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Fluorinated poly(arylene ether sulfone)s for polymeric optical waveguide devices

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Abstract

Pentafluorophenyl sulfone was prepared by oxidation of pentafluorophenyl sulfide. Ethynyl terminated fluorinated poly(arylene ether sulfone) (EFPAESO) was synthesized via nucleophilic aromatic substitution from 4,4′-(hexafluoroisopropylidene) diphenol or 4,4′-(trifluoromethylphenylisopropylidene) diphenol with an excess of pentafluorophenyl sulfone, followed by reaction with 3-ethylnylphenol. The molecular weights (M_ns) of the polymers determined by GPC with polystyrene standard were in the range of 6,400–17,200 and polydispersities (M_w/M_ns) were in the range of 2.25–3.19. This EFPAESO showed very high thermal stability up to 479 °C for 5% weight loss in TGA in air. T_g of the polymer was changed from 148 to 196 °C after curing. The cured films showed good chemical resistance and high thermal-stability. At 1550 nm wavelength, the refractive indices of the copolymer films were in the range of 1.5037–1.5504 and birefringences were in the range of 0.0021–0.0025. The optical loss for EFPAESO was less than 0.37 dB/cm at 1550 nm wavelength.
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1. Introduction

Poly(arylene ether sulfone) is one of the most important polymer of poly(arylene ether)s that are available commercially. The reasons are that poly(arylene ether sulfone)s have an array of desirable properties including good processability, chemical stability, high thermal-stability, T_g of 180–250 °C, and good solubility in a variety of organic solvents [1–4]. Their properties are caused from a good balance between sulfone groups and ether on polymer backbone. These two groups exhibit different bond angles, 109° for sulfone and 125° for ether group. The combination of these two groups allow flexibility due to ether group and enhancing the thermal-stability due to sulfone group which impart a high dipole moment [5–7].

Fluorine containing polymers are of great interest for use in aerospace, optical and electronic applications because of their unique properties and high temperature performance [8–20]. They have excellent thermal and chemical stability, low dielectric constant, low refractive index, and low moisture absorption [21,22]. Due to these properties, many fluorinated polymers have been studied in last decades. Especially, polymers containing perfluorinated aromatic units have been studied extensively in the last decade because perfluorinated aromatic units increase thermal stability and T_g. They have been studied for applications as films, coatings for optical and microelectronic devices like optical waveguide devices [23].

The present study is focused on the synthesis and characterization of highly fluorinated poly(arylene ether sulfone) (FPAESO) designed from low loss optical waveguide materials containing ethynyl end group as thermal crosslinkable groups. To obtain high molecular weight ethynyl terminated fluorinated poly(arylene ether sulfone) (EFPAESO), the effect of reaction temperature and time was investigated and evaluated in order that these materials can be used as polymers for passive optical waveguide devices.

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2. Experimental

2.1. Materials

Pentafluorophenyl sulfide, potassium carbonate, potassium permanganate, sulfuric acid and acetic acid were purchased from Aldrich Chemical Co. and used without further purification. 3-Ethynyl phenol was synthesized by the reported method [24]. 4,4′-(hexafluoroisopropylidene)-diphenol (6FBPA) was purchased from Fluorochem Chemical Co. and purified by recrystallization from benzene before use. 1,1-Bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (3FBPA) was prepared by previously published procedures [25]. N,N′-dimethylacetamide (DMAc) was purified by vacuum distillation from sodium hydride. Methanol and n-hexane were obtained from Oriental Chemical Industries (Korea) and used as received.

