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Synthesis of Highly Fluorinated Poly(arylene ether sulfide) for Polymeric Optical Waveguides

Kwan-Soo Lee and Jae-Suk Lee*

Department of Materials Science and Engineering and Center for Advanced Materials Research and Education (CAMRE), Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea

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Ethynyl-terminated fluorinated poly(arylene ether sulfide) (E-FPAESI) was synthesized via nucleophilic aromatic substitution from dihydroxy monomer and pentafluorophenyl sulfide, followed by the reaction with 3-ethynylphenol. Dihydroxy monomer was synthesized in four steps via bromination, Grignard, Suzuki cross-coupling, and demethylation techniques. The number-average molecular weights and polydispersities of the E-FPAESI were in the ranges of 7700−23 000 and 1.53−2.89, respectively. The glass transition temperatures of the polymers varied from 126 to 171 °C and upon curing in the range of 168−236 °C. E-FPAESI exhibited high thermal stability up to 451−483 °C. The refractive indices and birefringences of the spin-coated polymer films were in the ranges of 1.4943−1.5047 and 0.0004−0.0009 at 1550 nm wavelength, respectively. The optical loss for E-FPAESI was about 0.45 dB/cm at 1550 nm wavelength.

Introduction

Polymeric optical waveguide devices for optical telecommunications have attracted considerable attention due to their ease of processing and relatively low cost as compared to silica-based materials.[1] To obtain a polymer optical device with good performance, the polymer should have several requirements, which are low optical loss in the infrared region, sufficient thermal stability, easily controlled refractive index, low birefringence, and good adhesion to the silicon substrate.[2] However, it was reported that the overtone absorption of C−H vibrations of hydrocarbon polymers contributes significantly to the overall optical loss in the infrared communication region. It is well established that the substitution of hydrogen atoms, typically fluorine, shifts the absorption overtone to longer wavelengths and reduces optical loss at 1550 nm.[3]

Fluorine-containing polymers have been developed for optical waveguides because of their excellent thermal and chemical stability, low optical loss, low refractive index, low dielectric constant, low moisture absorption, and easy processability.[4] In view of these useful properties, many fluorinated polymers have been studied as optical waveguide materials in past decades. Representative fluorine-containing polymers are the fluorinated polyimides, poly(arylene ether)s, acrylic polymers, perfluorocyclobutane (PFCB) aryl ether polymers, and poly(siloxane)s.[1f,5−10]

Among the fluorinated polymers for optical waveguide application, the fluorinated poly(arylene ether)s[5,7] are one of the most suitable candidates because of their flexible ether

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* To whom correspondence should be addressed. Phone: +82-62-970-2306. Fax: +82-62-970-2304. E-mail: jslee@gist.ac.kr.

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group in the polymer backbone as compared to fluorinated polyimides. Fluorinated poly(arylene ether)s are of lower birefringence and more conveniently processed than polyimides due to their flexible backbone. Furthermore, the presence of the perfluorophenylene moiety in the polymer backbone offers good thermal stability and mechanical properties similar to those of polyimides. Aromatic polysulfides are one of the 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, flame resistance, low moisture absorption, and good affinity for inorganic fillers.[11] Srinivas et al. studied the thermal properties of poly(arylene ether sulfide)s and observed that the polymers are of high thermal stability in air as well as in nitrogen. X-ray studies showed the poly(arylene ether sulfide) materials to be semicrystalline.[12] Thermal degradation of poly(arylene sulfide)s was reported by Peters and Still. They found that the quantity of the pyrolysis fraction produced from the polymers was dependent on the environment, in which the degradation occurred.[13] Because of these excellent properties, poly(phenylene sulfide) has been studied extensively.

In this study, we present the synthesis and characterization of new ethynyl-terminated fluorinated poly(arylene ether sulfide) (E-FPAESI) with the aim of achieving high optical clarity at the telecommunication wavelength of 1550 nm, sufficient thermal stability, and a chemical resistance to withstand typical fabrication processing and operation conditions for waveguide materials. For E-FPAESI to meet the above demands, a new fluorinated monomer was synthesized for harnessing useful optical properties with low refractive index and birefringence. Furthermore, an ethynyl moiety at the end of the polymer as thermal cross-linkable groups was introduced to increase thermal stability, chemical resistance, and to decrease the birefringence.[2a,5,7a−f,14]

