns (G4000H and G5000H) was used and calibrated using a set of polystyrene standards in THF. 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.

Optical Properties. Polymer films for refractive index measurements were prepared from 30% (w/w) polymer solutions in cyclohexanone. The polymer solution was 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 (2 h) to remove the residual solvent. The refractive indices of the polymer films were determined at 633 and 1537 nm using the prism coupling technique with an uncertainty of ±0.0004. A soft lithography techniques has been used to prepare waveguide ridge structures using the following procedure:[28] A negative poly(dimethylsiloxane) (PDMS) mold is made from the replication of a silica “master” template, which was formed using standard photolithography and reactive etching processes. Then, a polymer solution with about 30 wt % solid content in cyclohexanone was cast on a silicon substrate and stamped by the PDMS mold. The samples were baked with the mold in a vacuum oven under a slight flow of nitrogen at 150 °C for about 4 h to completely evaporate the residual solvent.

Synthesis of P(6C$_F$-BPA)SO-75/25 from Copolymerization of DFPSO with 6C$_F$-Diol and 6F-BPA in the Presence of CsF. To a solution of DFPSO (0.8008 g, 2.01 mmol), 6C$_F$-diol (0.3934 g, 1.50 mmol), and 6F-BPA (0.1681 g, 0.50 mmol) in anhydrous DMAc (6 mL) was added CsF (0.911 g, 6.0 mmol). The mixture was stirred at room temperature for 2.1 h. After filtration to remove inorganic salt, the polymer solution was added dropwise into HCl/methanol (0.5 mL/200 mL) with stirring. The resulting fibrous white polymer was collected by filtration, washed thoroughly with water and methanol, and dried at room temperature under vacuum for 12 h.

The other polymers from both $6C_F$-diol and 7_bC_F-diol with the corresponding feed ratio of diol/bisphenol as indicated in the sample name were prepared using the same procedure outlined above with the reaction times listed in Table 1. Meanwhile, the feed ratio of DFPSO to the sum of the diol and bisphenol for all the polymers was 2.01/2.00. Their characterizations are as follows.

P($6C_F$)SO. Yield, 88%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 5.20 (t, $J = 13.2$ Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ −121.88 (4F, m), −124.35 (4F, m), −139.89 (4F, d, $J = 16.0$ Hz), −155.81 (4F, d, $J = 16.8$ Hz). T_g: 87 °C. T_m: 168.3 and 177.7 °C. M_n: 30 600 Da. M_w/M_n: 3.1.

P($6C_F$-BPA)SO-75/25. Yield, 88%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx1, d, $J = 8.8$ Hz), 7.32 (4Hx1, d, $J = 8.8$ Hz), 5.20 (4Hx3, t, $J = 13.2$ Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.16 (6Fx1, s), −121.87 (4Fx3, s), −124.35 (4Fx3, s), −138.59 (1Fx1, d, $J = 17.8$ Hz), −138.86 (1Fx3, d, $J = 18.0$ Hz), −139.61 (1Fx3, d, $J = 18.0$ Hz), −139.90 (1Fx9, d, $J = 17.6$ Hz), −153.37 (4Fx1, m), −155.80 (4Fx3, m). T_g: 114.5 °C. M_n: 45 400 Da. M_w/M_n: 4.2.

P($6C_F$-BPA)SO-50/50. Yield, 81%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx1, d, $J = 8.8$ Hz), 7.32 (4Hx1, d, $J = 8.8$ Hz), 5.20 (4Hx3, t, $J = 13.2$ Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.16 (6Fx1, s), −121.87 (4Fx1, s), −124.34 (4Fx1, s), −138.59 (1Fx1, d, $J = 16.0$ Hz), −138.85 (1Fx1, d, $J = 17.8$ Hz), −139.60 (1Fx1, d, $J = 16.8$ Hz), −139.88 (1Fx1, d, $J = 17.2$ Hz), −153.33 (4Fx1, m), −155.79 (4Fx1, m). T_g: 138.0 °C. M_n: 27 800 Da. M_w/M_n: 2.9.

P($6C_F$-BPA)SO-25/75. Yield, 83%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx1, d, $J = 8.8$ Hz), 7.32 (4Hx1, d, $J = 8.8$ Hz), 5.20 (4Hx3, t, $J = 13.2$ Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.16 (6Fx3, s), −121.86 (4Fx1, s), −124.34 (4Fx1, s), −138.58 (1Fx9, d, $J = 16.0$ Hz), −138.85 (1Fx3, d, $J = 16.2$ Hz), −139.60 (1Fx3, d, $J = 16.0$ Hz), −139.88 (1Fx1, d, $J = 15.8$ Hz), −153.30 (4Fx1, m), −155.78 (4Fx1, m). T_g: 163.7 °C. M_n: 25 400 Da. M_w/M_n: 2.8.