2.2. Characterization

Proton (^{1}H), carbon (^{13}C), and fluorine (^{19}F) NMR spectra were measured on a JEOL JNM-LA 300 WB FT-NMR in CDCl$_3$ or DMSO depending on the solubility of the materials being analyzed. ^{1}H NMR chemical shifts were referenced to tetramethysilane at 0 ppm, ^{13}C NMR chemical shifts were referenced to deuterated chloroform at 77.0 ppm or deuterated DMSO at 49 ppm and ^{19}F NMR chemical shifts were referenced to fluorinated chloroform at 0 ppm, respectively. IR of the monomers and polymers were characterized by using a Perkin–Elmer IR 2000. We confirmed the structure of synthetic monomer through molecular weights by GC/MS (HP 7892). The mass detector was used EI$^+$. Molecular weights of the polymer were analyzed by a size exclusion chromatography (Waters model 515). THF served as a mobile phase. Polymer solutions (concentrations of approx. 2 mg/ml) were filtered with a syringe through a 0.2 μm Teflon membrane filter and injected to styragel columns containing various pore sizes. The chromatography conditions were a 1.0 ml/min flow rate and a temperature of 40 °C for both SEC and detectors. Molecular weights of all samples were calculated by using polystyrene as standard. The thermal properties of resulting polymers were determined with a TA Instrument 2100 series. Thermal degradation temperatures were measured in the range of 40–750 °C and at the heating rate of 10 °C/min. T_g of polymers were measured in the range of 40–250 °C with the heating rate of 5 °C/min. Finally, in order to study the crosslinking behavior of ethynyl terminated polymers, we carried differential scanning calorimetry (DSC) measurement in the range of 40–350 °C. The thickness of the obtained films was measured by a depth profiler (α-step 500). The refractive indices were measured by using the prism-coupling method [26].

### 2.3. Synthesis and purification of pentafluorophenyl sulfone

A two-neck, 100 ml flask, equipped with a condenser, a magnetic stirrer, and a nitrogen inlet adapter, was charged with pentafluorophenyl sulfide (10.00 g, 27.6 mmol), KMnO$_4$ (6.05 g, 4 equiv.), and 120 ml of acetic acid. After 10 min of stirring at room temperature, 15 ml of H$_2$SO$_4$ was slowly dropped while cooling with ice bath. The reaction mixture was then stirred at room temperature for 10 h. The brown reaction mixture was dissolved in 150 ml of water to deactivate of unreacted KMnO$_4$. The product was extracted with methylene chloride and methylene chloride was removed using evaporator. White solid was purified by recrystallization from n-hexane. The product was filtrated, washed twice with n-hexane, and dried to yield white crystals. The yield was more than 95% after purification. Scheme 1 shows the synthetic procedure for pentafluorophenyl sulfone. ^{19}F NMR (CDCl$_3$): δ −132.89 (m, 2F), −138.23 (m, 1F), −154.52 (m, 2F); ^{13}C NMR (CDCl$_3$): δ 136.33 (m, 1C), 139.79 (m, 1C), 143.85 (m, 2C), 147.14 (m, 2C); FT-IR (KBr, cm^{-1}): 1647, 1501 (C=C); 1372, 551 (S=O); 1304, 1102, 995 (C–F); MS (cl): [M + H]$^+$, 398 Da.

