Synthesis and characterization of low-birefringent crosslinkable fluorinated poly(arylene ether sulfide)s containing pendant phenyl moiety

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ABSTRACT

Fluorinated poly(arylene ether sulfide) (FPAESI) and ethynyl-terminated fluorinated poly(arylene ether sulfide) (E-FPAESI) were synthesized via step-growth polymerization from prepared dihydroxy monomer and pentafluorophenylsulfide, then E-FPAESI was followed by a reaction with 3-ethynylphenol. The number-average molecular weights and polydispersities of FPAESI and E-FPAESI were in the range of 12,000–26,000 and 1.75–3.18, respectively. The glass transition temperatures of the polymers varied from 138 to 178 °C depending on the molecular weight of the polymer used and were changed to the range of 191–245 °C after curing. The FPAESIs and E-FPAESIs exhibited high thermal stability up to 445–450 °C and 457–462 °C, respectively. The refractive index and birefringence of spin-coated polymer films were determined by the prism-coupling method. The refractive indices and birefringences of the films were in the range of 1.5849–1.5880 and 0.0014–0.0035 at a 1550 nm wavelength, respectively. The effect of E-FPAESI structure on the birefringence is compared with various reported poly(arylene ether sulfide)s.

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1. Introduction

Poly(arylene ether)s are one of the most important classes of commercially available macromolecules [1]. Poly(arylene ether)s such as poly(arylene ether sulfone)s [1–3], poly(arylene ether ketone)s [1,4], poly(arylene ether sulfide)s [5], and poly(arylene ether phosphine oxide)s [4,6] are considered to be high-performance engineering materials having high glass transition temperatures, thermal stability, good mechanical properties, low flammability, and good processability. Due to this interesting combination of useful properties, several poly(arylene ether)s were technically produced and commercialized over the course of the past two decades.

Fluorine-containing polymers have often been studied in many high technology fields, such as surfaces and coatings [7], photonic and electronic applications [8–10], and membrane and energy conversion applications [11], because of their thermal and oxidative stabilities, chemical inertness, low refractive indices,

good surface properties, and easy processability [12,13]. Due to their unique properties and high temperature performance, these polymers are suitable for optical applications like waveguide materials. Representative fluorinated polymers are the fluorinated poly(arylene ether)s, polyimide, acrylic polymers, perfluoro-cyclobutyl (PFCB)-containing polymers, and poly(siloxane)s [8,14–29]. Specifically, among the fluorinated polymers, the fluorinated poly(arylene ether)s [8,9,17–22] are well-suited as a candidate for waveguide materials due to their flexible ether group in the polymer backbone as compared to fluorinated polyimides. Fluorinated poly(arylene ether)s are of lower birefringence and are more conveniently processed than polyimides, which have a stiff backbone. Furthermore, the fluorinated phenylene moieties in the polymer backbone give rise to good thermal stability and mechanical properties similar to those of polyimides.

Poly(arylene ether sulfide)s are important commercial high-performance polymers with the characteristics of good thermooxidative stability, good mechanical properties, fire resistance, low moisture absorption, and good affinity for inorganic fillers [5]. Due to these excellent properties having fluorine- and sulfide-containing polymers, our group has also steadily studied fluorinated poly(arylene ether sulfide)s for polymeric waveguide materials [17–19].

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One of the defects for polymeric waveguide applications is their appreciably high birefringence. In fact, the polarization-dependent loss which is induced by the optical components with large birefringence can cause degradation of the transmission quality or failure of the optical data. For example, the birefringence of polarization-independent wavelength division multiplexing (WDM) should even close to be zero. Hence, the design of waveguide materials with zero birefringence is important and has still remained a challenge.

In this study, we focused on the synthesis and characterization of novel crosslinkable fluorinated poly(arylene ether sulfide)s with the goals of achieving low birefringence (for clarity of information transportation at the telecommunication region of 1550 nm), sufficient thermal stability, and a chemical resistance to withstand the typical fabrication processing and operating conditions of waveguide materials. In order to achieve these properties, pendant diphenylated dihydroxy monomer and fluorinated monomer were used to increase the glass transition temperature and to lower the refractive index and birefringence of the polymer. In addition, a crosslinkable polymer system was employed to improve the thermal stability and chemical resistance, as well as to lower the birefringence with giving more amorphous structure.

2. Experimental

2.1. 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. Magesium (Mg) powder was obtained from Kanto Chemical Co. Magnesium was used after activation and vacuum drying at 100 °C for 24 h. Magnesium sulfate and hydrochloric acid were obtained form Oriental Chemical Industries (Korea). 3-Ethynylphenol was prepared according to the literature [17,30]. 1,4-Dibromo-2,5-dimethoxybenzene (1) and 2,5-dimethoxy-1,4-benzenediboronic acid (2) were prepared according to the methods reported in the literature [18].