P(7_bC_F)SO. Yield, 85%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 5.22 (m). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −82.24 (3F, s), −119.93 (2F, s), −122.79 (2F, s), −126.97 (2F, s), −139.98 (4F, d, $J = 16.8$ Hz), −156.00 (4F, d, $J = 18.4$ Hz), −183.60 (1F, s). T_g: 94.7 °C. M_n: 22 500 Da. M_w/M_n: 2.5.

P(7_bC_F-BPA)SO-75/25. Yield, 90%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx1, $J = 8.0$ Hz), 7.32 (4Hx1, m), 5.22 (4Hx3, m). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.17 (6Fx1, s), −82.19 (3Fx3, s), −119.86 (2Fx3, s), −122.74 (2Fx3, s), −126.91 (1Fx3, s), −138.60 (2Fx1, d, $J = 16.6$ Hz), −138.91 (2Fx3, d, $J = 17.2$ Hz), −139.61 (2Fx3, d, $J = 18.0$ Hz), −139.95 (2Fx9, d, $J = 17.6$ Hz), −153.34 (4Fx1, m), −155.96 (4Fx3, m), −183.58 (1Fx3, m). T_g: 121.3 °C. M_n: 45 400 Da. M_w/M_n: 3.8.

P(7_bC_F-BPA)SO-50/50. Yield, 81%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx1, d, $J = 8.0$ Hz), 7.33 (2Hx1, d, $J = 8.0$ Hz), 7.32 (2Hx1, d, $J = 8.0$ Hz), 5.23 (4Hx1, m). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.16 (6Fx1, s), −82.17 (3Fx1, s), −119.84 (2Fx1, s), −122.73 (2Fx1, s), −126.90 (1Fx1, s), −138.59 (2Fx1, d, $J = 16.6$ Hz), −138.90 (2Fx1, d, $J = 16.8$ Hz), −139.60 (2Fx1, d, $J = 18.4$ Hz), −139.93 (2Fx1, d, $J = 18.0$ Hz), −153.31 (4Fx1, m), −155.92 (4Fx1, m), −183.56 (1Fx1, m). T_g: 145.5 °C. M_n: 20 400 Da. M_w/M_n: 3.3.

P(7_bC_F-BPA)SO-25/75. Yield, 85%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4Hx3, d, $J = 8.0$ Hz), 7.33 (4Hx3, m), 5.24 (4Hx1, m). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.15 (6Fx3, s), −82.16 (3Fx1, s), −119.81 (2Fx1, s), −122.72 (2Fx1, s), −126.88 (1Fx1, s), −138.57 (2Fx9, d, $J = 16.4$ Hz), −138.88 (2Fx3, d, $J = 17.3$ Hz), −139.58 (2Fx3, d, $J = 18.0$ Hz), −139.90 (2Fx1, m), −153.29 (4Fx3, m), −155.88 (4Fx1, m), −183.55 (1Fx1, m). T_g: 167.6 °C. M_n: 28 500 Da. M_w/M_n: 2.9.

P(BPA)SO. Yield, 89%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 7.45 (4H, d, $J = 8.4$ Hz), 7.32 (4H, d, $J = 8.0$ Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ (ppm) −65.15 (6F, s), −138.55 (4F, d, $J = 16.4$ Hz), −153.27 (4Fx1, m). T_g: 185.2 °C. M_n: 32 300 Da. M_w/M_n: 3.3.

Conclusion

We have prepared novel highly fluorinated aromatic−aliphatic copolyethers by copolymerizations of DFPSO with 6F-BPA and $6C_F$-diol or 7_bC_F-diol with different feed ratios of [diol]/[6F-BPA]. The reactions were completed in 2−5 h in the presence of CsF in DMAc at room temperature to produce polymers with M_n up to 45 000 Da. A ^{19}F NMR study shows that the copolymers have slightly lower 7_bC_F −DFPSO−7_bC_F triad content than that predicted for statistically random copolymers, indicating a slightly lower reactivity of the diol than that of 6F-BPA. The introduction of highly fluorinated alkylene units into the polymers effectively reduces T_g from 185.2 to 87.0 °C and the refractive index from 1.5120(n_{TE})/1.5089(n_{TM}) to 1.4643(n_{TE})/1.4629(n_{TM}) for P($6C_F$-BPA)SO copolymers. The branched alkylene (7_bC_F) units in P(7_bC_F-BPA)SO copolymers produced slightly higher T_g values than their linear analogues and a more efficient reduction of refractive indices to 1.4487(n_{TE})/1.4471(n_{TM}). Meanwhile, the resultant polymers also show a reduced birefringence with the increase of the alkylene content. The values decreased from 3.1×10^{-3} to 1.4×10^{-3} for P($6C_F$-BPA)SO copolymers and from 3.1×10^{-3} to 1.6×10^{-3} for P(7_bC_F-BPA)SO copolymers. The potential for patterning these polymers into ridge structures with dimensions on the order of a few micrometers for photonic applications has been demonstrated using soft lithography techniques.

