

## Direct UV-written highly fluorinated aromatic-aliphatic copolyethers for optical waveguides

Ying Wan<sup>a</sup>, Yang Zhang<sup>b</sup>, Zuosen Shi<sup>a</sup>, Wenhui Xu<sup>a</sup>, Xiaolong Zhang<sup>a</sup>, Lisha Zhao<sup>a</sup>, Zhanchen Cui<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Supermolecular Structure and Materials, Jilin University, Changchun 130012, PR China

<sup>b</sup> Beijing Research Institute of Chemical Industry, SINOPEC, Beijing 100013, PR China

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### ABSTRACT

A bisphenol monomer (4-methoxy) phenylhydroquinone (Me-HQ) was prepared and further polymerized with 2,2,3,3,4,4,5,5,6,6,7,7-dodeca-fluoro-1,8-octanediol (12F-diol) and decafluorobiphenyl (DFBP) to obtain highly fluorinated aromatic-aliphatic copolyethers containing methoxy groups. After demethylation and the reaction with epoxy chloropropane, a series of novel highly fluorinated aromatic-aliphatic copolyethers bearing epoxy groups (FA-APE EP) at different feed ratios of (Me-HQ)/(12F-diol) were obtained. The chemical structures of all the copolymers were analyzed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra. A series of highly fluorinated photoresists were prepared by composing of fluorinated copolyethers, diphenyliodonium salt as a photoacid generator (PAG) and solvent. After UV-curing, the cross-linked films exhibited excellent chemical resistance and high thermal stability (*T<sub>d</sub>* ranged from 230 to 278 °C). The refractive indices of the films could be controlled between 1.5127 and 1.4749 at 1550 nm by varying the feed ratio of comonomers. A clear negative pattern was obtained through direct UV exposure and chemical development. For waveguides without upper cladding, the propagation loss of the channel waveguides was measured to be 0.18 dB/cm at 1550 nm.

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### 1. Introduction

Organic polymers appear to be promising candidates for optical waveguide devices due to their easy processability, low cost fabrication potential, and structure-property tenability [1–4]. Various techniques such as reactive ion-beam etching, photobleaching and ion-implantation processes have been used to fabricate polymeric channel waveguides. However, these methods involve many processing steps and can lead to long fabrication time and low yield [5,6]. Compared to these techniques, direct UV photolithographic process exhibits more advantageous, due to its low cost, high yield and large dimension fabrication [7,8]. In order to fabricate polymeric waveguides using direct UV photolithography process, stable UV-curable polymers with high optical transparency in the infrared wavelength region is an important factor [9–12]. NANO™ SU-8 2000 is a chemically amplified negative photoresist, which is used widely as both the waveguide core and the grating structures, but the optical loss of this material at 1550 nm is above 1 dB/cm due to the high overtone absorptions of the C–H bonds [13–16]. It is

well known that using fluorine atom to replace hydrogen atom in the polymer can theoretically reduce the intrinsic optical loss by about 5 orders of magnitude at telecommunication wavelength region (1.3 and 1.55 μm) [17–21]. As a result, fluorinated polymers have been considered to be one of the potential candidates for optical applications [22–25].

Among all the fluorinated polymers, fluorinated poly(arylene ether)s are well known as candidates for optical materials because of their low optical loss, low moisture absorption, easy processability, high chemical and thermal stability [26–29]. However, most of the polymers from this type developed so far are only partially fluorinated materials with relatively low fluorine contents because of the use of non-fluorinated or partially fluorinated bisphenols for polymer preparation. This limitation hampers the potential to further reduce the intrinsic optical loss at communications wavelength of this series of polymers. Recently, Ding et al have successfully prepared a series of highly fluorinated aromatic-aliphatic copolyethers by copolycondensation of decafluorodiphenylsulfone with bisphenol and highly fluorinated diols [21]. The resulting copolyethers exhibited improved thermal stability, and the refractive indexes of these copolyethers could be controlled by varying the feed ratio. However, due to no cross-linkable groups existing in the polymers, well-developed waveguide structures with smooth ridge walls from these polymers could only be demonstrated using a soft

\* Corresponding author. College of Chemistry, Jilin University, 2699 Qianjin Road, Changchun 130012, PR China. Tel.: +86 431 85168217; fax: +86 431 85193423.  
E-mail address: [cuizc@jlu.edu.cn](mailto:cuizc@jlu.edu.cn) (Z. Cui).

lithography technique. Compared to direct UV photolithographic process, the soft lithography technique shows many disadvantages such as high cost, difficult preparation technology and so on. Therefore, it seems more meaningful to obtain optical waveguide materials which can be directly UV-cured, by introducing cross-linkable groups into the highly fluorinated copolyethers system.

This study focuses on the synthesis of highly fluorinated aromatic-aliphatic copolyethers containing epoxy group with a goal of achieving optical clarity at the telecommunication wavelength region and being directly UV-cured. Highly fluorinated copolyethers containing methoxy groups were first prepared, and then the methoxy groups were converted to reactive hydroxy groups, which reacted with epoxy chloropropane resulting in copolyethers bearing epoxy groups (FA-APE EP). We introduced a simple process for fabricating the low loss waveguides by composing of fluorinated polyethers, diphenyliodonium salt as a photoacid generator (PAG) and solvent. After coating on the Si/SiO<sub>2</sub> wafer and exposing to UV light (200–300 nm), highly cross-linked structure was formed for the FA-APE EP resist. The cross-linking density and refractive index could be controlled by varying the ratios of bisphenol and diols.