2.2. Synthesis of monomer

2.2.1. 2,5-Dimethoxy-(1,1′; 4′,1″)-terphenyl (3)
With a stirred solution of the monomer 2 (1.50 g, 6.64 mmol), bromobenzene (2.08 g, 13.25 mmol) in THF (50 mL) and 2 M K_2CO_3

aqueous solution (25 mL), the catalyst Pd(PPh$_3$)$_4$ (0.50 g, 5 mol%) was added. The reaction mixture was refluxed at 80 °C under a nitrogen atmosphere for 8 h. The solution was extracted with methylene chloride and water and dried over anhydrous magnesium sulfate. Evaporation in a vacuum gave a white solid. The crude product was purified by column chromatography. The analytical data obtained were as follows: Yield: 93%. mp: 147–149 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 3.79 (s, 6H), 6.98 (s, 2H), 7.35 (t, 2H, J = 7.34 Hz), 7.44 (t, 4H, J = 7.26 Hz), 7.59 (d, 4H, J = 6.97 Hz). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): δ = 56.41 (s, **CH**$_3$O–), 114.81 (s, CH$_3$O–C–**CH**–), 127.08 (s, –CH–CH–**CH**–CH–CH–), 128.06 (s, –CH–**CH**–CH–**CH**–CH–), 129.43 (s, –**CH**–CH–CH–CH–**CH**–), 130.43 (s, CH$_3$O–C–**C**–), 138.31 (s, CH$_3$O–C–C–**C**–), 150.65 (s, CH$_3$O–**C**–). MS (EI, m/z): calcd for C$_{20}$H$_{18}$O$_2$, 290.36; found, 290 [M]$^+$. Anal. calcd. for C$_{20}$H$_{18}$O$_2$: C, 82.73; H, 6.25. Found: C, 82.77; H, 6.28.

2.2.2. (1,1′; 4′,1″)-terpheny-2,5-diol (4)
A solution of the monomer 3 in glacial acetic acid (100 mL) was reacted with hydrobromic acid (50 mL) for 48 h at 125 °C. The solution was poured into deionized water (1 L) and filtered to obtain a white powder. The material was recrystallized from methylene chloride. The analytical data were as follows: Yield: 90%. mp: 222–224 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 6.85 (s, 2H), 7.30 (t, 2H, J = 7.32 Hz), 7.41 (t, 4H, J = 7.51 Hz), 7.55 (d, 4H, J = 4.03 Hz), 8.96 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 118.21 (s, HO–C–**CH**–), 127.14 (s, –CH–CH–**CH**–CH–CH–), 128.45 (s, –CH–**CH**–CH–**CH**–CH–), 128.68 (s, HO–C–**C**–), 129.55 (s, –**CH**–CH–CH–CH–**CH**–), 138.74 (s, HO–C–C–**C**–), 147.53 (s, HO–**C**–). IR (KBr, thin film, cm^{-1}): 3438 (–OH). MS (EI, m/z): calcd for C$_{18}$H$_{14}$O$_2$, 262.30; found, 262 [M]$^+$. Anal. calcd. for C$_{18}$H$_{14}$O$_2$: C, 82.42; H, 5.38. Found: C, 82.58; H, 5.60.