2.4. Synthesis of EFPAESO

EFPAESO was synthesized via nucleophilic aromatic substitution of 6FBPA with pentafluorophenyl sulfone. Scheme 2 represents a typical structure of EFPAESO. 6FBPA (2.00 g, 5.95 mmol) and K$_2$CO$_3$ (0.82 g, 1.0 equiv.), in DMAc (24 ml) and benzene (20 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. The benzene was reflux into the Dean–Stark trap. After removing benzene, the reaction mixture was cooled to 80 °C and then pentafluorophenyl sulfone was added. To complete the polymerization reaction, this temperature was maintained for 12 h. In order to attach ethynyl group at the end of polymer, 3-ethynylphenol (0.12 g, 4.00 equiv.), benzene (10 ml) and K$_2$CO$_3$ were added to the reaction mixture and then reaction was continued at 120 °C for 2 h. After removing benzene, the reaction was continued for 2 h. The reaction mixture was cooled and then precipitated into 400 ml of acidic methanol–water (1:1 solution). The polymer was dissolved in dimethylformamide and reprecipitated into methanol, filtered and washed with methanol. The white solid was dried under vacuum at 100 °C for 3 days. The yield of polymer was above 95%; EFPAESO; ^{1}H
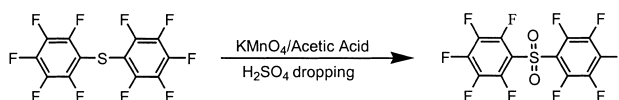
Scheme 1. Synthesis of pentafluorophenyl sulfone.
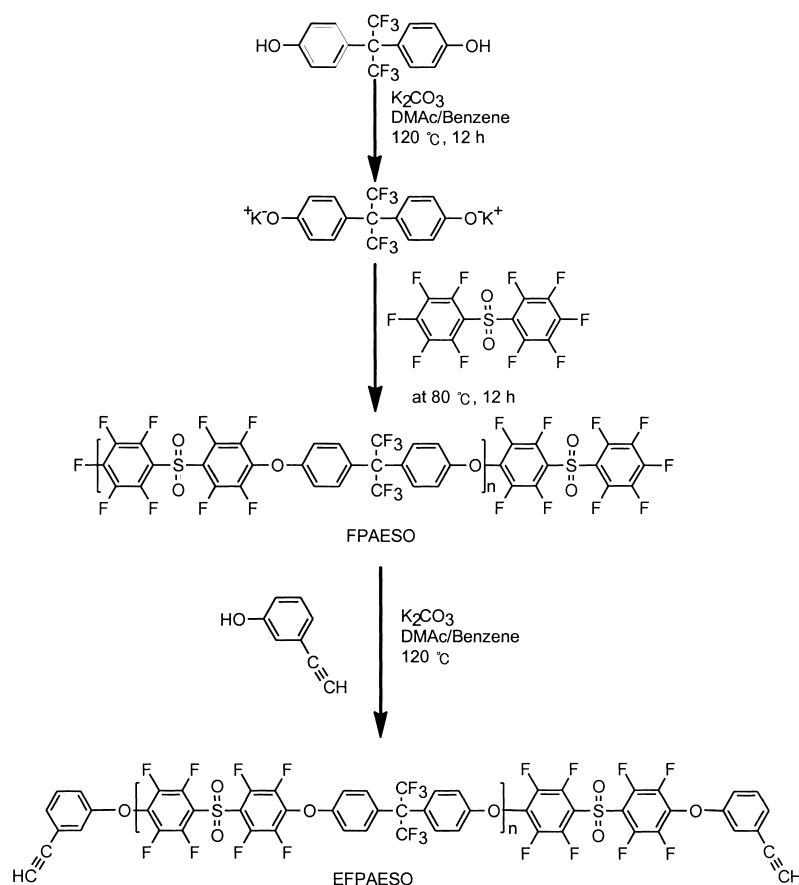
Scheme 2. Synthesis of EFPAESO.

NMR (CDCl$_3$): δ 3.02 (ethynyl H), 6.96, 7.35; ^{19}F NMR (CDCl$_3$): δ −63.3 (b, 6F), −134.5 (b, 2F), −145.5 (b, 2F); ^{13}C NMR (CDCl$_3$): δ 63.7 [−**C**(CF$_3$)$_2$−], 78.9, 81.9 (C of ethynyl), 116.4, 130.8, 131.7, 156.3 (phenyl of 6FBPA), 122.1, 128.2, 128.8 (−CF$_3$), 115.8, 134.7, 139.6, 142.9, 143.6, 147.1 (phenyl of pentafluorophenyl sufone).

2.5. Preparation of copoly(arylene ether sulfone)s

The copolymers were prepared from the two bisphenols, 6FBPA and 3FBPA, with pentafluorophenyl sulfone. The synthetic procedure of copoly(arylene ether sulfide)s was same as described above. Copoly(arylene ether sulfone); ^{1}H NMR (CDCl$_3$): δ 3.03 (ethynyl H), 6.92, 7.11, 7.34; ^{19}F NMR (CDCl$_3$): δ −56.7 (b, 3F), −63.3 (b, 6F), −134.5 (b, 2F), −145.5 (b, 2F); ^{13}C NMR (CDCl$_3$): δ 63.7 [−**C**(CF$_3$)$_2$− and −**C**(CF$_3$)(C$_6$H$_6$)−], 78.9, 81.9 (C of ethynyl), 116.4, 130.8, 131.7, 156.7 (phenyl of 6FBPA), 122.1, 128.2, 128.8 (−CF$_3$), 115.8, 134.7, 139.7, 143.0, 143.6, 147.2 (phenyl of pentafluorophenyl sulfone).