Experimental Section

Materials. Pentafluorophenyl sulfide, potassium carbonate, methylene chloride, bromine, iodine, 1,4-dimethoxybenzene, tetrahydrofuran (THF), 1,2-dibromoethane, trimethyl borate, hydrobromic acid (48%), acetic acid (glacial), tetrakis(triphenylphosphine)-palladium(0), *N*,*N*-dimethylacetamide (DMAc), and benzene were purchased from Aldrich Chemical Co. and used without further purification. Magnesium (Mg) powder was obtained from Kanto Chemical Co. Magnesium was used after activation and vacuum-drying at 100 °C for 24 h. 3,5-Bis(trifluoromethyl)bromobenzene was purchased from Fluorochem Ltd. and used without purification. Magnesium sulfate and hydrochloric acid were obtained from Oriental Chemical Industries (Korea). 3-Ethynylphenol was prepared according to the literature.[7a,14]

Measurements. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a JEOL JNM-LA 300 WB FT-NMR in $CDCl_3$ and deuterated DMSO (DMSO-d_6). Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra were referenced to tetramethysilane (TMS) at 0 ppm as an internal reference and fluorinated trichlorofluoromethane at 0 ppm as an external reference, respectively. FT-IR spectroscopy was performed with a Perkin-Elmer IR 2000 series. GC/MS spectra were measured on a SHIMADZU GCMS-QP2010 and used for measurement of molecular weight using EI^+ mass detector. The molecular weights and molecular weight distributions were determined by size exclusion chromatography (Waters model 515) and calculated using polystyrene as a standard at 40 °C. THF was used as the mobile phase. The thermal properties of resulting polymers were determined with a TA Instrument 2100 series, covering the thermal degradation temperature of 40−750 °C at a heating rate of 10 °C/min. Glass transition temperatures (T_g) of polymers were measured in the range of 40−350 °C at a heating rate of 5 °C/min using the differential scanning calorimeter (DSC) measurement. The thickness of the cast films was measured by a depth profiler (α-Step 500). The refractive index and birefringence were determined using a prism coupler (SAIRON Technology, Korea) with a 1550 nm diode laser as a monitoring beam.[15] The optical loss of the thermal cured film in the waveguide was determined by an immersion method[16] on a waveguide using a loss measurement device (model SPA-4000/SPA-Lite, SAIRON, Korea).

1,4-Dibromo-2,5-dimethoxybenzene (1). 1,4-Dimethoxybenzene (10.29 g, 74.50 mmol) was dissolved in dry methylene chloride (50 mL) under N_2. To the solution was slowly added bromine (9.21 mL, 178.80 mmol) dropwise over 2 h at room temperature with intercepting light. The solution was stirred for 1 h and poured into an excess amount of 1 M KOH aqueous solution to remove unreacted bromine. The brownish colored solution became yellowish upon stirring. The solution was extracted with methylene chloride (150 mL) three times and washed with water, then dried over anhydrous magnesium sulfate, and the solvent was removed in a rotary evaporator to give a white solid. The crude product was purified by recrystallization from ethanol. The yield was above 95% after purification. Melting point: 144−149 °C. ^{1}H NMR ($CDCl_3$): $\delta = 3.85$ (6H, s), 7.10 (2H, s). MS (EI, *m/z*): 296 (M^+, 100%). Anal. Calcd for $C_8H_8Br_2O_2$: C, 32.47; H, 2.72. Found: C, 32.49; H, 2.81.

2,5-Dimethoxy-1,4-benzenediboronic Acid (2). 1,4-Dimethoxy-2,5-dibromobenzene (20 g, 67.57 mmol) was added to the mixture of Mg powder (6.57 g, 0.27 mol), 1,2-dibromoethane (0.10 mL) (for activation of Mg), and dry THF (100 mL). The reaction mixture

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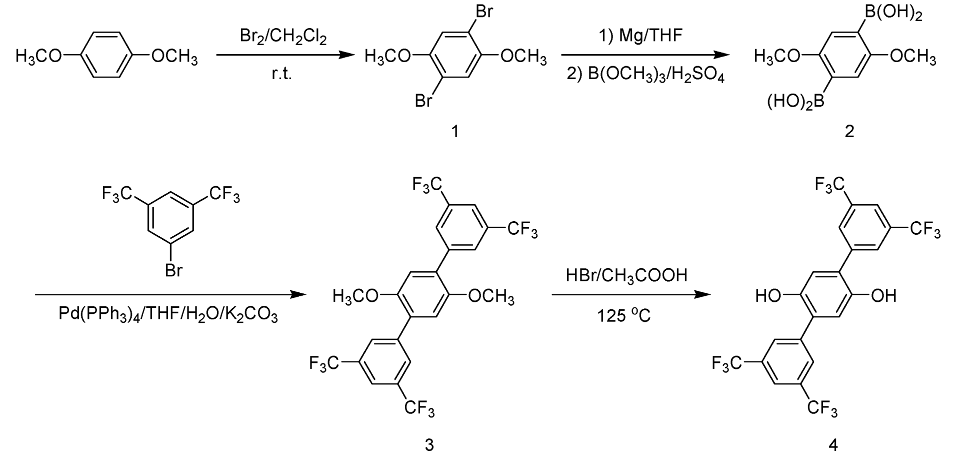
Scheme 1. Synthesis of the Dihydroxy Monomer