2.3. Synthesis of FPAESI and E-FPAESI

As shown in Scheme 2, FPAESIs were synthesized via the step-growth polymerization of compound 4 with pentafluorophenyl sulfide. Dihydroxy monomer 4 (1.85 mmol) and pentafluorophenyl sulfide (0.68 g, 1.86 mmol) with K$_2$CO$_3$ (0.28 g, 1.10 equiv), in a DMAc (10 mL) and benzene (10 mL) mixture, were placed in a 50 mL 2-neck flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean–Stark trap. The mixture was reacted at 120 °C for 12 h to ensure complete dehydration with refluxing benzene into the Dean–Stark trap. E-FPAESI was synthesized by capping the end of the FPAESI with an ethynyl group. Typically, 3-ethynylphenol (0.87 g, 4.00 equiv) and benzene (10 mL) were added to the reaction mixture, and the reaction was allowed to proceed at 120 °C for 2 h. After removing benzene, the reaction mixture was cooled and
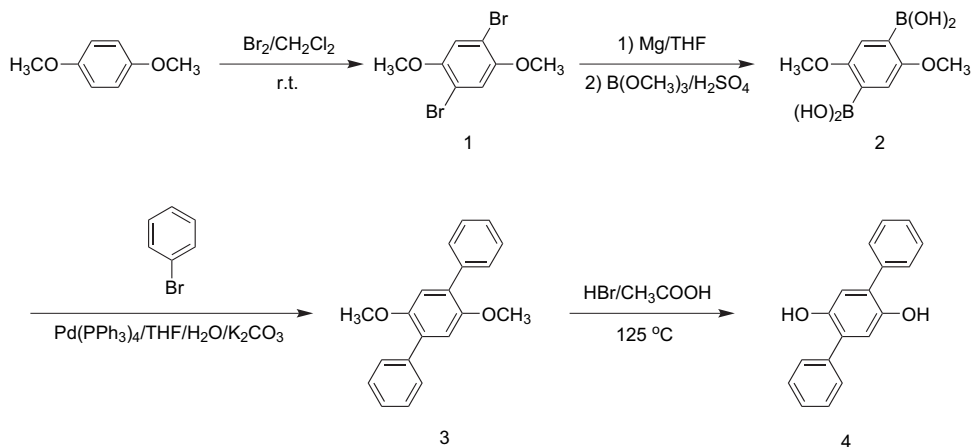
Scheme 1. Synthesis of the dihydroxy monomer.
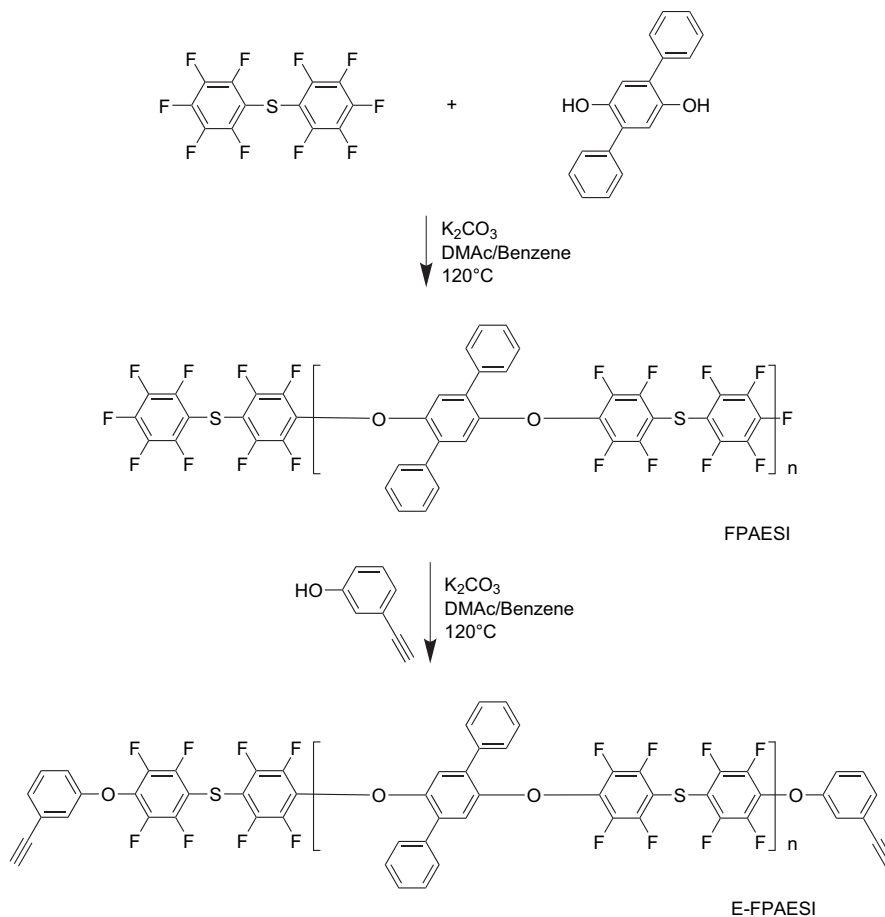
Scheme 2. Synthesis of FPAESI and E-FPAESI.

then precipitated into methanol/water (400 mL, 1:1 solution). The resulting product 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 (300 MHz, CDCl$_3$, δ, ppm): 3.02 (ethynyl H), 7.04 (br, 2H), 7.35–7.37 (br, 6H), 7.44 (br, 4H). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 117.48, 118.56, 128.11, 128.37, 129.14, 132.04, 135.64, 135.82, 139.27–142.61 (d, $J = 252.96$ Hz), 145.79–149.14 (d, $J = 253.28$ Hz), 150.05. ethynylphenyl part: 78.10, 82.35, 115.31, 123.52, 127.09, 129.23, 129.51, 148.15. ^{19}F NMR (300 MHz, CDCl$_3$, δ, ppm): −150.09 (4F, s), −129.87 (4F, s). IR (KBr, thin film, cm^{-1}): 3300 (acetylenic CH peak).

