Fluorinated Poly(arylene ether sulfide) for Polymeric Optical Waveguide Devices

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ABSTRACT: Fluorinated poly(arylene ether sulfide)s containing an ethynyl group (E-FPAESI) were synthesized by nucleophilic aromatic substitution from 4,4′-(hexafluoroisopropylidene)diphenol (6FBPA) and an excess of pentafluorophenyl sulfide, followed by reaction with 3-ethynylphenol. The molecular weights (M_n's) and polydispersities (M_w/M_n's) of the E-FPAESI determined by GPC with polystyrene standard were in the range 14 200−25 200 and 2.23−2.47, respectively. The polymer films were fabricated by spin-coating and cross-linked by thermal curing. The cured films had good chemical resistance for common solvents such as acetone, tetrahydrofuran (THF), methylene chloride, chloroform, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The glass transition temperature of E-FPAESI was changed from 120 to 160 °C after curing and showed high thermal stability up to 489 °C. At 1.55 μm wavelength, the refractive indices and birefringences of the films were in the range 1.5200−1.5515 and 0.0034−0.0044, respectively, depending on feed ratio of 6FBPA and 4,4′-(trifluoromethylphenylisopropylidene)diphenol (3FBPA). The optical loss for E-FPAESI was measured to be less than 0.40 dB/cm.

Introduction

Fluorine-containing polymers are of considerable interest for optical and electronic applications in recent years[1−3] because of their thermal and chemical stability, easy processability, low dielectric constant, refractive index, optical loss, and moisture absorption.[4−6] It was reported that transmission losses in polymers are caused from the vibration absorption of the C−H bond. Many researchers could minimize the loss at 1.3 and 1.55 μm by substituting hydrogen with heavy atoms such as fluorine, deuterium, and chlorine.[7,8] Also, thermal and chemical stability of fluorinated polymers were improved by the introduction of cross-linkable groups at the chain ends.[3]

Many kinds of polymers have been developed for optical waveguides.[1−3,9−16] Representative materials for passive waveguides are fluorinated poly(arylene ether)s[3] and aromatic polyimides.[2] Fluorinated polyimides are suitable candidates for real device application due to their excellent thermal and mechanical properties. But polyimides due to their stiff backbone need improvements to lower the birefringence.[8] Fluorinated poly(arylene ether)s are more accessible than polyimides. Because of the flexibilizing ether group in the polymer backbone, poly(arylene ether)s are more easily processed than polyimides. In addition, they have good thermal stability and mechanical properties similar to those of polyimides due to the perfluorophenylene moiety.[3,4,17] Aromatic polysulfides are one of high-performance polymers with the characteristics of good thermooxidative stability, high glass transition temperatures, and excellent mechanical stability. Especially, poly(phenylene sulfide) is an important commercial high-performance polysulfide with excellent mechanical properties, fire resistance, low moisture absorption, and good affinity for inorganic fillers. Because of these excellent properties, poly(phenylene sulfide) has been extensively studied.[18,19]

This study focuses on the synthesis of fluorinated poly(arylene ether sulfide) (FPAESI) with a goal of achieving optical clarity at the telecommunication wavelength region of 1.3 and 1.55 μm, sufficient thermal stability, and a chemical resistance to withstand typical fabrication processing and operation conditions. To satisfying the above demands, fluorinated monomers were used. A cross-linked polymer system was employed to increase thermal stability and chemical resistance.

Experimental Section

Materials. Pentafluorophenyl sulfide, 6FBPA, 4-bromophenol, phenylacetylene, potassium carbonate, *tert*-butyldimethylsilyl chloride, imidazole, triphenylphosphine, bis(triphenylphosphine)palladium(II) chloride ($PdCl_2(PPh_3)_2$), and copper(I) iodide (CuI) were purchased from Aldrich Chemical Co. and used without further purification. 3FBPA was kindly donated by the Virginia Polytechnic Institute. *N*,*N*-Dimethylacetamide (DMAc) was obtained from Oriental Chemical Industries (Korea) and purified by vacuum distillation from sodium hydride.