was refluxed for 2 h and cooled using liquid nitrogen. When the temperature of the reaction mixture reached −70 °C, trimethyl borate (30.3 mL, 0.27 mol) was added. The reaction mixture was stirred for 12 h at room temperature. Next, 700 mL of 2 M H_2SO_4 solution was added. The organic layer was extracted with diethyl ether, washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated off. The residue was recrystallized from a H_2O/acetonitrile mixture. The product yield was above 60%. Melting point: >250 °C. ^{1}H NMR (DMSO-d_6): $\delta = 3.77$ (6H, s), 7.16 (2H, s), 7.80 (4H, s). ^{13}C NMR (DMSO-d_6): $\delta = 55.84$, 116.86, 124.56, 157.47. Anal. Calcd for $C_8H_{12}B_2O_6$: C, 43.68; H, 5.38. Found: C, 42.55; H, 5.36.

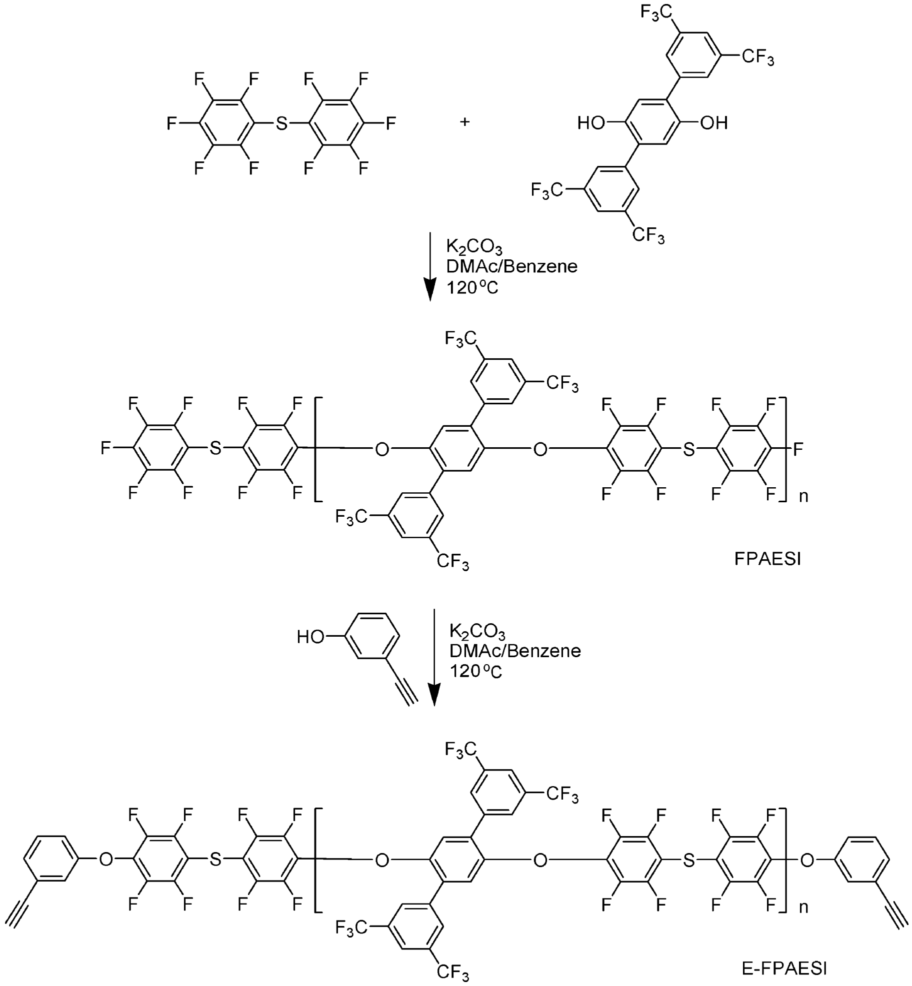
2,5-Dimethoxy-3,5,3″,5″-tetrakis-trifluoromethyl-(1,1′;4′,1″)-terphenyl (3). To a stirred solution of monomer **2** (1.50 g, 6.64 mmol), 3,5-bis(trifluoromethyl)bromobenzene (3.89 g, 13.28 mmol) in 50 mL of THF, and 2 M K_2CO_3 solution in 25 mL of water was added the catalyst $Pd(PPh_3)_4$ (0.50 g, 5 mol %). The reaction mixture was heated at 80 °C under nitrogen atmosphere for 8 h. The solution was extracted with methylene chloride and washed with water. The extracts were dried over anhydrous magnesium sulfate. Evaporation in a vacuum gave a white solid. The crude product was purified by recrystallization from a methylene chloride. The yield of **3** was 93%. Melting point: 193−195 °C. ^{1}H NMR ($CDCl_3$): $\delta = 3.85$ (6H, s), 6.98 (2H, s), 7.87 (2H, s), 8.01 (4H, s). ^{13}C NMR ($CDCl_3$): $\delta = 56.45$ (s, **C**H_3O−), 114.24 (s, CH_3O−C−**C**H−), 120.97−121.17 (m, −C(CF_3)−**C**H−C(CF_3)−, $J = 3.87$ Hz), 118.02−128.84 (q, −**C**F_3, $J = 272.55$ Hz), 128.73 (s, CH_3O−C−**C**−), 129.62 (m, −**C**H−C(CF_3)−CH−C(CF_3)−**C**H−), 130.81−132.14 (q, −**C(**CF_3)−, $J = 33.25$ Hz), 139.83 (s, −**C**−CH−C(CF_3)−CH−C(CF_3)−), 150.70 (s, CH_3O−**C**−). ^{19}F NMR ($CDCl_3$): $\delta = -60.03$ (12F, s). IR (KBr, cm^{-1}): 3503 (−OH). MS (EI, *m/z*): 562 (M^+, 100%). Anal. Calcd for $C_{24}H_{14}F_{12}O_2$: C, 51.26; H, 2.51. Found: C, 51.17; H, 2.44.