2.6. Preparation of polymer film and thermal curing

EFPAESO was dissolved into cyclohexanone at concentration of 30–40 wt%. Then the solution was filtered with a syringe through a 0.2 μm Teflon membrane filter. The filtered yellow solution was spin coated on the Si wafer substrates at the spin rate of 1,000 rpm for 2 min. After coating, the film was baked at 270 °C for 2 h on a hotplate. Adjusting concentration of polymer solution controlled the film thickness (7–10 μm).

2.7. Measurement of propagation loss

To fabricate single-mode optical waveguides, 4 μm-thick EFPAESO (6FBPA–3FBPA = 8:2, M_n; 17,000) film was spin-coated onto 8.6 μm-thick EFPAESO (6FBPA–3FBPA = 10:0, M_n; 17,200) on Si substrate and baked at 270 °C for 4 h under nitrogen atmosphere. On the EFPAESO (6FBPA–3FBPA = 8:2) layer, 100 nm-thick silicon nitride was deposited by PECVD using SiH$_4$ and N$_2$ at 160 °C. To define the waveguide patterns on the silicon nitride layer, 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 core layer to form ridge waveguide (4.0 μm deep and 6.0 μm wide) by O$_2$ RIE. Finally, an uppercladding layer was formed over the core by spin-coating and curing.

The loss spectrum of the optical waveguides was

measured in the range of 1100–1700 nm. Broad-band light source (HP 83437A) was directly launched into fabricated straight waveguide through the single-mode fiber, and output light was monitored through the single-mode fiber with an optical spectrum analyzer (HP 86140B).

Loss measurements were performed using a laser diode with the 1550 nm wavelength. The propagation losses were obtained by the cutback method [27]. The input light was launched into the device through the single-mode fiber and the output light was end-fired coupled to a photodetector.

3. Result and discussion

3.1. Pentafluorophenyl sulfone

Activated halide monomer (pentafluorophenyl sulfone) (mp 129 °C) was synthesized via the oxidation reaction of pentafluorophenyl sulfide (mp 88–89 °C) as showed in Scheme 1. In ^{19}F NMR, there are three different fluorine atoms. All peaks clearly corresponded to the proposed structure. The peak assigned to the *meta*-fluorine was observed at −154.52 ppm. The *ortho*-fluorine was observed at −132.89 ppm and the *para*-fluorine at −138.23 ppm. The fluorine atoms at *para*- and *meta*- positions were found at the down field comparing with pentafluorophenyl sulfide because of the electron withdrawing group of the sulfonyl group. From mass spectrum, the mother ion of pentafluorophenyl sulfone (398 Da) and pentafluorophenyl (167 Da) were shown. From the above results, we could correctly define pentafluorophenyl sulfone structure.

3.2. EFPAESO

Polycondensation of pentafluorophenyl sulfone (activated dihalide) with 6FBPA in benzene–DMAc mixed solvent was carried out in the presence of potassium carbonate as a condensation agent. The molecular structure of EFPAESO was confirmed by ^{19}F NMR in CDCl$_3$, and compared with 6FBPA and pentafluorophenyl sulfone Fig. 1 shows the ^{19}F NMR spectrum of EFPAESO and there are three fluorine atoms. The peak at −63.33 ppm was due to the hexafluoroisopropyl group of 6FBPA, while the peaks at −134.57 and −145.52 ppm were due to perfluoroaromatic group of pentafluorophenyl sulfone moiety. In ^{19}F NMR spectrum of the polymer, the peak of *para*-fluorine of pentafluorophenyl sulfone was disappeared due to replacement of the fluorine atoms by bisphenate. This result indicates that nucleophilic aromatic substitution had taken place.