Acknowledgment. This manuscript is NRCC publication number 49128. Jianfu Ding thanks Jacques Roovers for fruitful discussions and his suggestions.

References and Notes

(1) Eldada, L. *Opt. Eng.* **2001**, *40*, 1165−1178.
(2) Ma, H.; Jen, A. K.-J.; Dalton, L. R. *Adv. Mater.* **2002**, *14*, 1339−1365.
(3) Blythe, A. R.; Vinson, J. R. *Polym. Adv. Technol.* **2000**, *11*, 601−611.
(4) Zhou, M. *Opt. Eng.* **2002**, *41*, 1631−1643.
(5) Pitois, C.; Wiesmann, D.; Lindgren, M.; Hult, A. *Adv. Mater.* **2001**, *13*, 1483−1487.
(6) Mercer, F.; Goodman, T.; Wojtowicz, J.; Duff, D. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1767−1770.
(7) Goodwin, A. A.; Mercer, F. W.; McKenzie, M. T. *Macromolecules* **1997**, *30*, 2767−2774.
(8) Miyatake, K.; Oyaizu, K.; Tsuchida, E.; Hay, A. S. *Macromolecules* **2001**, *34*, 2065−2071.
(9) Kimura, K.; Tabuchi, Y.; Yamashita, Y.; Cassidy, P. E.; Fitch, J. W., III; Okumura, Y. *Polym. Adv. Technol.* **2000**, *11*, 757−765.
(10) Lee, H.-J.; Lee, E.-M.; Lee, M.-H.; Oh, M.-C.; Ahn, J.-H.; Han, S. G.; Kim, H. G. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2881−2887.
(11) Lee, H.-J.; Lee, M.-H.; Oh, M.-C.; Ahn, J.-H.; Han, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2355−2361.
(12) Kim, J.-P.; Kang, J.-W.; Kim, J.-J.; Lee, J.-S. *Polymer* **2003**, *44*, 4189−4195.
(13) Liu, F.; Ding, J.; Li, M.; Day, M.; Robertson, G.; Zhou, M. *Macromol. Rapid Commun.* **2002**, *23*, 844−848.
(14) Ding, J.; Day, M. *Macromolecules* **2006**, *39*, 6054−6062.
(15) Ding, J.; Day, M.; Robertson, G. P.; Roovers, J. *Macromol. Chem. Phys.* **2004**, *205*, 1070−1079.
(16) Ding, J.; Liu, F.; Li, M.; Day, M.; Zhou, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4205−4216.
(17) Qi, Y.; Ding, J.; Day, M.; Jiang, J.; Callender, C. L. *Polymer* **2006**, *47*, 8263−8371.
(18) Qi, Y.; Ding, J.; Day, M.; Jiang, J.; Callender, C. L. *Chem. Mater.* **2005**, *17*, 676−682.
(19) Ding, J.; Qi, Y.; Day, M.; Jiang, J.; Callender, C. L. *Macromol. Chem. Phys.* **2005**, *206*, 2396−2400.
(20) Ding, J.; Du, X.; Day, M.; Jiang, J.; Callender, C. L.; Stupak, J. *Macromolecules* **2007**, *40*, 3145−3153.
(21) Imai, Y.; Yamanaka, K.; Ishikawa, H.; Kakimoto, M. *Macromol. Chem. Phys.* **1999**, *200*, 95−99.

(22) Imai, Y.; Ishikawa, H.; Park, K.-H.; Kakimoto, M.-A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2055−2061.

(23) Jöhnck, M.; Müller, L.; Neyer, A.; Hofstraat, J. W. *Eur. Polym. J.* **2000**, *36*, 1251−1264.

(24) Han, K.; Jang, W.-H.; Rhee, T. H. *J. Appl. Polym. Sci.* **2000**, *77*, 2172−2177.

(25) Jang, W.; Shin, D.; Choi, S.; Park, S.; Han, H. *Polymer* **2007**, *48*, 2130−2143.

(26) Kobayashi, J.; Matsuura, T.; Sasaki S.; Maruno, T. *J. Lightwave Technol.* **1998**, *16*, 610−614.

(27) Takasaki, T.; Kuwana, Y.; Takahashi, T.; Hayashida, S. *J. Polym. Sci., Part A: Polym. Chem*. **2000**, *38*, 4832−4838.

(28) Xia, Y. N.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153−184.

MA071766N