2.4. Preparation of polymer films

The polymers were dissolved in cyclohexanone (30–50%, w/v). The solutions were filtered with a 0.2 μm Teflon syringe filter. The filtered 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 170–180 °C for 1 h on a hot plate. The concentration of the polymer solutions was properly controlled for the thickness of the films (6–8 μm). The prepared polymer films (E-FPAESI) were cured at 270 °C for 2 h on a hot plate that rendered the films insoluble.

2.5. 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. FT-IR spectroscopy was performed with a Perkin–Elmer IR 2000 series. GC/MS spectra were measured on an SHIMADZU GCMS-QP2010 and used for measurement of the molecular weight using the 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 the resulting polymers were determined with a TA Instrument 2100 series, covering the thermal degradation temperature of 40–800 °C at a heating rate of 10 °C/min. The glass transition temperatures (T_g) of the 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 [31].

3. Results and discussion

3.1. Monomer synthesis

Dihydroxy monomer **4** was designed to increase the T_g and lowering the birefringence of the polymers. Usually the birefringence of polymer materials comes mainly from the preferred orientation of the rigid groups and polymer chains, although the orientation may be induced by stress during the formation of the

final polymer films [8–10,32,33]. We prepared the terphenyl dihydroxy monomer as a counterpart of pentafluorophenyl sulfide. In the polymer structure, it has two bulky and rigid side phenyl groups, which can increase the free volume of the polymer. They also reduce the birefringence due to inefficient chain packing. In addition, the introduction of the side phenyl group may confer a high T_g. Dihydroxy monomer **4** was synthesized via bromination, Grignard, Suzuki cross-coupling, and demethylation techniques in four steps as shown in Scheme 1. These monomer structures were confirmed using ^{1}H, ^{13}C, and ^{19}F NMR in CDCl$_3$ or DMSO-d_6, as well as with GC/MS spectra.

3.2. Polymer synthesis and characterization

Our group has studied the effects of reaction temperature and reaction time on the molecular weights of FPAESI. The reports in previous papers support the observed results [17–20]. The reactivity of *para*-fluorines in pentafluorophenyl sulfide is better than that of *ortho*-fluorines with activated monomer. Unfortunately, when the reaction temperature increases to above 130 °C, the *ortho*-fluorines in the pentafluorophenyl sulfide also react with the *para*-fluorines during the polymerization. In order to avoid side reactions such as branching or crosslinking, the polymerization should take place at a reaction temperature below 130 °C. Thus, step-growth polymerization of pentafluorophenyl sulfide with the dihydroxy monomer **4** in DMAc/benzene was conducted in the presence of K$_2$CO$_3$, acting as a mild base at the 120 °C reaction temperature for 4 h. Our group also introduced 3-ethynylphenol as a thermal crosslinkable group [17–20] in the polymer chain end for the fabrication of waveguides, resulting in good thermal stability, chemical resistance, and low birefringence.

After polymerization, the ^{19}F NMR (Fig. 1) 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 down-field to −150.09 ppm due to a decrease of electron density. These phenomena confirmed that the polymerization of monomer **4** with pentafluorophenyl sulfide was successfully achieved. In the ^{1}H NMR spectra, aromatic peaks were observed at 7.44, 7.35–7.37 and 7.04 ppm due to monomer **4**, and the ethynyl peak appeared at 3.02 ppm after introducing the ethynyl phenol into the polymer chain end. The ^{13}C NMR spectra also supported that the polymer was successfully synthesized (Fig. 1).

FPAESI was very soluble in typical organic solvents such as NMP, DMF, DMSO, DMAc, THF, methyl ethyl ketone, cyclohexanone, chloroform, and toluene. These solubility tests supported that the FPAESI was synthesized without serious branching or crosslinking side reactions. However, the polymer was not soluble in any solvents after thermal crosslinking. In the FT-IR spectra (Fig. 2), the thermally crosslinkable ethynyl peak at 3300 cm$^{−1}$ disappeared after curing at 270 °C for 2 h, while other FT-IR peaks were not affected.

Usually the crystalline structure acts as a defect interrupting the guiding light and also affects the refractive index and the birefringence of the polymer [8,9]. We concluded that E-FPAESI is indeed an amorphous polymer from the DSC and wide-angle X-ray crystallography studies (Fig. 3).