Characterization. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a JEOL JNM-LA 300 WB FT-NMR in $CDCl_3$. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra were referenced to tetramethysilane (TMS) at 0 ppm, deuterated chloroform at 77.0 ppm, and fluorinated chloroform at 0 ppm, respectively. FT-IR spectroscopy was performed with a Perkin-Elmer IR 2000 series. The molecular weights and molecular weight distributions were determined by size exclusion chromatography (Waters model 515) and calculated using polystyrene as standard. Tetrahydrofuran was used as the mobile phase. The thermal properties of resulting polymers were determined with a TA Instrument 2100 series. Thermal degradation temperatures were measured in the range 40−700 °C at a heating rate of 10 °C/min. Glass transition temperatures

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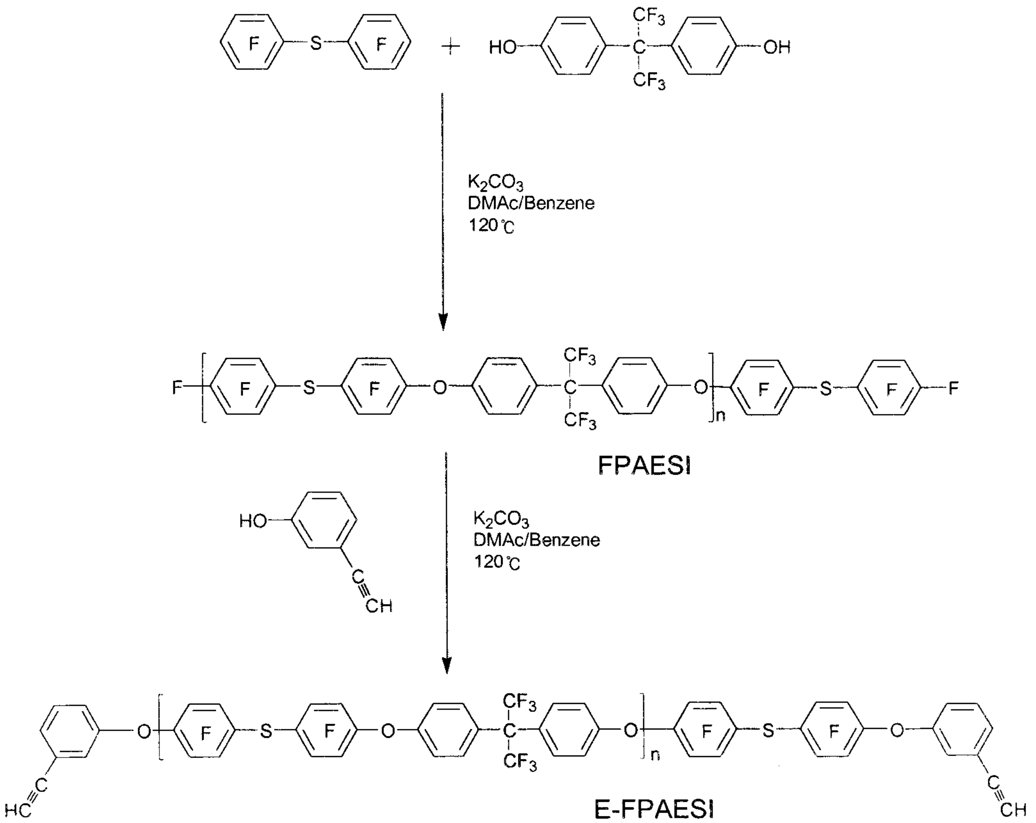
Scheme 1. Synthesis of FPAESI and E-FPAESI



(T_g) of polymers were measured in the range 40−350 °C at a heating rate of 5 °C/min. To study the cross-linking behavior of ethynyl-terminated polymers, differential scanning calorimeter (DSC) measurements were carried out in the range 40−350 °C. The thickness of the cast films was measured by a depth profiler (α-Step 500). The refractive indices were measured by using the prism-coupling method.[20]

Synthesis of 1-Bromo-3-(*tert*-butyldimethylsiloxy)benzene. 3-Bromophenol (5.00 g, 280 mmol) was added dropwise to a DMF (23.61 g, 299 mmol) solution of *tert*-butyldimethylsilyl chloride and imidazole under a nitrogen atmosphere. The solution was stirred for 24 h, and then water (300 mL) was added to the reaction mixture. The mixture was extracted three times with diethyl ether. Solvent was removed by rotary evaporator after drying the solution over anhydrous $MgSO_4$. The crude product was purified by vacuum distillation with 90% yield [bp = 90 °C/2 mmHg; ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 6H), 0.97 (s, 9H), 6.76 (m, 1H), 7.00 (m, 1H), 7.08 (m, 2H)].