3,5,3″,5″-Tetrakis-trifluoromethyl-(1,1′;4′,1″)-terphenyl-2,5-diol (4). A solution of the monomer **3** in 100 mL of glacial acetic acid was reacted with 50 mL of 48% hydrobromic acid for 48 h at 125 °C. The solution was poured into approximately 1 L of deionized water to obtain a white powder by filtration. The material was purified by recrystallization from methylene chloride and subsequent treatment with activated carbon in methanol. The yield of **4** was 87%. Melting point: 176−178 °C. ^{1}H NMR ($CDCl_3$): $\delta = 4.77$ (2H, s), 6.94 (2H, s), 7.90 (2H, s), 8.05 (4H, s). ^{13}C NMR ($CDCl_3$): $\delta = 118.17$ (s, HO−C−**C**H−), 117.92−128.76 (q, −**C**F_3, $J = 272.75$ Hz), 121.05−121.43 (m, −C(CF_3)−**C**H−C(CF_3)−), 127.01 (s, HO−C−**C**−), 129.35 (m, −**C**H−C(CF_3)−CH−C(CF_3)−**C**H−), 131.12−132.48 (q, −**C**(CF_3)−, $J = 33.36$ Hz), 139.03 (s, −**C**−CH−C(CF_3)−CH−C(CF_3)−), 146.92 (s, HO−**C**−). ^{19}F NMR ($CDCl_3$): $\delta = -60.03$ (12F, s). MS (EI, *m/z*): 534 (M^+, 100%). Anal. Calcd for $C_{22}H_{10}F_{12}O_2$: C, 49.46; H, 1.89. Found: C, 49.32; H, 1.85.