The molecular structures of EFPAESO was characterized by FT-IR and compared with FPAESO (Fig. 2). FT-IR spectra of EFPAESO show ethynyl peak at 3316 cm^{-1} after end capping reaction, and the peak was disappeared after curing. While other FT-IR peaks are not affected. This
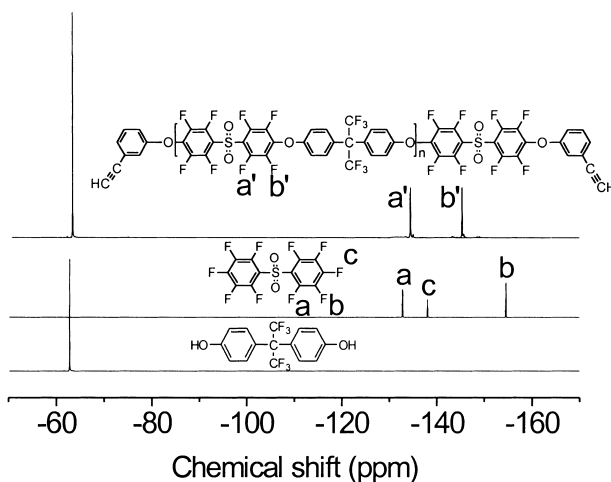

Fig. 1. ^{19}F-NMR of EFPAESO.

indicates that the polymer is very stable at high temperature (270 °C) for 2 h.

3.3. Effect of the molar ratio on the molecular weight

In case of condensation polymerization, the molecular weight of polymer can be controlled by monomer feed ratio [28]. Molecular weight is important for controlling physical properties of polymer. We observed that the molecular weights of EFPAESO 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_ns) and polydispersities (M_w/M_ns) of the resulting EFPAESO were in the range of 6,400–17,200 and 2.25–3.19 with polystyrene standards, respectively. The molecular weights of the resulting polymers could be successfully controlled by the monomer imbalance.

3.4. Thermal properties of polymers

The thermal stability of EFPAESO was investigated by thermogravimetric analysis (TGA) at heating rate of 10 °C/min in air atmosphere. These results are shown in Fig. 3. EFPAESO has high thermal stability and crosslinked
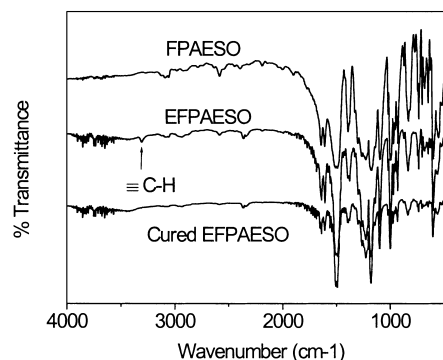

Fig. 2. FT-IR spectra EFPAESO.

Table 1
Molecular weight of EFPAESO depending on monomer feed ratio

	Feed ratio[a]	M_n		M_w/M_n	Yield (%)	T_g (°C)
		Calcd	Obsd			
EFPAESO-1	0.9003	7,164	6,400	2.75	97	148
EFPAESO-2	0.9216	9,164	10,400	2.25	95	156
EFPAESO-3	0.9406	12,164	15,300	3.19	92	164
EFPAESO-4	0.9522	15,164	17,200	2.75	93	172

[a] The feed mole ratio of 6FBPA–Pentafluorophenyl sulfone (mol/mol).

EFPAESO was showed higher thermal degradation temperature. EFPAESO showed a two-step degradation behavior in air. This was due to the sulfone group in the polymer backbone.

The T_g of polymers were measured by DSC at a heating rate of 5 °C/min under nitrogen atmosphere. EFPAESO has high T_g as shown in Table 1. Table 1 shows the molecular weight dependence of T_g of the polymers. As the number average molecular weight of EFPAESO is increased from 6,400 to 17,200, the value of T_g increases from 148 to 172 °C. EFPAESO has high T_g. This occurs as a result of reduction of chain flexibility due to sulfone group. The ether group improves the flexibility, while the sulfone group imparts a high dipole moment and reduced flexibility which enhance the T_g. The chain rigidity is derived from the relatively inflexible and immobile phenyl and sulfone groups. Those properties, along with the high T_g, make possible continuous use in the 150–200 °C range.