The molecular weight of the polymer in the case of step-growth polymerization can be controlled by the monomer feed ratio [34]. 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 molecular weights and their thermal properties are summarized in Table 1. The number-averages of the molecular weights (M_n) and polydispersities (M_w/M_n) were in the ranges of 11,600–25,700 and 1.75–3.18, respectively.
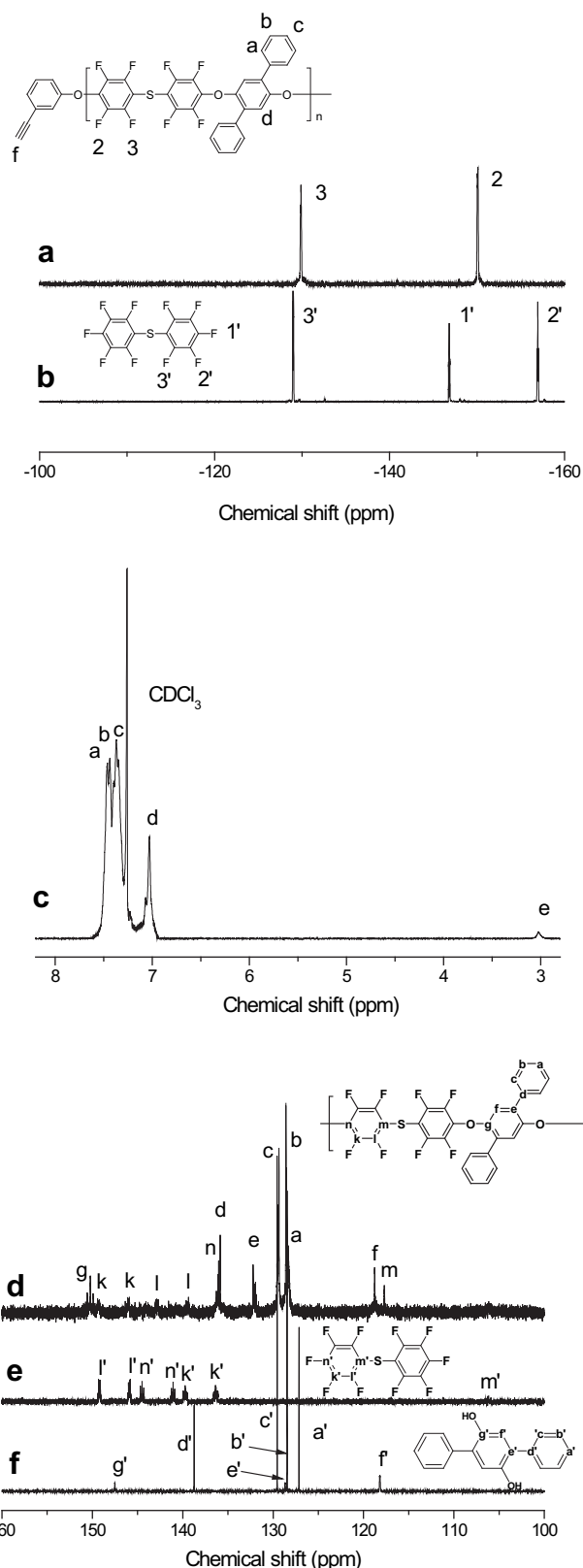

Fig. 1. NMR spectra of the monomer and polymer (^{19}F NMR of E-FPAESI (a) and pentafluorophenylsulfide (b), ^{1}H NMR of E-FPAESI (c), and ^{13}C NMR of FPAESI (d), pentafluorophenylsulfide (e) and monomer 4 (f)).
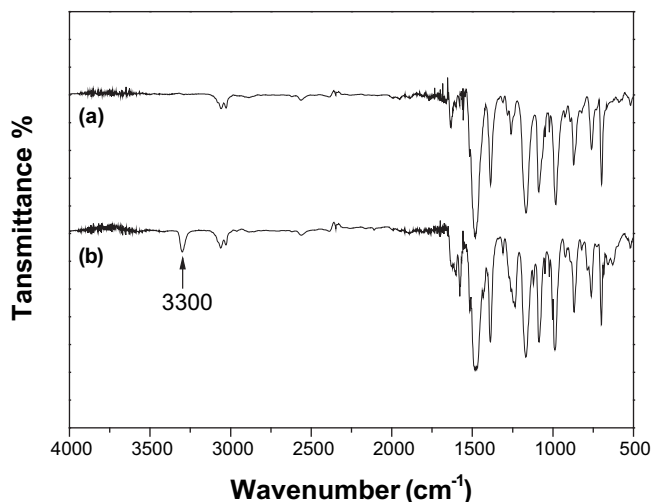
Fig. 2. FT-IR spectra of E-FPAESI before thermal curing (b), and after thermal curing (a) at 270 °C for 2 h.

The molecular weights of the resulting polymers could be successfully controlled by the stoichiometric amounts of the monomers.