Synthesis of FPAESI and E-FPAESI. FPAESI was synthesized via nucleophilic aromatic substitution of dihydroxy monomer **4** with pentafluorophenyl sulfide as shown in Scheme 2. Dihydroxy monomer **4** (0.99 g, 1.85 mmol) and pentafluorophenyl sulfide (0.68 g, 1.86 mmol) with K_2CO_3 (0.28 g, 1.10 equiv) in a DMAc (10 mL) and benzene (10 mL) mixture were placed in a 50 mL two-neck flask equipped with a magnetic stirrer, a nitrogen inlet, and Dean−Stark trap. The reaction mixture was heated to 120 °C, and this temperature was maintained for 12 h to ensure complete dehydration. Benzene was refluxed into the Dean−Stark trap, following which the reaction mixture was stirred at this temperature for a further period of 2 h. To synthesize E-FPAESI, the end of the FPAESI was capped by an ethynyl group. In a typical procedure, 3-ethynylphenol (0.87 g, 4.00 equiv) and benzene (10 mL) were added to the reaction mixture, and then the reaction was continued at 120 °C for 2 h. After benzene was removed, the reaction mixture was cooled and then precipitated into 400 mL of acidic methanol/water (1:1 solution). The polymer was dissolved in THF and reprecipitated into methanol, filtered, and washed with methanol. The resulting white solid was dried under vacuum at 80 °C for 3 days. The yields of FPAESI and E-FPAESI were above 90%. E-FPAESI, ^{1}H NMR ($CDCl_3$): $\delta = 3.02$ (ethynyl H), 6.97 (2H, b), 7.86 (2H, b), 7.70 (4H, b). ^{13}C NMR ($CDCl_3$): $\delta = 115.98$, 117.60−128.40 (q, −**C**F_3, $J = 272.13$ Hz), 122.36 (m, −C(CF_3)−**C**H−C(CF_3)−), 129.34, 130.56, 131.46−132.80 (q, −**C**CF_3, $J = 33.77$ Hz), 137.13, 137.27, 139.34−142.73 (d, $J = 255.76$ Hz), 145.91−149.22 (d, $J = 247.38$ Hz), 150.00. Ethynylphenyl part, 77.24, 78.05, 115.13, 123.78, 127.28, 129.35, 129.60, 149.99. ^{19}F NMR ($CDCl_3$): $\delta = -149.90$ (4F, s), −128.95 (4F, s), −60.28 (12F, s). IR (KBr, cm^{-1}): 3311 (acetylenic CH peak). Anal. Calcd for $(C_{34}H_8F_{20}O_2S_1)_n$: C, 47.46; H, 0.94; S, 3.73. Found: C, 47.56; H, 1.08; S, 3.76.

Preparation of Polymer Films. The polymer solutions were prepared in cyclohexanone (30−50%, w/v). The solutions were filtered with a syringe through a 0.2 μm Teflon membrane filter. The filtered yellow solutions were spin-coated on the SiO_2/Si wafer substrates at the spin rate of 1000 rpm for 2 min. After being coated, the films were baked at 170 °C for 1 h on a hot plate. Adjusting the concentration of polymer solutions controlled thickness of the films (6−8 μm). In case of the E-FPAESI, the prepared polymer films were cured at 270 °C for 2 h on a hot plate that rendered the films insoluble.

Scheme 2. Synthesis of FPAESI and E-FPAESI



Results and Discussion

Synthesis of Dihydroxy Monomer (4). Fluorinated dihydroxy monomer **4** was designed for reducing the refractive index and the birefringence of the polymers. Usually the incorporation of fluorine atoms in the polymers can affect the refractive index and the optical loss. It was reported that the refractive index of polymers is related to the free volume, the electronic polarizability, and the difference between the used optical wavelength and the maximum absorption wavelength. The birefringence of polymer materials comes mainly from the preferred orientation of rigid groups and polymer chains, although the orientation may be induced by stress during the formation of the final polymer films.[2,5,17] We prepared terphenyl dihydroxy monomer substituted with CF_3 moieties as a counterpart of pentafluorophenyl sulfide. In the polymer structure, it has two bulky side phenyl groups containing four CF_3 moieties, which can increase the free volume of the polymer, and they decrease the refractive index due to the greater steric volume of fluorine in comparison to hydrogen. They also reduce the birefringence due to inefficient chain packing. In addition, introduction of the side phenyl group may make the polymer have a high T_g.

Dihydroxy monomer **4** was synthesized via bromination, Grignard, Suzuki cross-coupling, and demethylation techniques in four steps (Scheme 1). The molecular structures of this material were confirmed using ^{1}H, ^{13}C, and ^{19}F NMR spectra in $CDCl_3$ or DMSO-d_6, and GC/MS spectra.

Synthesis of FPAESI and E-FPAESI. The effect of reaction temperature and reaction time on the molecular weights of FPAESI has been studied. Observed results were supported by the previously reported paper.[7a] The *para*-fluorines in pentafluorophenyl sulfide have better reactivity than the *ortho*-fluorines with activated monomer. Unfortunately, increasing the reaction temperature above 130 °C, the *ortho*-fluorines in pentafluorophenyl sulfide were also reacted with the *para*-fluorines during the polymerization. This result indicated that the polymerization should be accomplished at the reaction temperature below 130 °C to avoid side reactions such as branching or cross-linking. Thus, polycondensation of pentafluorophenyl sulfide with monomer **4** in DMAc/benzene was conducted in the presence of K_2CO_3, which acted as a mild base at a reaction temperature of 120 °C for 4 h. Our group also introduced 3-ethynylphenol as a thermal cross-linkable group[7a−d] for the fabrication of waveguides, which have good thermal stability, chemical resistance, and low birefringence.