## 2. Experimental section

### 2.1. Materials

2,2,3,3,4,4,5,5,6,6,7,7-dodeca-fluoro-1,8-octanediol (12F-diol), Decafluorobiphenyl (DFBP), (4-methoxy)aniline, diphenyliodonium hexafluorophosphate (PI), 1,4-benzoquinone were purchased from ABCR, Fluka and Aldrich and used without further purification. Epoxy chloropropane and other reagents were purchased from Beijing Chemical Co. (Beijing, China). All of the solvents were used after purification according to conventional methods.

### 2.2. Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 500 MHz for <sup>1</sup>H, 125 MHz for <sup>13</sup>C, and 470 MHz for <sup>19</sup>F. The chemical shifts relative to tetramethylsilane (TMS) for <sup>1</sup>H NMR, <sup>13</sup>C NMR and CFCl<sub>3</sub> for <sup>19</sup>F NMR as internal reference were reported on the ppm scale. For <sup>13</sup>C NMR, in order to yield the signal and multiplicity information for all carbon types including the signals of quaternary carbons, a pulse sequence DEPTQ experiment was performed. IR spectra (KBr) were taken on an AVATAR 360 transform infrared (FT-IR) spectrophotometer. Elemental analysis was performed by Shanghai Institute Organic Chemistry. The molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography-Refractive index-Multi-angle laser light scattering detection (GPC-RI-MALLS) techniques on a Waters 410 GPC, Optilab rex and wyatt DAWN HELEOS with tetrahydrofuran (THF) as the solvent at 25 °C at a flow rate of 1.0 mL/min using polystyrene as a standard. Differential scanning calorimetry (DSC) was performed with NETZSCH 4 at a scan rate of 10 °C/min under nitrogen. Thermal stability, as measured by 5% weight loss of the polymer samples, was analyzed using Perkin–Elmer TGA-7 analyzer at a heating rate of 10 °C/min in nitrogen. Atomic force microscopy (AFM) observations of the film surfaces were carried out with a commercial instrument (Digita Instrument, Nanoscope IIIa, Multimode) under ambient conditions at room temperature. All tapping mode images were measured at room temperature in air with the microfabricated rectangle crystal silicon cantilevers (Nanosensor). The topography images were obtained at a resonance frequency of approximately 365 kHz for the probe oscillation. Refractive index measurements were done using an M-2000VI ellipsometer (J.A. Woolam Co., Inc).

The UV–vis–NIR absorption spectrum was recorded on SHIMADZU UV-3600 spectrophotometer (slit width 5 nm). Scanning electron microscopy (SEM) was performed on a JEOL FESEM 6700F electron microscope with primary electron energy of 3 kV.

### 2.3. Synthesis of monomer and copolymers

#### 2.3.1. Synthesis of (4-methoxy)phenylhydroquinone (Me-HQ)

(4-methoxy)phenylhydroquinone (Me-HQ) was prepared by the procedure previously reported (Scheme 1) [30]. First, the (4-methoxy)phenylbenzoquinone (Me-BQ) was prepared from (4-methoxy)aniline and 4-benzoquinone. Yield: 90%. Mp: 114–115 °C. *m/z*: 214. IR (KBr, cm<sup>-1</sup>): 1651 (C=O), 2970 (-OCH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 7.54 (2H, d), 7.02 (2H, d), 6.94 (1H, d), 6.89 (2H, d), 3.81 (3H, s). Then the (4-methoxy)phenylhydroquinone (Me-HQ) was obtained by reduction with Zn and HCl. Yield: 62%. Mp: 113–114 °C. *m/z*: 216. IR (KBr, cm<sup>-1</sup>): 3385 (-OH), 2970 (-OCH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, DMSO, TMS): δ (ppm) 8.49 (2H, d), 7.47 (2H, m), 6.93 (2H, m), 6.72 (1H, m), 6.67 (1H, d), 6.51 (1H, m), 3.79 (3H, s). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>: C, 72.22; H, 5.56. Found: C, 71.32; H, 4.86.

#### 2.3.2. Synthesis of highly fluorinated aromatic-aliphatic copolyethers containing methoxy group (FA-APE Me)

A typical synthetic procedure for the preparation of **FA-APE Me 1** is as follows. decafluorobiphenyl (3.34 g, 10 mmol), Me-HQ (2.16 g, 10 mmol) and CsF (4.55 g, 30 mmol) were added into a 100 mL three-neck flask equipped with a magnetic stirrer, a condenser and a nitrogen inlet. Then, 30 mL dimethylacetamide (DMAc) was charged into the reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 50 °C and maintained at this temperature for 6 h. After filtration to remove inorganic salt, the polymer solution was added dropwise into HCl/methanol (0.5 mL/200 mL) with stirring. The resulting white precipitate was collected by filtration, washed thoroughly with methanol, and dried at room temperature under vacuum.