3.3. Thermal properties

The glass transition temperature (T_g) typically depends on the molecular weight of the polymer. Table 1 shows the molecular weight dependence of the glass transition temperature (T_g) of the polymers. When increasing the M_n of FPAESI from 11,600 to 25,700, the T_g increased from 138 to 178 °C. DSC analysis was also performed to study the effect of curing on the T_g. These results are shown in Fig. 4. The T_g of the polymers increased with an increasing degree of curing. Thus, with increasing number of DSC scans, the T_g increased from 140 to 191 °C. An intense exothermic peak at the first scan was regarded as the reaction of the ethynyl moiety. At the second scan, this intense exothermic peak disappeared because the ethynyl groups were crosslinked with each other upon heating.

The thermal stabilities (T_d, temperature at 5% weight loss) of FPAESI and E-FPAESI were investigated by TGA at a heating rate of

Table 1
Synthetic data for FPAESI and E-FPAESI.

Polymer	Feed ratio[a]	M_n		M_n/M_w	Yield (%)	T_g (°C)[e]	T_d (°C)[f]
		Calcd[b]	Obsd[c]				
FPAESI 1	0.9390	10,174	11,625	3.17	95	138	445
FPAESI 2	0.9600	15,077	16,055	3.18	96	173	447
FPAESI 3	0.9701	20,047	21,725	2.21	95	177	449
FPAESI 4	0.9762	25,092	25,712	2.04	93	178	450
E-FPAESI 1	0.9480	11,683[d]	12,018[d]	2.59	95	140–188–191[g]	457
E-FPAESI 2	0.9762	25,092[d]	25,067[d]	1.75	97	178–231–245[g]	462

[a] The feed mole ratio of dihydroxy monomer 4/pentafluorophenylsulfide (mol/mol).
[b] Calculated number-average of the molecular weight from the feed ratio {M_n = repeating unit/(1 − feed ratio) + molecular weight of the end groups (pentafluorophenyl sulfide)} [20].
[c] Determined by GPC calibrated with polystyrene standards at 40 °C.
[d] The molecular weights of E-FPAESIs were measured before crosslinking.
[e] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen (second scan).
[f] Onset temperature for 5% weight loss measured by TGA with a heating rate of 10 °C/min in air.
[g] Glass transition temperatures with changing scan number (first - second - third scan).

10 °C/min in air, and the results are shown in Table 1. Polymers with similar molecular weight with and without the crosslinkable end-capping moiety were studied for T_d, and the results are shown in Fig. 5. Although the observed molecular weight of E-FPAESI (E-FPAESI 2) was lower than that of FPAESI (FPAESI 4), E-FPAESI exhibited higher thermal stability than FPAESI due to the cross-linked structure [30].

3.4. Optical properties

The polymer used as the core material must have a higher refractive index than that of the cladding material according to the device design and waveguide geometry. For either a single-mode or multi-mode waveguide, the appropriate index difference between the core and the cladding is strongly dependent on the dimension of the waveguide and the wavelength of the light source [8].

The replacement of C–H bonds with C–F bonds has been reported to give a high optical transparency of the polymeric material in the near-infrared (NIR) telecommunication region [7–9,32,33,35]. The refractive index could change with the free volume
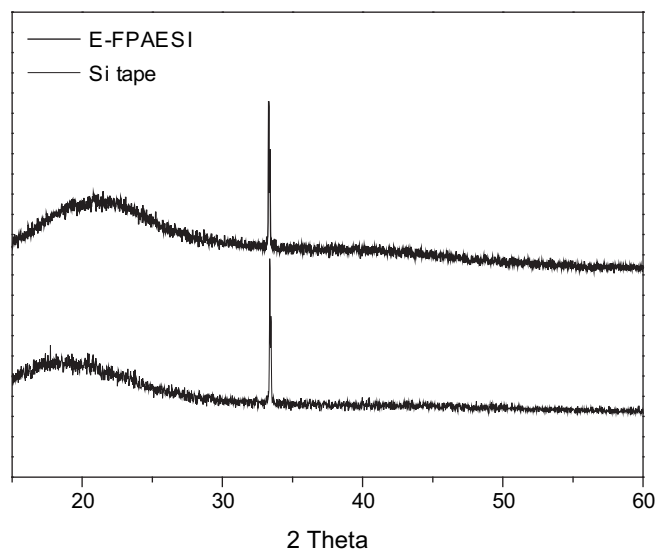