3-Ethynylphenol. (Trimethylsilyl)acetylene (22.78 g, 223 mmol) was added into the reaction flask containing 1-bromo-3-(*tert*-butyldimethylsiloxy)benzene (40.00 g, 186 mmol) and triphenylphosphine (2.45 g, 9.35 mmol) in DMAc under a steady flow of nitrogen. Bis(triphenylphosphine)palladium(II) chloride (1.30 g, 1.85 mmol) and triethylamine (140 mL) were added. The reaction mixture was heated to 60 °C, and then copper(II) iodide (0.44 g, 2.22 mmol) was added with 150 mL of triethylamine. The reaction mixture was heated to 80 °C and maintained for 6 h with stirring. After cooling to room temperature, the reaction mixture was filtered to remove inorganic salts. The concentrated product was poured into acidic water and extracted with methylene chloride. The organic layer was dried over anhydrous $MgSO_4$, and then solvents were removed by the rotary evaporator. 1-(Tert-butyldimethysiloxy)-3-((trimethylsilyl)ethynyl)benzene was obtained by vacuum distillation with 74% yield [bp = 110 °C/5 mmHg; ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 6H), 0.25 (s, 9H), 0.98 (s, 9H), 6.80 (m, 1H), 6.94 (s, 1H), 7.11 (m, 2H)]. Tetrabutylammonium fluoride (45.0 mL, 1.0 M solution in THF, 45.12 mmol) was added dropwise to the solution of 1-(tertbutyldimethysiloxy)-3-((trimethylsilyl)ethynyl)benzene in 15 mL of THF. After being stirred for 4 h, the solution was poured into water. The organic layer was extracted with ether and dried over anhydrous $MgSO_4$. After removal of the solvent, the mixture was distilled under vacuum to provide 3-ethynylphenol with 60% yield [bp = 55 °C/2 mmHg; ^{1}H NMR ($CDCl_3$): δ 3.02 (s, 1H), 4.95 (bs, OH), 6.83 (m, 1H), 6.94 (m, 1H), 7.03 (m, 1H), 7.12 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 77.3, 83.2 (ethynyl), 116.3, 116.7, 123.3, 124.9, 129.7, 155. 1 (phenyl)].[3]

Synthesis of FPAESI and E-FPAESI. FPAESI and E-FPAESI were synthesized via step growth polymerization of 6FBPA with pentafluorophenyl sulfide as shown in Scheme 1. 6FBPA (1.00 g, 3.0 mmol) and pentalfluorophenyl sulfide (1.16 g, 1.12 equiv) were dissolved in DMAc (10 mL) in a 50 mL two-neck flask equipped with a magnetic stirrer, a nitrogen inlet, and Dean−Stark trap. The reaction mixture was vigorously stirred. To the clear reaction mixture, K_2CO_3 (0.49 g, 1.50 equiv) was added followed by benzene (10 mL). The reaction bath was heated to 120 °C, and this temperature was maintained for 2 h to ensure complete dehydration. Benzene gets refluxed into the Dean−Stark trap. After removing benzene, the reaction mixture was stirred at this temperature for a further period 2 h. To attach an ethynyl group at the end of polymer, 3-ethynylphenol (0.12 g, 4.00 equiv) and benzene (10 mL) were added to the reaction mixture, and then reaction was continued for 2 h. The reaction mixture was cooled and then precipitated into 400 mL of methanol/water (1:1 solution). The filtrate was dissolved in THF and reprecipitated into methanol. The precipitated polymer was filtered and washed with methanol. The white solid was dried under vacuum (60 °C) for 3 days. The yield of polymer was above 90%. FPAESI; ^{1}H NMR ($CDCl_3$): δ 6.98 (b, 1H), 7.36 (b, 1H); ^{19}F NMR ($CDCl_3$): δ −63.48 (b, 3F), −131.44 (b, 2F), −151.20 (b, 2F); ^{13}C NMR ($CDCl_3$): δ 63.8, 107.4, 116.5, 118.3, 122.2, 125.9, 129.7, 130.9, 133.1, 134. 7, 140.0, 143.4, 145.9, 149.3, 157.1; E-FPAESI; ^{1}H NMR ($CDCl_3$): δ 3.02 (ethynyl H), 6.98, 7.34; ^{19}F NMR ($CDCl_3$): δ −63.43 (b, 3F), −131.44 (b, 2F), −151.20 (b, 2F); ^{13}C NMR ($CDCl_3$): δ 63.7 [$-\mathbf{C}(CF_3)_2-$], 78.2, 82.3 (C of ethynyl), 115.8, 128.1, 131.5, 156.7 (phenyl of 6FBPA), 122.1, 125.9, 128.8 ($-\mathbf{C}F_3$), 107.3, 134.7, 140.0, 143.4, 145.6, 149.3 (phenyl of pentafluorophenyl sulfide).