Yield: 95.3%. *M<sub>n</sub>* = 10733; *M<sub>w</sub>/M<sub>n</sub>* = 1.46. IR (KBr, cm<sup>-1</sup>): 3020 (-CH<sub>3</sub>), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 7.52 (2H, d, 8.5 Hz), 7.13 (1H, s), 6.99 (2H, s), 6.97 (2H, s), 3.85 (3H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 160.0, 153.7, 150.6, 146.2, 144.2, 143.1, 142.5, 141.1, 140.5, 136.4, 135.9, 133.6, 130.8, 128.7, 119.2, 117.5, 115.9, 114.3, 103.2, 102.2, 55.7. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>): δ (ppm) -138.1 (4F, m), -153.3 (4F, m). Anal. Calcd for C<sub>25</sub>H<sub>10</sub>F<sub>8</sub>O<sub>3</sub>: C, 58.82; H, 1.96, F, 29.80. Found: C, 58.75; H, 1.98; F, 30.29.

The other copolymers from both decafluorobiphenyl, Me-HQ and 12F-diol with the corresponding feed ratio of [Me-HQ]/[Me-HQ + 12F-diol] were prepared using the same procedure outlined above listed in Table 1. Their characterizations are as follows.

**FA-APE Me 2.** Yield: 92.6%. *M<sub>n</sub>* = 10625; *M<sub>w</sub>/M<sub>n</sub>* = 2.03. IR (KBr, cm<sup>-1</sup>): 3020 (-CH<sub>3</sub>), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 7.51 (6H, m), 7.12 (3H, s), 6.97 (6H, s), 6.96 (6H, s), 4.74 (4H, m), 3.84 (3H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 160.0, 153.7, 150.6, 146.1, 144.1, 143.1, 142.4, 141.1, 140.4, 139.3, 136.4, 136.0, 133.6, 130.8, 128.7, 119.2, 117.6, 115.9, 114.3, 103.2, 102.3, 70.4, 55.7. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>): δ (ppm) -122.4 (12F, m), -138.9 (16F, m), -153.4 (16F, m). Anal. Calcd for C<sub>95</sub>H<sub>34</sub>F<sub>44</sub>O<sub>11</sub>: C, 52.15; H, 1.55; F, 38.24. Found: C, 53.25; H, 1.48; F, 39.12.

**FA-APE Me 3.** Yield: 95.1%. *M<sub>n</sub>* = 11636; *M<sub>w</sub>/M<sub>n</sub>* = 1.96. IR (KBr, cm<sup>-1</sup>): 3020 (-CH<sub>3</sub>), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 7.50 (2H, d, 10 Hz), 7.11 (1H, s), 6.97 (2H, s), 6.95 (2H, s), 4.79 (4H, m), 3.83 (3H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS): δ (ppm) 160.0, 153.7, 150.6, 146.1, 144.1, 143.1, 142.3, 141.1, 140.3, 138.2, 136.5, 136.0, 133.6, 130.8, 128.7, 119.2, 117.6, 115.9, 114.2, 103.2, 102.3, 70.4, 55.7. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>): δ (ppm) -122.6



Scheme 1. Synthesis of (4-methoxy)phenylhydroquinone (Me-HQ).

(12F, m),  $-138.5$  (8F, m),  $-153.5$  (8F, m). Anal. Calcd for  $C_{45}H_{14}F_{28}O_5$ : C, 46.31; H, 1.20; F, 45.45. Found: C, 47.22; H, 1.41; F, 43.64.

**FA-APE Me 4.** Yield: 93.6%.  $M_n = 11257$ ;  $M_w/M_n = 1.78$ . IR (KBr,  $cm^{-1}$ ): 3020 (–CH<sub>3</sub>), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>, TMS):  $\delta$  (ppm) 7.52 (2H, d, 10 Hz), 7.11 (1H, s), 6.99 (2H, s), 6.97 (2H, s), 4.20 (12H, m), 3.84 (3H, s). <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>, TMS):  $\delta$  (ppm) 160.2, 154.0, 150.6, 146.0, 144.0, 143.3, 142.6, 141.3, 140.7, 138.5, 135.8, 133.4, 130.8, 128.5, 118.7, 118.0, 116.0, 114.2, 102.9, 101.9, 70.4, 55.1. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-122.3$  (36F, m),  $-138.5$  (16F, m),  $-153.6$  (16F, m). Anal. Calcd for  $C_{85}H_{22}F_{68}O_9$ : C, 41.16; H, 0.89; F, 52.14. Found: C, 42.11; H, 1.00; F, 53.25.

### 2.3.3. Synthesis of highly fluorinated aromatic-aliphatic copolyethers containing hydroxyl group (FA-APE OH)

A typical synthetic procedure for the preparation of **FA-APE OH 1** is as follows. 1.0 g FA-APE Me 1 was dissolved into 20 mL CH<sub>2</sub>Cl<sub>2</sub> in a 100 mL three-neck flask equipped with a magnetic stirrer and a nitrogen inlet. The solution was cooled down to 0 °C (ice bath) and 1 mL BBr<sub>3</sub> dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. Then the mixture was poured into 200 mL methanol, and the obtained copolyether was filtered and washed with methanol and deionized water several times. Finally, the resulting copolymers were dried at room temperature under vacuum for 48 h.