3.5. Effect of curing on the thermal properties

It is known that the degree of curing increases, the T_g of polymers increases [23]. In this work, DSC analysis was performed to study the effect of curing on the T_g and the curing properties of the polymers (Fig. 4). As the scan number of DSC increased, the T_g increased from 148 to 196 °C. An intense exothermic peak in the first scan was seen due to the reaction of ethynyl moiety. In the third scan (as the degree of curing was increased), the intense exothermic peak disappeared. This means that the curing
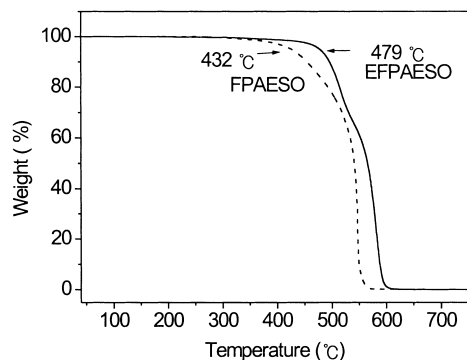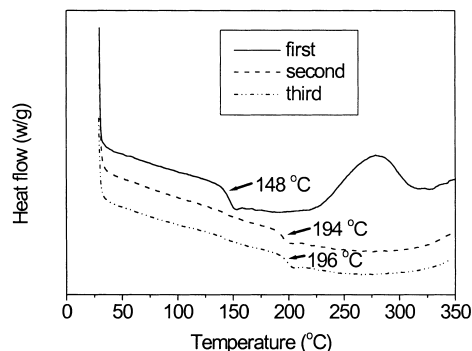

Fig. 4. Effect of the degree of curing on the T_g of EFPAESO (M_w; 6,400) bearing crosslinkable ethynyl moiety.

of ethynyl-terminated polymers was occurred at this temperature.

3.6. Control of refractive index of the cured polymer films

To study the effect of fluorine content on refractive index of EFPAESO, the copolymers were prepared by using different molar ratios of 6FBPA and 3FBPA with pentafluorosulfone. Fig. 5 shows the refractive index of the EFPAESO and their copolymers at 1550 nm. The refractive index of EFPAESO can be controlled from 1.5037 to 1.5504 by changing 6FBPA and 3FBPA content. The birefringences of EFPAESO were in the range of 0.0021–0.0025.

3.7. Optical properties

Fig. 6 shows the near IR light absorption spectrum of a 4.4 cm-long waveguide dependence on wavelength. There are C–H bond vibrational absorption peaks ($2\nu_{C-H}$, 1650 nm and $3\nu_{C-H}$, 1100 nm) and related peak ($2\nu_{C-H} + \delta_{C-H}$, 1400 nm). However, it has small light absorption at telecommunication wavelength of 1300 and 1550 nm due to high fluorine content. To determine the propagation loss of the EFPAESO, measurements were

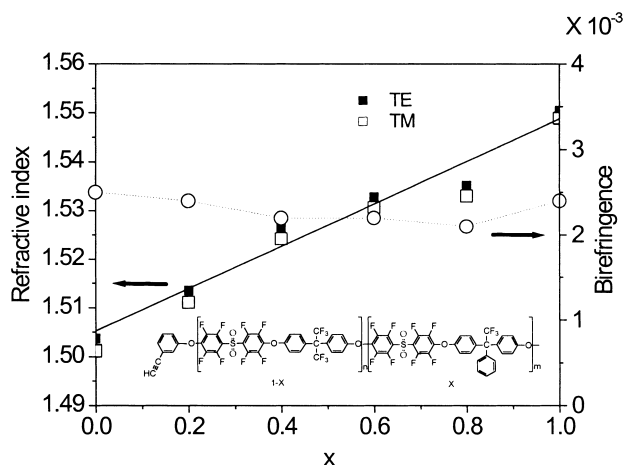Fig. 3. TGA thermograms of the FPAESO and EFPAESO (M_w; 6,400).