Preparation of Copoly(arylene ether sulfide)s. The copolymers were prepared from the two bisphenols, 6FBPA and 3FBPA, with pentafluorophenyl sulfide. The synthetic procedure of copoly(arylene ether sulfide)s was done by the same method described as above. Copoly(arylene ether sulfide); ^{1}H NMR ($CDCl_3$): δ 3.08 (ethynyl H), 6.92, 7.11, 7.34; ^{19}F NMR ($CDCl_3$): δ −56.4 (b, 3F), −61.7 (b, 3F), −130.1 (b, 2F), −149.6 (b, 2F); ^{13}C NMR ($CDCl_3$): δ 63.7 [$-C(CF_3)_2-$ and $-C(CF_3)$-(C_6H_6)−], 78.2, 82.3 (C of ethynyl), 115.8, 128.1, 131.5, 156.7 (phenyl of 6FBPA), 122.1, 125.9, 128.8 ($-CF_3$), 107.3, 134.7, 140.0, 143.4, 145.6, 149.3 (phenyl of pentafluorophenyl sulfide).

Preparation of Polymer Films and Thermal Curing. E-FPAESI was dissolved in 1,1,2,2-tetrachloroethane at concentrations of 10−30 wt %. The solutions were filtered with a syringe through a 0.2 μm Teflon membrane filter. The filtered light yellow solutions were spin-coated on silicon wafer substrates at a spin rate of 1000 rpm for 2 min. After coating, the films were baked at 180 °C for 1 h on a hot plate. Adjusting concentration of polymer solution controlled the film thickness. The thickness of the obtained films varied from 0.7 to 6.8 μm. The prepared polymer films were cured at 270 °C for 2 h on a hot plate to prepare insoluble films.

Measurement of Propagation Loss. To fabricate single-mode optical waveguides with the 6.8 μm thickness, E-FPAESI film was spin-coated onto 15 μm thick SiO_2 on Si substrate and baked at 180 °C for 1 h and followed by 270 °C for 2 h. On the EFPAESI layer, 100 nm thick silicon nitride masks were deposited by plasma enhanced chemical vapor deposition (PECVD) using $SiCl_4$ and N_2 at 150 °C. To define the waveguide patterns on the silicon nitride layer, an AZ5214 photoresist was spin-coated onto the silicon nitride layer and patterned using conventional photolithography. The silicon nitride mask was patterned by reactive ion etching (RIE) using CF_4 gas with the developed photoresist as an etch mask, and the pattern was transferred to the core lay to form ridge waveguide (5.2 μm deep and 7.0 μm wide) by O_2 RIE. As the upper cladding layer, a type of fluorinated polymer, 14 μm thick perfluorocyclobutane (PFCB, n_{TE} = 1.487), was spin-coated and baked at 250 °C for 1 h.