Yield: 90.2%  $M_n = 10736$ ;  $M_w/M_n = 2.05$ . IR (KBr,  $cm^{-1}$ ): 3460 (–OH), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, DMSO, TMS):  $\delta$  (ppm) 9.65 (1H, s), 7.40 (2H, d, 8 Hz), 7.33 (1H, s), 7.29 (1H, s), 7.19 (1H, s), 6.84 (2H, d, 10 Hz). <sup>13</sup>C NMR (125 MHz, DMSO, TMS):  $\delta$  (ppm) 158.4, 153.8, 150.4, 146.2, 144.2, 143.1, 142.6, 141.4, 140.6, 136.3, 135.9, 133.4, 131.2, 126.7, 119.0, 118.7, 116.4, 116.1, 102.8, 102.0. <sup>19</sup>F NMR (470 MHz, DMSO, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-138.2$  (4F, m),  $-153.4$  (4F, m). Anal. Calcd for  $C_{24}H_8F_8O_3$ : C, 58.06; H, 1.61, F, 30.65. Found: C, 58.74; H, 1.90; F, 30.33.

**PA-AE OH 2.** Yield: 93.4%.  $M_n = 10225$ ;  $M_w/M_n = 1.92$ . IR (KBr,  $cm^{-1}$ ): 3460 (–OH), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, DMSO,

TMS):  $\delta$  (ppm) 9.65 (3H, s), 7.40 (6H, d, 5 Hz), 7.34 (3H, s), 7.30 (3H, s), 7.20 (3H, d, 10 Hz), 6.85 (6H, d, 10 Hz), 5.24 (4H, s). <sup>13</sup>C NMR (125 MHz, DMSO, TMS):  $\delta$  (ppm) 158.4, 153.8, 150.5, 146.2, 144.2, 143.2, 142.6, 141.2, 140.6, 136.3, 135.7, 133.3, 131.2, 126.7, 119.0, 118.7, 116.3, 116.1, 102.7, 102.0, 70.4. <sup>19</sup>F NMR (470 MHz, DMSO, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-122.5$  (12F, m),  $-138.5$  (16F, m),  $-153.4$  (16F, m). Anal. Calcd for  $C_{92}H_{28}F_{44}O_{11}$ : C, 51.49; H, 1.31, F, 38.99. Found: C, 53.03; H, 1.30; F, 36.22.

**PA-AE OH 3.** Yield: 94.1%.  $M_n = 11261$ ;  $M_w/M_n = 1.85$ . IR (KBr,  $cm^{-1}$ ): 3460 (–OH), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, DMSO, TMS):  $\delta$  (ppm) 9.66 (1H, s), 7.40 (2H, d, 5 Hz), 7.34 (1H, s), 7.29 (1H, d, 5 Hz), 7.20 (1H, s), 6.84 (2H, d, 5 Hz), 5.26 (4H, s). <sup>13</sup>C NMR (125 MHz, DMSO, TMS):  $\delta$  (ppm) 158.4, 153.8, 150.5, 146.2, 144.2, 143.8, 142.6, 141.2, 140.6, 138.5, 136.3, 133.3, 131.2, 126.7, 119.0, 118.6, 116.4, 116.1, 102.7, 102.0, 70.4. <sup>19</sup>F NMR (470 MHz, DMSO, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-122.6$  (12F, m),  $-138.5$  (8F, m),  $-153.5$  (8F, m). Anal. Calcd for  $C_{44}H_{12}F_{28}O_5$ : C, 45.83; H, 1.04, F, 46.18. Found: C, 46.12; H, 1.13; F, 46.02.

**PA-AE OH 4.** Yield: 91.4%.  $M_n = 11602$ ;  $M_w/M_n = 1.73$ . IR (KBr,  $cm^{-1}$ ): 3460 (–OH), 1120–1300 (C–F). <sup>1</sup>H NMR (500 MHz, DMSO, TMS):  $\delta$  (ppm) 9.66 (1H, s), 7.40 (2H, d, 5 Hz), 7.35 (1H, s), 7.29 (1H, d, 5 Hz), 7.20 (1H, s), 6.84 (2H, d, 5 Hz), 5.26 (12H, s). <sup>13</sup>C NMR (125 MHz, DMSO, TMS):  $\delta$  (ppm) 158.4, 153.8, 150.5, 146.2, 144.3, 143.9, 142.6, 141.2, 140.6, 138.5, 136.3, 133.3, 131.2, 126.6, 119.0, 118.6, 116.4, 116.1, 102.6, 102.1, 70.4. <sup>19</sup>F NMR (470 MHz, DMSO, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-122.4$  (36F, m),  $-138.5$  (16F, m),  $-153.6$  (16F, m). Anal. Calcd for  $C_{84}H_{20}F_{68}O_9$ : C, 40.91; H, 0.81; F, 52.44. Found: C, 42.14; H, 0.96; F, 53.11.

### 2.3.4. Synthesis of highly fluorinated aromatic-aliphatic copolyethers containing epoxy group (FA-APE EP)

FA-APE OH (5.10 g, 0.01 mol hydroxyl groups) and epoxy chloropropane (20 g, 0.216 mol) were added into a 100 mL three-necked flask equipped with a mechanical stirrer and a water condenser. The mixture was heated to 60 °C with stirring, and this temperature was maintained for 6 h. During this time, sodium hydroxide (0.80 g, 0.02 mol) was added every half hour. The excess of epoxy chloropropane was distilled off under reduced pressure. The reaction mixture was cooled to room temperature and then dissolved in benzene (40 mL). The resulting sodium chloride was removed by filtration with a glass filter, then benzene was distilled. The obtained copolymer was washed with methanol and dried at room temperature under vacuum.