After polymerization, the ^{19}F NMR (Figure 1) spectrum shows that the *para*-fluorine peak at around −146.82 ppm of pentafluorophenyl sulfide disappeared and the *meta*-fluorine peak at around −156.94 ppm of pentafluorophenyl sulfide shifted downfield to −149.90 ppm due to a decrease

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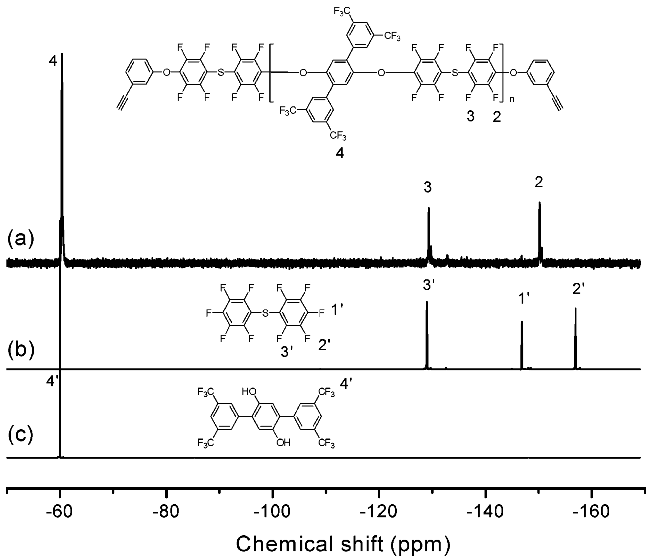

Figure 1. ^{19}F NMR of monomer **4** (c), pentafluorophenylsulfide (b), and E-FPAESI (a).

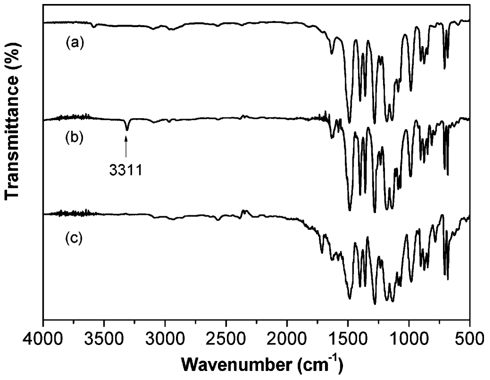

Figure 2. FT-IR spectra of FPAESI (a), E-FPAESI before thermal curing (b), and after thermal curing (c) at 270 °C for 2 h.

of electron density. These phenomena confirmed that polymerization of monomer **4** with pentafluorophenyl sulfide was successfully achieved. In ^{1}H NMR spectra, three aromatic peaks at 7.93, 7.86, and 6.97 ppm due to monomer **4** were observed, and the ethynyl peak appeared at 3.02 ppm after introducing the ethynyl phenol into polymer chain end. FT-IR spectra (Figure 2) of E-FPAESI as compared to FPAESI showed an ethynyl peak at 3311 cm^{-1} after the end-capping reaction. This peak disappeared after curing at 270 °C for 2 h, while other FT-IR peaks are not affected. This indicates that the polymer is very stable at high temperature (270 °C). FPAESI was soluble in typical solvents such as NMP, DMF, DMAc, THF, methyl ethyl ketone, cyclohexanone, and toluene. These solubility tests supported that the FPAESI was synthesized without serious branching or cross-linking side reactions. Usually crystalline structure behaves as a defect for guiding light and also affects the refractive index and the birefringence of the polymer.[5] We conclude from DSC and wide-angle X-ray crystallography studies that E-FPAESI is indeed an amorphous polymer.

In case of condensation polymerization, the molecular weight of polymer can be controlled by monomer feed ratio.[18] We observed that the molecular weights of FPAESIs and E-FPAESIs determined by GPC were in accordance with the calculated molecular weights. The results of the analysis are summarized in Table 1. The number-average molecular weights (M_n) and polydispersities (M_w/M_n) of the resulting polymers were in the ranges 5400−24 100 and 1.53−2.89, respectively. The molecular weights of the resulting polymers could be successfully controlled by the monomer feed ratio imbalance.