Loss measurements were performed using a laser diode with the 1.55 μm wavelength. The light was launched into the waveguides by the end-fire coupling to characterize the optical loss. The near-field pattern from straight waveguide has Gaussian intensity distribution, indicating that the optical waveguide operates in the single mode. Propagation loss of the straight waveguides was measured by the cut-back method.[21]

Results and Discussion

FPAESI. The effect of reaction temperature on the molecular weights of FPAESI was examined at 120 and 140 °C for 4 h reaction. At 140 °C of reaction temperature, the reacting solution gelated very quickly after removing benzene in azotropic solvent. But side reactions such as gelation and decreasing of molecular weight were not showed at 120 °C of reaction temperature. The effect of reaction time on the molecular weights of FPAESI was also examined varying reaction time from 2 to 6.5 h, keeping the reaction conditions such as monomer molar ratio, activation time of hydroxyl group of 6FBPA, and reaction temperature constant. The polymerization is very fast and essentially completes after 2 h at 120 °C. This result indicated that the fluorine in the para position in pentafluorophenyl sulfide is very reactive with activated 6FBPA. The molecular weight of FPAESI remained almost unchanged up to 6.5 h.

The molecular structure of FPAESI was characterized by NMR in $CDCl_3$. All peaks shifted downfield in ^{1}H NMR spectra following polymerization, due to replacement of hydrogen atoms by the perfluorophenylene group. Furthermore, all the peaks in the polymer spectrum are broader than those of the monomer. The ^{19}F NMR spectrum for FPAESI is dominated by peaks centered at −63.48, −131.44, and −151.20 ppm corresponding to the CF_3, ortho fluorine, and meta fluorine atoms, respectively. The fluorine peak related with the para position almost disappeared. In ^{13}C NMR, the para carbon peak shifted from 141.1 and 144.1 to 134.7 ppm, and the doublet was replaced by a singlet due to the coupling with fluorine atom. FPEASI was soluble in common solvents such as acetone, tetrahydrofuran, DMF, and DMSO. It means that the FPAESI was synthesized without gelation.

Table 1. Synthetic Data of FPAESI

	feed ratio[a]	M_n calcd	M_n obsd	M_w/M_n	yield (%)	T_g (°C)
FPAESI-1	0.9043	7 000	10 200	1.99	98	97
FPAESI-2	0.9322	10 000	14 300	2.30	98	124
FPAESI-3	0.9543	15 000	21 600	2.14	95	140
FPAESI-4	0.9655	20 000	25 400	2.45	88	157

[a] The feed mole ratio of 6FBPA/pentafluorophenyl sulfide (mol/mol).

Table 2. Synthetic Data of E-FPAESI

	feed ratio[a]	M_n calcd	M_n obsd	M_w/M_n	yield (%)	refractive index (TE/TM)
E-FPAESI-1	0.9322	10 164	14 200	2.23	97	1.5220/1.5180
E-FPAESI-2	0.9543	15 164	18 100	2.65	95	1.5211/1.5170
E-FPAESI-3	0.9723	25 164	25 200	2.47	93	1.5190/1.5145

[a] The feed mole ratio of 6FBPA/pentafluorophenyl sulfide (mol/mol).

In the case of condensation polymerization, the molecular weight of polymer can be controlled by the monomer feed ratio. FPAESIs were synthesized from different monomer feed ratios as shown in Table 1. It was found that molecular weights of FPAESI correspond well with the calculated molecular weights. The number-average molecular weights (M_n's) and polydispersities (M_w/M_n's) of the resulting polymers were in the range 10 200−25 400 and 1.99−2.45, respectively. The molecular weights of the resulting polymers could be successfully controlled by the monomer feed ratio imbalance.

E-FPAESI. For the fabrication of waveguide device, a cross-linked polymer system is needed because polymer film gets dissolved in multicoated thin-film process. To achieve the thermal and chemical resistance of FPAESI, cross-linkable 3-ethynyl group was chosen at the polymer chain ends.

The molecular structure of ethynyl-terminated FPAESI was characterized by ^{1}H NMR and ^{13}C NMR in $CDCl_3$. ^{1}H NMR spectra of E-FPAESI showed two aromatic peaks at 6.9 to 7.4 ppm due to the 6FBPA moiety. Subpeaks at this region and 3.02 ppm were due to the ethynyl moiety, and all the carbon peaks of FPAESI could be assigned. Particularly, the terminal ethynyl carbon peaks were registered at 78.2 and 83.3 ppm. Figure 1 shows the FT-IR spectra of FPAESI, E-FPAESI, and cured E-FPAESI. The acetylenic C−H peak at 3308 cm^{-1} appeared after 3-ethynylphenol was attached to FPAESI. This peak completely disappeared after curing at 270 °C for 2 h. However, the absorption bands of the film relating to benzene ring, sulfide, ether, and trifluoromethyl group were not changed during the curing process.