Yield: 91.7%.  $M_n = 10961$ ;  $M_w/M_n = 1.86$ . IR (KBr,  $cm^{-1}$ ): 1120–1300 (C–F), 929.3 ( $\Delta$ ). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 7.49 (2H, d, 10 Hz), 7.33 (1H, s), 7.29 (1H, s), 7.19 (1H, s), 6.88 (2H, d, 10 Hz), 4.27 (1H, d, 10 Hz), 4.03 (1H, s), 3.41 (1H, s), 2.92 (1H, s), 2.76 (1H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 158.4, 153.8, 150.1, 145.7, 143.7, 142.7, 141.9, 140.7, 139.9, 136.1, 135.5, 133.0, 130.5, 128.9, 118.8, 117.2, 115.6, 114.6, 101.8, 68.8, 50.1, 44.7. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>):  $\delta$  (ppm)  $-138.2$  (4F, m),  $-153.4$  (4F, m). Anal. Calcd for  $C_{27}H_{12}F_8O_4$ : C, 58.70; H, 2.17, F, 27.54. Found: C, 58.54; H, 2.21; F, 39.31.

**FA-APE EP 2.** Yield: 94.3%.  $M_n = 11726$ ;  $M_w/M_n = 2.33$ . IR (KBr,  $cm^{-1}$ ): 1120–1300 (C–F), 929.8 ( $\Delta$ ). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,

**Table 1**  
Characterization of the fluorinated aromatic-aliphatic copolyethers.

Copolymer	12F-diol in feed (mol%) <sup>a</sup>	Yield (%)	12F-diol conversion (mol%)	$M_n^b$	$M_w/M_n$
PA-AE Me 1	0	95.3	—	10,733	1.46
PA-AE Me 2	25	92.6	93.1	10,625	2.03
PA-AE Me 3	50	95.1	94.2	11,636	1.96
PA-AE Me 4	75	93.6	94.1	11,257	1.78
PA-AE OH 1	0	90.2	—	10,736	2.05
PA-AE OH 2	25	93.4	91.9	10,225	1.92
PA-AE OH 3	50	94.1	93.7	11,261	1.85
PA-AE OH 4	75	91.4	92.4	11,602	1.73
PA-AE EP 1	0	91.7	—	10,961	1.86
PA-AE EP 2	25	94.3	93.6	11,726	2.33
PA-AE EP 3	50	92.5	94.3	12,989	2.38
PA-AE EP 4	75	90.4	91.6	11,829	1.58

<sup>a</sup> Molar ratio of [12F-diol]/[Me-HQ + 12F-diol].

<sup>b</sup> Number average molecular weight determined by GPC.

TMS):  $\delta$  (ppm) 7.50 (6H, d, 10 Hz), 7.11 (3H, s), 6.99 (12H, d, 10 Hz), 4.76 (4H, s), 4.26 (3H, d, 10 Hz), 4.00 (3H, s), 3.36 (3H, s), 2.91 (3H, s), 2.76 (3H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) 158.5, 153.3, 150.1, 145.7, 143.7, 142.7, 141.9, 140.7, 139.9, 138.0, 136.1, 135.5, 133.0, 130.5, 128.9, 118.8, 117.2, 115.6, 114.6, 101.8, 70.0, 68.8, 50.1, 44.7.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ):  $\delta$  (ppm)  $-122.5$  (12F, m),  $-138.5$  (16F, m),  $-153.4$  (16F, m). Anal. Calcd for  $\text{C}_{101}\text{H}_{40}\text{F}_{44}\text{O}_{14}$ : C, 52.42; H, 1.73, F, 36.16. Found: C, 53.04; H, 1.65; F, 34.32.

**FA-APE EP 3.** Yield: 92.5%.  $M_n = 12989$ ;  $M_w/M_n = 2.38$ . IR (KBr,  $\text{cm}^{-1}$ ): 1120–1300 (C–F), 929.8 ( $\Delta$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) 7.51 (2H, d, 10 Hz), 7.11 (1H, s), 6.98 (4H, d, 10 Hz), 4.76 (4H, s), 4.26 (1H, d, 10 Hz), 4.00 (1H, s), 3.36 (1H, s), 2.91 (1H, s), 2.76 (1H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) 158.7, 153.5, 150.1, 145.8, 143.4, 142.8, 141.9, 140.7, 139.8, 138.2, 136.1, 135.5, 133.0, 130.5, 128.9, 118.8, 117.2, 115.7, 114.6, 101.9, 70.0, 68.8, 50.1, 44.8.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ):  $\delta$  (ppm)  $-122.6$  (12F, m),  $-138.5$  (8F, m),  $-153.5$  (8F, m). Anal. Calcd for  $\text{C}_{47}\text{H}_{16}\text{F}_{28}\text{O}_6$ : C, 46.69; H, 1.32, F, 44.04. Found: C, 48.55; H, 1.26; F, 45.18.

**FA-APE EP 4.** Yield: 90.4%.  $M_n = 11829$ ;  $M_w/M_n = 1.58$ . IR (KBr,  $\text{cm}^{-1}$ ): 1120–1300 (C–F), 929.5 ( $\Delta$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) 7.51 (2H, d, 10 Hz), 7.11 (1H, s), 6.97 (4H, d, 10 Hz), 4.75 (12H, s), 4.26 (1H, d, 10 Hz), 4.00 (1H, s), 3.36 (1H, s), 2.91 (1H, s), 2.75 (1H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  (ppm) 158.4, 153.3, 150.0, 145.6, 143.7, 142.8, 141.6, 140.3, 139.6, 138.0, 136.1, 135.5, 133.0, 130.5, 128.5, 118.8, 117.1, 115.5, 114.6, 101.9, 70.0, 68.9, 50.0, 44.5.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ):  $\delta$  (ppm)  $-122.4$  (36F, m),  $-138.5$  (16F, m),  $-153.6$  (16F, m). Anal. Calcd for  $\text{C}_{87}\text{H}_{24}\text{F}_{68}\text{O}_{10}$ : C, 41.43; H, 0.95, F, 51.27. Found: C, 42.06; H, 0.93; F, 50.36.