Thermal Properties. Thermal stability (T_d, temperature at 5% weight loss) of FPAESI and E-FPAESI was investigated by TGA at a heating rate of 10 °C/min in air, and the results are shown in Table 1. Polymers with similar molecular weight with and without cross-linkable end-capping moiety were studied for T_d, and the results are shown in Figure 3. E-FPAESI exhibited higher thermal stability than FPAESI due to cross-linking.[14]

Table 1 shows the molecular weight dependence of the glass transition temperature (T_g) of the polymers. As the M_n of FPAESI is increased from 5400 to 24 100, the value of the T_g increased from 110 to 172 °C. The DSC analysis was also performed to study the effect of curing on the T_g. These results are shown in Figure 4. As the degree of curing increased, the T_g of polymers increased. Thus, polymers had higher T_g than before, as the DSC scan time is increased. An intense exothermic peak at the first scan was regarded as the reaction of ethynyl moiety. In the second scan, this intense exothermic peak disappeared because the ethynyl groups were cross-linked with each other upon heating.

Optical Properties. Based on the device design and waveguide geometry, the polymer used as the core material must have a higher refractive index than that of the cladding material. The appropriate index difference between core and cladding for either a single-mode or a multi-mode waveguide is strongly dependent on the dimension of the waveguide and the wavelength of the light source.[5a]

It was reported that the replacement of C−H bonds with C−F bonds gives high optical transparency of the polymeric material in the near-infrared (NIR) telecommunication region.[2,3,5−10,17] The refractive index could change with the free volume (packing density), polarizability of the material, temperature, and humidity. Yet the birefringence ($\Delta n = n_{TE} - n_{TM}$, where n_{TE} and n_{TM} represent transverse electric and transverse magnetic nodes in waveguide, respectively) is related to the optical anisotropy of the polymer material.[2,3,5−10,17]

Table 2 shows the refractive index and the birefringence of the spin-coated fluorinated polymers at 1550 nm as measured by the prism-coupling method.[19] Similar to other conventional spin-coated polymer films,[7−9] FPAESIs and E-FPAESIs showed a lower n_{TM} than n_{TE} because of their preferred orientation of the polymer chain in the direction parallel to the substrate during the spin-coating procedure. As shown in Table 2, the refractive index of fluorinated polymers changed from 1.5012 to 1.4943 depending on M_n of the fluorinated polymers. As the M_n of the polymers

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Table 1. Synthetic Data of FPAESI and E-FPAESI

polymer	feed ratio[a]	M_n calcd[b]	M_n obsd[c]	M_n/M_w	yield (%)	T_g (°C)[d]	T_d (°C)[e]
FPAESI 1	0.8144	5002	5434	2.53	93	110	440
FPAESI 2	0.9107	10 002	10 871	1.94	92	143	450
FPAESI 3	0.9261	12 010	12 373	1.53	90	151	451
FPAESI 4	0.9651	25 021	24 082	2.50	91	172	470
E-FPAESI 1	0.8144	5002	7707	1.71	93	126	480
E-FPAESI 2	0.9413	15 025	17 977	2.36	95	164	482
E-FPAESI 3	0.9562	20 011	22 293	2.89	95	171−228−236[f]	483

[a] The feed mole ratio of dihydroxy monomer **4**/pentafluorophenylsulfide (mol/mol). [b] Calculated number-average molecular weight from the feed ratio {M_n = repeating unit/(1 − feed ratio) + molecular weight of the end groups (pentafluorophenyl sulfide)}.[18] [c] Determined by GPC calibrated with polystyrene standards at 40 °C. [d] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen (second scan). [e] Onset temperature for 5% weight loss measured by TGA with a heating rate of 10 °C/min in air. [f] Glass transition temperature with change in the scan time (first−second−third scan).

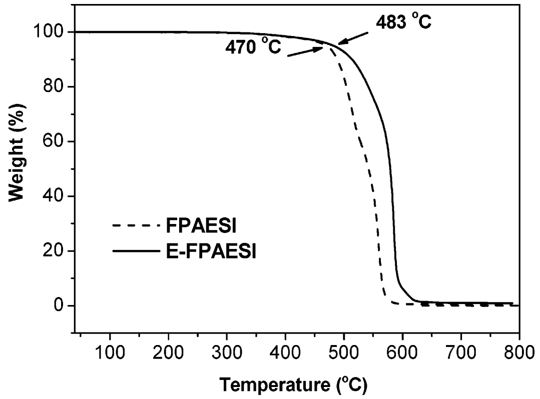

Figure 3. TGA of FPAESI **4** (M_n: 24 100) and E-FPAESI **3** (M_n: 22 300).