The number-average molecular weights (M_n's) and polydispersities (M_w/M_n's) of E-FPAESI are shown in

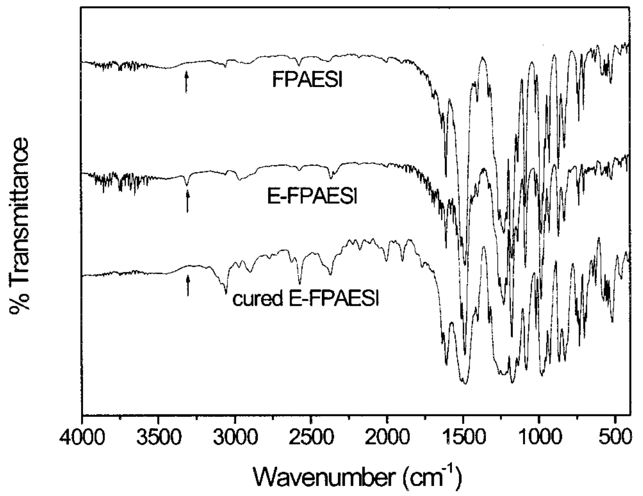


Figure 1. FT-IR spectra of FPAESI, E-FPAESI, and cured E-FPAESI.

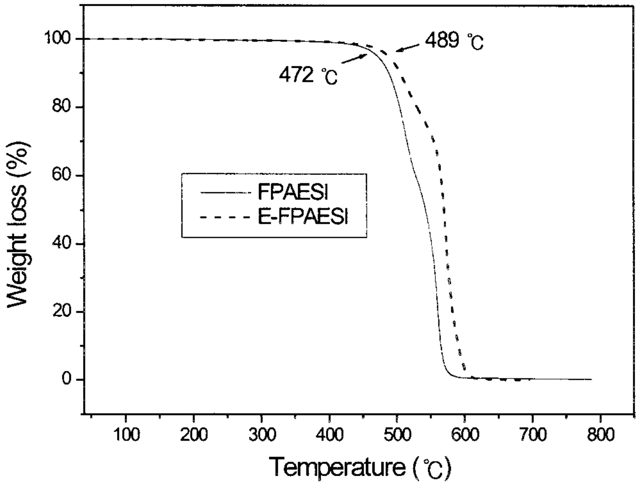


Figure 2. Thermograms of the fluorinated FPAESI (M_n: 14K) and E-FPAESI (M_n: 14K).

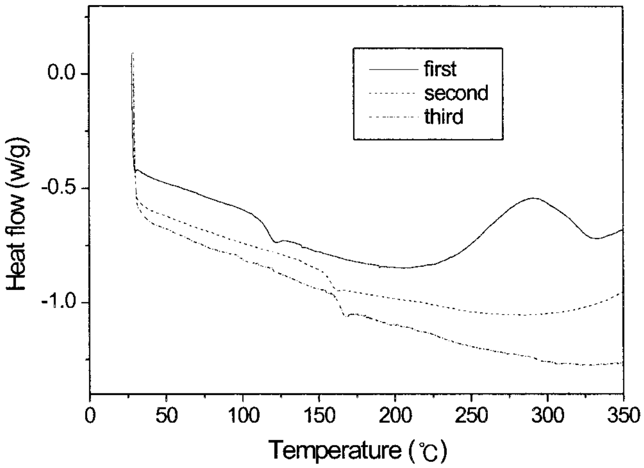


Figure 3. Effect of the degree of curing on the glass transition temperature of E-FPAESI (M_n: 14K).