#### 2.4. Film preparation for the measurement of refractive index

The FA-APE EP 1–4 solutions were prepared in cyclopentanone (60–80 wt%), diphenyliodonium hexafluorophosphate (PI) was added as the initiator (8 wt% relative to the copolymer). The solutions were filtered by a syringe through a 0.22  $\mu\text{m}$  Teflon membrane filter and spin-coated onto a silicon wafer substrates. The resulting films (3–7  $\mu\text{m}$  in thickness) were baked at 90  $^\circ\text{C}$  for 30 min, then irradiated by UV light (1000 V) for 8 min. The films were finally heated slowly to 120  $^\circ\text{C}$  and maintaining this temperature for 1 h.

#### 2.5. Photopatterning

For good adherence of the FA-APE EP 1–4 solutions, the Si/SiO<sub>2</sub> wafer was first ultrasonically cleaned in organic solvents and then soaked in an etchant consisting of  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7:3$  at 90  $^\circ\text{C}$  for 30 min. Then the Si/SiO<sub>2</sub> wafer was rinsed in deionized water, dried using nitrogen gas, and spin-coated with the polymer solution. The thickness of the polyether layer on the substrate was controlled by the spinning speed and solid content of the polymer.

To fabricate optical waveguide by direct photolithography using a contact print of a simple grating mask, a polymer layer was spin-coated onto the Si substrate with a 2  $\mu\text{m}$  SiO<sub>2</sub> layer. The film (about 5  $\mu\text{m}$  thick) was dried at 90  $^\circ\text{C}$  for 30 min to remove all the solvent. Photopatterning of the film was performed by exposing the film to the UV light through a mask for 7 min, followed by a post-baking at 100  $^\circ\text{C}$  for 1 h and developing with dimethylformamide (DMF). The development time depended on the thickness of the layer.

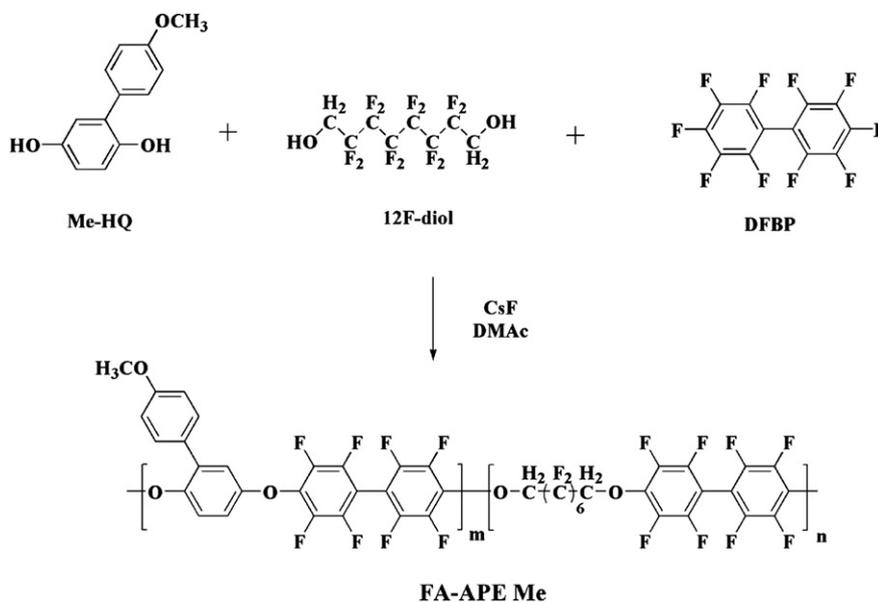
### 3. Results and discussion

#### 3.1. Monomer (Me-HQ) synthesis

Because of the highly symmetrical chain structure and high flexibility of the fluorinated alkyne segments, the copolyethers exhibit a tendency to crystallize. The crystalline morphology of polymer materials will increase the heterogeneity of their optical properties and lead to a significant optical loss due to light scattering [27,31]. Me-HQ was chosen as a bisphenol monomer, because it not only provided branched side-chain in the polymers to avoid crystallizing, but also provided reactive site to introduce cross-linkable epoxy group.