Fig. 5. Relationship between the refractive index and dihydroxyl monomer content of EFPAESO.
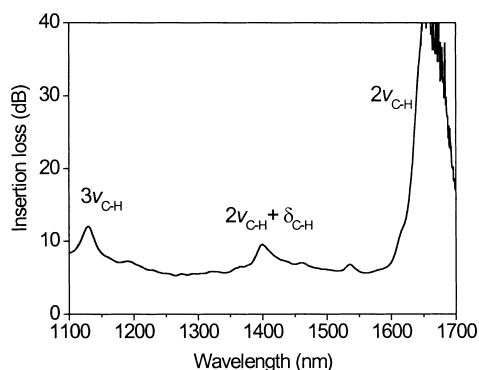
Fig. 6. Near-infrared absorption spectrum of a 4.4 cm-long waveguide.

performed in such single mode channel waveguide at 1550 nm. Fig. 7 shows the relationship between the insertion loss and the waveguide length, which was obtained by the cut-back method at the wavelength of 1550 nm. The insertion loss shows a linear relationship with the waveguide length. The propagation loss, which was obtained from the slope, was less than 0.37 dB/cm. These results indicate that the EFPAESO waveguide has good optical properties at the wavelength of 1550 nm. This propagation loss of EFPAESO is comparable to that of poly(arylene ether sulfide) (0.4 dB/cm) [24]. Fig. 7 shows a typical near field pattern from a straight waveguide with the dimension of $4 \times 6 \ \mu m^2$ at 1550 nm. This pattern has a Gaussian intensity distribution, indicating that the optical waveguides operate in single mode.

The key requirements of optical waveguide materials include low optical loss in infrared region, high thermal stability, refractive index controllability and low birefringence. Especially, low birefringence is most important requirement in application of a wavelength division multiplex system, because the optical components having the high birefringenc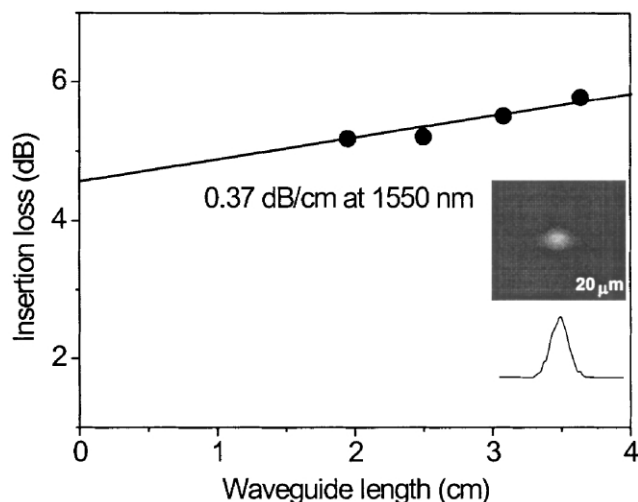e show a high polarization dependent loss (PDL) that cause a degradation of the transmission quality or a failure of the optical system. Therefore, optical polymers require low birefringence to achieve low PDL. The birefringence (0.0021–0.0025) of EPAESO is much lower than other poly(arylene ether)s such as poly(arylene ether sulfide) [24] and poly(arylene ether)s [29]. However, the optical loss of EPAESO is similar to other poly(arylene ether)s in the range of < 0.4 dB/cm, which is low enough to apply to optical components.

4. Conclusions

Single mode optical waveguides have been fabricated by using crosslinkable fluorinated poly(arylene ether sulfone)s [EFPAESO]. IR regions of transparence exist near 1300 and 1550 nm, the wavelength of interest for telecommunication. The refractive indices of the cured polymer films could be successfully controlled from 1.5037 to 1.5504 in the combination of 6FBPA and 3FBPA. The birefringence of EFPAESO copolymers was 0.0021–0.0025. These are much lower than those of fluorinated polyimides for optical waveguides [11]. EFPAESO had very low value of 0.37 dB/cm for propagation loss at 1550 nm. This result indicates that the EFPAESO is a good candidate as a core and cladding material for the optical waveguide devices.

Acknowledgements

Fig. 7. Effect of waveguide length on optical loss of the fabricated waveguide at 1550 nm.

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