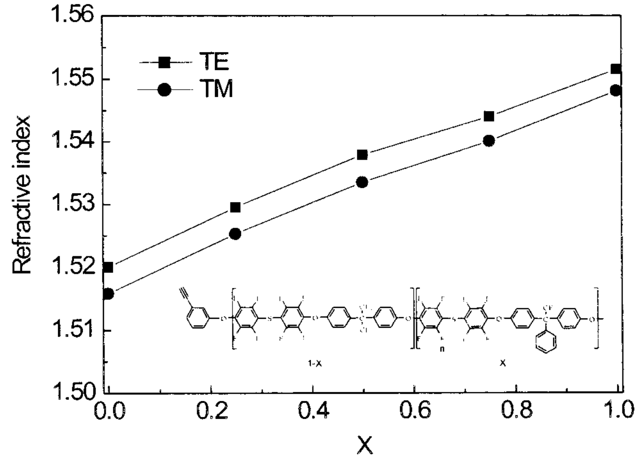


Figure 4. Relationship between the refractive index and 6FBPA and 3FBPA content of E-FPAESI.

Table 2. M_n's and M_w/M_n's of E-FPAESI were in the range 14 200−25 200 and 2.23−2.65, respectively. The M_n's were very similar to those of FPAESI. It was found that there was no side reaction such as cross-linking of the ethynyl group in the synthesis of E-FPAESI with increasing reaction time up to 6 h.

Thermal Properties. Table 1 shows the molecular weight dependence of glass transition temperature (T_g) of polymers. As the number-average molecular weight of FPAESI is increased from 10 200 to 25 400, the value of T_g increased from 97 to 157 °C. The results of thermogravimetric analysis are shown in Figure 2. E-FPAESI (5 wt % loss at 489 °C) exhibited higher thermal stability than FPAESI (5 wt % loss at 472 °C) due to cross-linking.

DSC analysis was performed to study the effect of curing on the glass transition temperature and the curing properties of the polymers. These results are shown in Figure 3. As the degree of curing increased, the glass transition temperature of polymers increased. Thus, with increasing number of DSC scans was increased, the glass transition temperature increased from 121 to 143 °C. Also, an intense exothermic peak at the first scan was seen due to the reaction of ethynyl moiety. At the second scan (as the degree of curing was increased), this intense exothermic peak disappeared because the ethynyl groups were reacted with each other by heating.

Optical Properties. Table 2 shows the refractive indices of the cured E-FPAESI films according to the M_n's. As the molecular weight of fluorinated polymers bearing cross-linkable ethynyl moiety increased, the mole fraction of fluorine increased due to the reduction of the terminal ethynyl group. As shown in Table 2, the refractive index of E-FPAESI changed from 1.5220 to 1.5190 on M_n's of E-FPAESI. The birefringences of E-FPAESI, $\Delta n = n_{TE} - n_{TM}$ (where n_{TE} and n_{TM} represent transverse electric and transverse magnetic modes in waveguide, respectively), were in the range 0.0040−0.0045. But difference of refractive index for E-FPAESI on M_n's was too small to apply optical device fabrication. To study the effect of fluorine content on refractive index of E-FPAESI, the copolymers were prepared by the appropriate molar ratio of 6FBPA and 3FBPA with pentafluorosulfide. As shown in Figure 4, the refractive index of E-FPAESI increased linearly with increasing 3FBPA at 1.55 μm. The refractive index of E-FPAESI changed from 1.5200 to 1.5515 on ratio of 3FBPA and 6FBPA. The birefringences of E-FPAESI were in the range 0.0034−0.0044. This results show that the refractive indices of the E-FPAESI can be controlled by combination of 6FBPA and 3FBPA content in the copolymer.

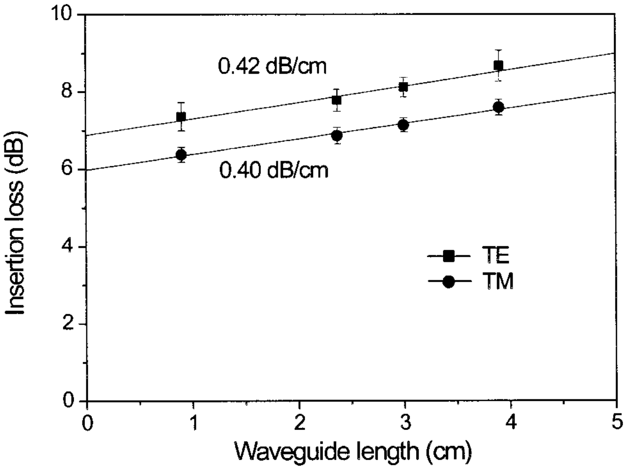


Figure 5. Effect of waveguide length on optical loss of the fabricated waveguide for TE and TM polarizations at 1.55 μm.