#### 3.2. Preparation of highly fluorinated aromatic-aliphatic copolyethers (FA-APE Me, FA-APE OH)

Fluorinated aromatic-aliphatic copolyethers containing pendent methoxy group (FA-APE Me) were synthesized using various feed ratios of Me-HQ/12F-diol (Scheme 2), and the ratio was controlled as shown in Table 1 for tuning the properties of the resulting copolyethers. To avoid serious branching or cross-linking side



**Scheme 2.** Synthesis of highly fluorinated aromatic-aliphatic copolyethers containing methoxy group (FA-APE Me).

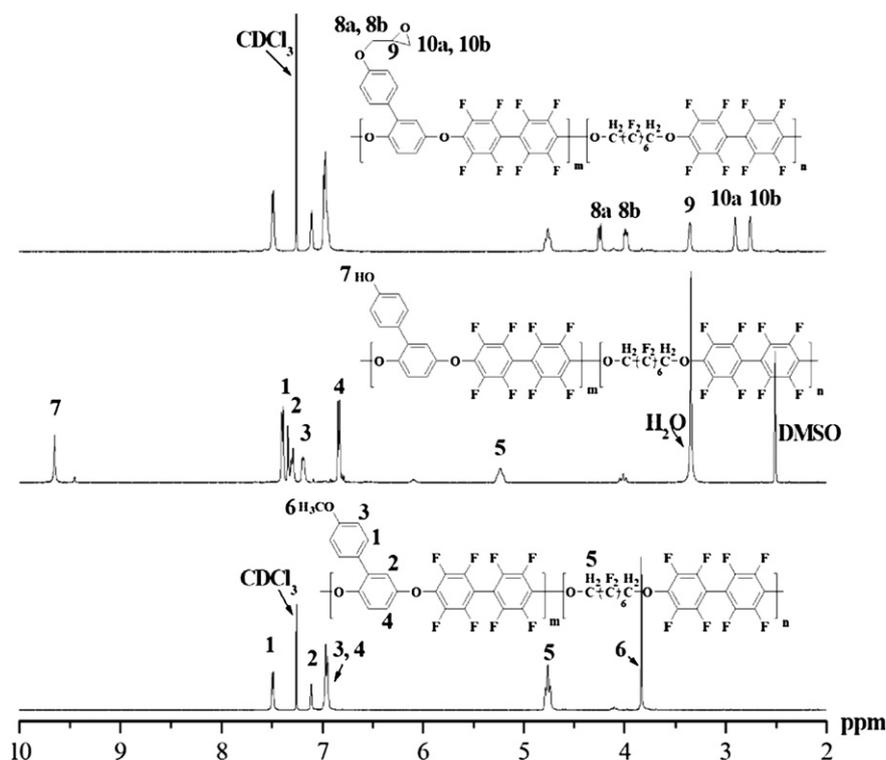


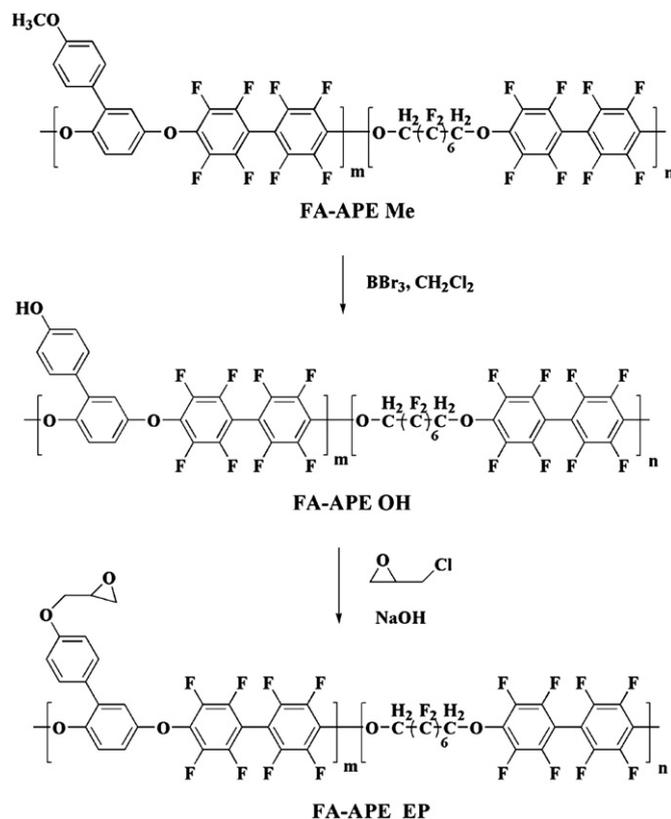
Fig. 1.  $^1\text{H}$  NMR spectra of FA-APE Me 3, FA-APE OH 3 and FA-APE EP 3 (from bottom to top).

reactions, the copolymerization was therefore carried out using a very mild reaction condition. This reaction involved the cesium fluoride as the catalyst, which enable the reaction temperature as low as  $50\text{ }^\circ\text{C}$ . FA-APE Me 1–4 showed a low-molecular-weight ( $M_n$ ) ranged from 10,600 to 11,600 as shown in Table 1. Low-molecular-weight polymer could have advantages in decreasing line edge roughness at very small feature sizes and it is helpful to dissolve more uniformly during development [32–36]. The chemical composition of the copolymers was confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra. Fig. 1 shows the  $^1\text{H}$  NMR spectrum of FA-APE Me 3. The signals around 6.95–7.50 ppm were attributed to the hydrogen atoms in phenyl, while the aliphatic peak at 3.83 ppm was ascribed to the methoxy group of Me-BQ units. The aliphatic proton signal observed at 4.79 ppm was attributed to the proton in the 12F-diol. The relative peak intensities correlated well with the ratios of 12F-diol contents. The results of the copolymerization reaction are summarized in Table 1, which indicates that both diol and bisphenol are completely incorporated into copolyethers.