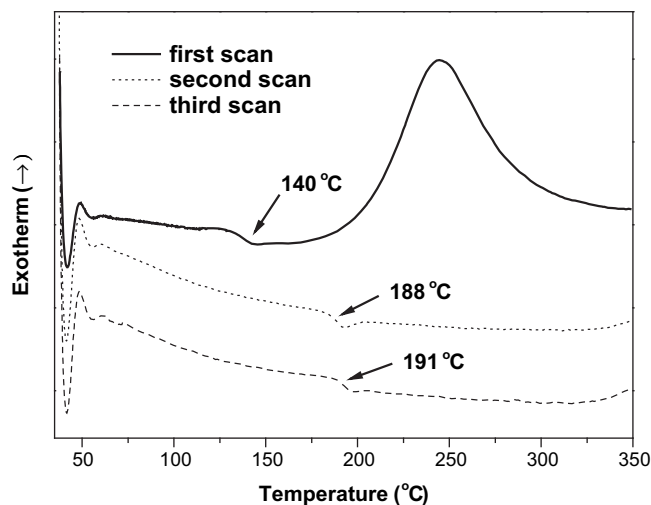**Fig. 3.** XRD data of E-FPAESI (solid) and silicon wafer (dot).

Fig. 4. Effect of the degree of curing on the T_g of E-FPAESI 1 (M_n: 12,018) bearing the crosslinkable ethynyl moiety.
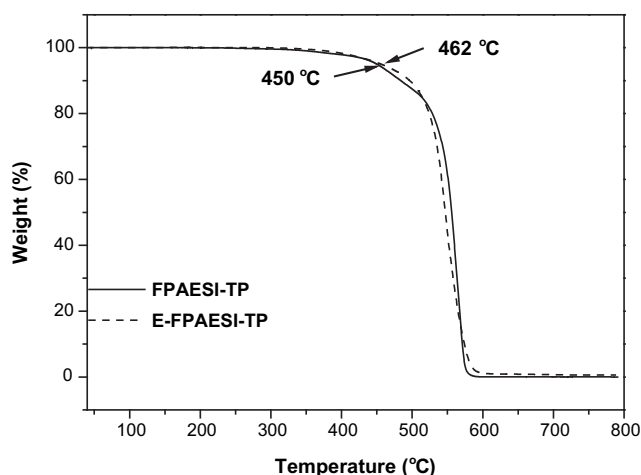
Fig. 5. TGA of FPAESI 4 (M_n: 25,712) and E-FPAESI 3 (M_n: 25,067).

Fig. 6. Schematic representation of the model of E-FPAESI, before thermal curing (a), and after thermal curing (b) at 270 °C for 2 h.

(packing density), polarizability of the material, temperature, and humidity. However, the birefringence ($\delta n = n_{TE} - n_{TM}$, where n_{TE} and n_{TM} represent the transverse electric and transverse magnetic nodes in the waveguide, respectively) is related to the optical anisotropic ratio (δ) of linear polarizability (microscopic view) and the molecular orientations (Ω) in the bulk material (marcroscopic view) [7–10,32,33,35]. Recently, various effective factors on birefringence have been investigated, including spin-coating and thermal treatment conditions, substrate material, film thickness, humidity and the solvent used [36–41]. All these factors are related to the molecular orientation in the bulk materials.

The refractive indices and the birefringence of the spin-coated fluorinated polymers at 1550 nm, as measured by the prism-coupling method, are shown in Table 2 [39,42]. Because of their preferred orientation of the polymer chain in the direction parallel to the substrate during the spin-coating procedure [36], FPAESIs and E-FPAESIs showed lower values for n_{TM} than n_{TE} compared to other conventional spin-coated polymer films [17–28]. As shown in Table 2, usually the higher the M_n of the polymers is, the lower the refractive index is. The refractive index of fluorinated polymers varied from 1.5849 to 1.5880 depending on the M_n of the fluorinated polymers. The crosslinked polymers (E-FPAESI)s especially behaved such that the refractive indices of the polymers decreased with the increasing M_n of the polymers [17]. But the birefringence of the fluorinated polymers, especially the crosslinked polymers (E-FPAESI)s, showed the opposite tendency to the refractive index [17]. These results support the theory that there is normally a trade-off between the birefringence and the glass transition temperature (T_g). Usually, the high T_g polymers containing a rigid aromatic group, such as poly(arylene ether), polyimide, and per-fluorocyclobutane (PFCB) aryl ether, tend to be orientated during
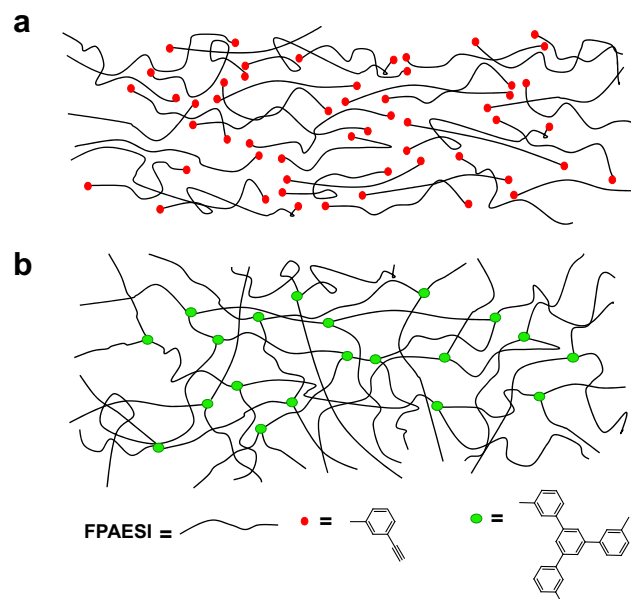
the chemical and physical processes [9,17–28]. Thus, the birefringence exhibited by E-FPAESI was much lower than that of FPAESI [18], due to the crosslinking effect that gives rise to rearrangement as shown in Fig. 6.