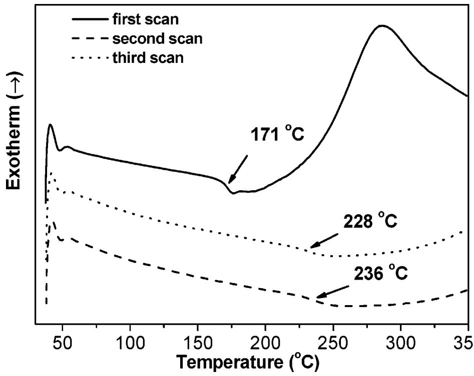

Figure 4. Effect of the degree of curing on the T_g of E-FPAESI **3** (M_n: 22 300) bearing cross-linkable ethynyl moiety.

Table 2. Refractive Index and Birefringence of Fluorinated Polymers at 1550 nm

polymer	refractive index TE mode (n_{xy})	refractive index TM mode (n_z)	n[a]	$n_{TE} - n_{TM}$ ($\times 10^{-3}$)[b]
FPAESI 1	1.5012	1.5007	1.5010	0.5
FPAESI 2	1.5037	1.5024	1.5033	1.3
FPAESI 3	1.5000	1.4985	1.4995	1.5
FPAESI 4	1.4949	1.4940	1.4946	0.9
E-FPAESI 1	1.5047	1.5043	1.5046	0.4
E-FPAESI 2	1.4954	1.4948	1.4952	0.6
E-FPAESI 3	1.4943	1.4934	1.4940	0.9

[a] Average refractive index, $n = (2n_{xy} + n_z)/3$. [b] Birefringence.

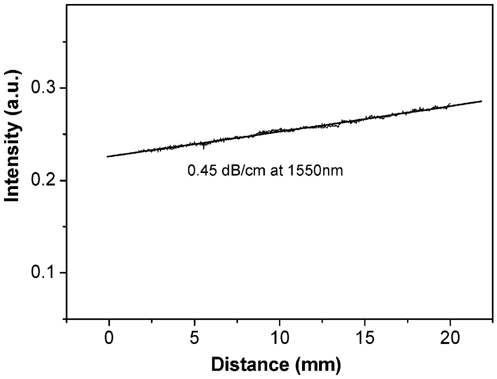

Figure 5. Optical loss of the cured film of waveguide along waveguide length (E-FPAESI 3).

increased, the refractive indices of polymers decreased. Yet the birefringence of fluorinated polymers showed a tendency opposite from that of the refractive index. These results supported that the relationship between the birefringence and the T_g is normally a tradeoff. Because high T_g polymers contain a rigid aromatic group such as poly(arylene ether), polyimide, and perfluorocyclobutane (PFCB), aryl ether polymers tend to be orientated during chemical and physical processes.[5b,7−9] The birefringences of polymers were in the range of 0.0004−0.0015 (Table 2). E-FPAESIs and FPAESIs showed lower birefringences as compared to the reported fluorinated polymers such as fluorinated polyimide and poly(arylene ether)s.[5,6g,7] The optical loss of the waveguide film along the wavelength is shown in Figure 5. The light loss calculated from the slop was 0.45 dB/cm at 1550 nm for the film, which is relatively lower than that reported for nonfluorinated materials at the same wavelength.[2b,5a,6f] The low optical loss was ascribed to substitution of C−H bonds by C−F bonds in the polymer chain. These results indicate that the E-FPAESI is a good candidate as a core material for the optical waveguide devices.

Conclusions

Ethynyl-terminated fluorinated poly(arylene ether sulfide) (E-FPAESI) for polymeric optical waveguide devices was successfully synthesized via nucleophilic aromatic substitution polycondensation of highly fluorinated dihydroxy monomer **4** with pentafluorophenyl sulfide in the presence of K_2CO_3 and the aprotic polar solvent (DMAc). Especially, monomer **4** was designed for reducing the refractive index and birefringence. The ethynyl moiety of the polymer chain end acted so as to not only lower the birefringence but also to improve the thermal stability up to 483 °C. After cross-linking, the resulting films were insoluble in common organic solvents. The T_g of E-FPAESI increased as the degree of cross-linking increased. The refractive indices of the cured polymer films were in the range of 1.5047−1.4943. The optical loss of E-FPAESI exhibited a very low value of 0.45 dB/cm at 1550 nm. These results indicate that E-FPAESI is a promising candidate as a core and cladding material for the optical waveguide devices.

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