Figure 5 shows a linear relationship of insertion loss with the waveguide length. The propagation losses, which were obtained from the slope, are less than 0.42 and 0.40 dB/cm for the TE and TM polarization, respectively. This result indicated that the E-FPAESI is a good candidate as a core material for the optical waveguide devices.

Conclusions

Cross-linkable poly(arylene ether sulfide)s for polymeric optical waveguide devices were successfully synthesized. The molecular weight of E-FPAESI was controlled by monomer feed ratio imbalance from 14 200 to 25 200. These amorphous polymers easily provided transparent thin films by spin-coating. The thermally cross-linked films of E-FPAESI showed high thermal stability up to 489 °C under an air atmosphere. After cross-linking, the resulting films were insoluble in common organic solvents such as acetone, THF, methylene chloride, chloroform, DMF, and DMSO. The glass transition temperatures of polymers increased as the degree of cross-linking increased. The refractive indices of the cured polymer films could be controlled from 1.5220 to 1.5515 by combination of 6FBPA and 3FBPA content in the copolymer at 1.55 μm wavelength (birefringence: 0.0034−0.0044). The optical loss was measured to be less than 0.40 dB/cm.

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Supporting Information Available: ^{1}H, ^{19}F, and ^{13}C NMR spectra of poly(arylene ether sulfide) and copoly(arylene ether sulfide). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Fischbeck, G.; Moosburger, R.; Kostrzewa, C.; Achen, A.; Petermann, K. *Electron. Lett.* **1997**, *33*, 518.
(2) Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Macromolecules* **1994**, *27*, 6665.
(3) 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.
(4) Goodwin, A. A.; Mercer, F. W.; McKenzie, M. T. *Macromolecules* **1997**, *30*, 2767.
(5) Nagal, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4740.
(6) Hudliky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed.; Ellis Horwood: Chichester, 1992; pp 531−557.
(7) Rosenberg, S. D.; Walburn, J. J.; Ramsden, H. E. *J. Org. Chem.* **1957**, *22*, 1606.
(8) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* **1992**, *25*, 3540.
(9) Smith, D. W.; Babb, D. A. *Macromolecules* **1996**, *29*, 852.
(10) Pitois, C.; Vukmirovic, S.; Hult, A.; Wiesmann, D.; Robertsson, M. *Macromolecules* **1999**, *32*, 2903.
(11) Kang, J. W.; Kim, J. S.; Kim, J. J. *Jpn. J. Appl. Phys.* **2001**, *40*, 3215.
(12) Kang, J. W.; Kim, J. S.; Lee, C. M.; Kim, E.; Kim, J. J. *Electron. Lett.* **2000**, *36*, 1641.
(13) Usui, M.; Imamura, S.; Sugawara, S.; Hayashida, S.; Sato, H.; Hikita, M.; Izawa, T. *Electron. Lett.* **1994**, *30*, 958.
(14) Kowalczyk, T. C.; Kosc, T.; Singer, K. D.; Cahill, P. A.; Seager, C. H.; Meinhardt, M. B.; Beuhler, A. J.; Wargowski, D. A. *J. Appl. Phys.* **1994**, *76*, 2505.
(15) Toyoda, S.; Ooba, N.; Hikita, M.; Kurihara, T.; Imamura, S. *Thin Solid Film* **2000**, *370*, 311.
(16) Yoshimura, R.; Hikita, M.; Tomaru, S.; Imamura, S. *J. Lightwave Technol.* **1998**, *16*, 1030.
(17) Hendricks, N. H.; Lau, K. S. Y. *Polm. Prepr.* **1996**, *37* (1), 150.
(18) Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; J. Wiley & Sons: New York, 1985; Vol. 11, pp 531−542.
(19) Fagerburg, D. R. *Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, FL, 1996; Vol. 9, pp 6517−6525.
(20) Ulrich, R.; Torge, R. *Appl. Opt.* **1973**, *12*, 2901.
(21) Lee, H. M.; Oh, M. C.; Park, H.; Hwang, W. Y.; Kim, J. J. *Appl. Opt.* **1997**, *36*, 9021.

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