Polymers (FPAESI 1 and E-FPAESI 1, or FPAESI 4 and E-FPAESI 2) with similar molecular weights, and with and without a cross-linkable end-capping moiety, were also studied for birefringence, and the results are shown in Table 2. The n_{TE}s of FPAESI 1 and FPAESI 4 corresponding to 1.5880 and 1.5853, respectively, were decreased to 1.5865 and 1.5849, respectively, after crosslinking (E-FPAESI 1 and E-FPAESI 2), while the n_{TM}s of FPAESI 1 and FPAESI 4 corresponding to 1.5845 and 1.5826, respectively, were increased to 1.5851 and 1.5837, respectively. These phenomena are mainly due to the flexible and kinked polymer backbone, whose bond angles are 121° for ether linkage and 108° for sulfide linkage [16], and the *meta*-substituted ethynyl moiety at the polymer chain end [21]. These results indicated that the E-FPAESIs are more amorphous than the FPAESIs, that the films underwent three-dimensional crosslinking with molecular orientation during the crosslinking processing (Fig. 6) [8–10,21,24], and that the bulky pendant phenyl moieties increase the free volume (decrease the packing density) between the E-FPAESI polymer chains [8,9]. This also means that the structure of the polymers changed to become more amorphous after crosslinking. In case of bisphenol-based poly(arylene ether sulfide)s, the birefringence decreased from 3.9×10^{-3} to 2.7×10^{-3} with the increased bulkiness of the bisphenol structure, as in a previous report [43]. Herein, their rigid side diphenyl groups give more disorientation in the bulk state of E-FPAESI, and the birefringence of the E-FPAESIs showed a lower value, in the range of $1.4–1.8 \times 10^{-3}$ in comparison with other reported E-FPAESIs.

In our research, the birefringence of fluorinated polymers showed a tendency opposite that of the T_g of the polymers. The birefringences of polymers were in the range of 0.0014–0.0035 (Table 2). E-FPAESIs showed lower birefringences compared to the reported fluorinated poly(arylene ether sulfide)s and fluorinated polyimides [8–10,14,15]. These results indicate that the E-FPAESI is good candidate as a core material for the optical waveguide.

Table 2
Refractive indices and birefringences of the fluorinated polymers at 1550 nm.

Polymer	Refractive index			$n_{TE} - n_{TM}$ ($\times 10^{-3}$)[b]
	TE mode (n_{xy})	TM mode (n_z)	n[a]	
FPAESI 1	1.5880	1.5845	1.5868	3.5
FPAESI 2	1.5855	1.5824	1.5845	3.1
FPAESI 3	1.5861	1.5827	1.5850	3.4
FPAESI 4	1.5853	1.5826	1.5844	2.7
E-FPAESI 1	1.5865	1.5851	1.5860	1.4
E-FPAESI 2	1.5849	1.5837	1.5845	1.8

[a] Average refractive index, $n = (2nxy + nz)/3$.
[b] Birefringence.

4. Conclusion

The crosslinkable fluorinated poly(arylene ether sulfide) (E-FPAESI) was successfully synthesized for polymeric optical waveguide materials via the step-growth polymerization of a rigid dihydroxy monomer **4** with pentafluorophenyl sulfide, followed by the reaction with 3-ethynylphenol as a thermal crosslinkable end group. The bulky and rigid dihydroxy monomer **4** was designed for reducing the refractive index and birefringence while maintaining a high T_g of the polymer. Furthermore, in order to lower the birefringence as well as improve the thermal stability, the ethynyl moiety at the polymer chain end was introduced. After crosslinking, the polymer films were not soluble in any common organic solvents. The T_g of E-FPAESI increased with an increasing degree of crosslinking. The refractive indices of the polymer films were in the range of 1.5849–1.5880. The birefringence of the crosslinked polymer films was much lower than that of non-crosslinked polymer films, due to its being more amorphous. These results indicate that the E-FPAESI is a good candidate as a core and cladding material for optical waveguide devices.

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