The conversion of the methoxy groups to reactive hydroxyl groups using  $\text{BBr}_3$  was conduct in  $\text{CH}_2\text{Cl}_2$  (Scheme 3). In the IR spectra, FA-APE OH polymers showed an absorption at  $3460\text{ cm}^{-1}$  attributed to the characteristic absorption of hydroxyl group, which could not be observed in the spectra of FA-APE Me polymers.  $^1\text{H}$  NMR spectrum of FA-APE OH 3 is shown in Fig. 1. In comparison with FA-APE Me 3, a signal appeared around 9.66 ppm, which corresponded to the hydrogen atom of hydroxyl group, and no peaks around 3.83 ppm were observed. These results indicate that the methoxy groups have been converted into hydroxyl groups completely.

### 3.3. Preparation of highly fluorinated aromatic-aliphatic copolyethers containing epoxy group (FA-APE EP)

Highly fluorinated aromatic-aliphatic copolyethers containing epoxy group (FA-APE EP) 1–4 were prepared from FA-APE OH 1–4



Scheme 3. Synthesis of fluorinated aromatic-aliphatic ether containing hydroxyl (FA-APE OH) and epoxy (FA-APE EP) group.

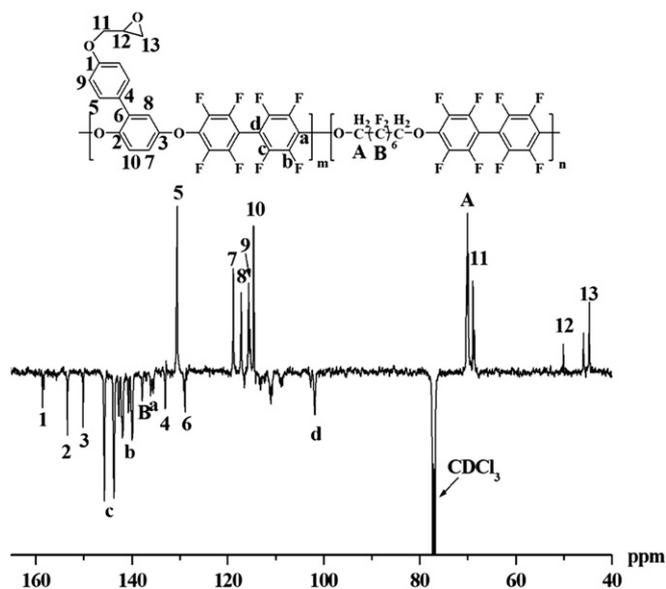


Fig. 2.  $^{13}\text{C}$  NMR spectrum of FA-APE EP 3.

and epoxy chloropropane as shown in Scheme 3. FA-APE EP copolymers were obtained as white solid materials which displayed excellent solubility in common organic solvents such as acetone, dichloromethane, chloroform, tetrahydrofuran, DMF and DMAc. The copolymer structures were confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra. The  $^1\text{H}$  NMR spectrum of FA-APE EP 3 is also shown in Fig. 1. In comparison with FA-APE OH 3, the signal at 9.66 ppm corresponding to the proton of hydroxyl group disappeared, and several new signals appeared in the 4.26–2.76 ppm region, which was ascribed to the protons in epoxy group, respectively. To confirm the structure of FA-APE EP 3 further,  $^{13}\text{C}$  NMR measurement was also carried out (Fig. 2). The signals at 145.7, 143.7, 142.7, 141.9, 140.7, 139.9, 136.1, 135.5, and 101.8 ppm were attributed to the carbon atoms of decafluorobiphenyl. The signals at 138.0 and 70.0 ppm corresponded to the carbon atoms of  $-\text{CF}_2-$  and  $-\text{CH}_2-$  from 12F-diol units. The characteristic peaks of epoxy group were observed at 68.8, 50.1, 44.7 ppm. The  $^{19}\text{F}$  NMR spectra of FA-APE EP series of copolymers displayed complicated patterns, but no change with the Me-HQ/12F-diol ratio was observed for the position of the peaks. As shown in Fig. 3, the

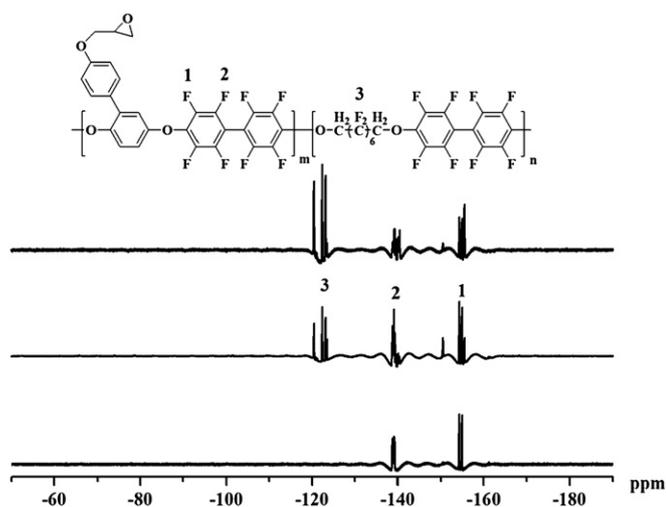


Fig. 3.  $^{19}\text{F}$  NMR spectra of FA-APE EP 1–3 (from bottom to top).

Table 2

Thermal properties and gel fractions of the fluorinated aromatic-aliphatic copolyethers.

Copolymer	12F-diol in feed (mol%) <sup>a</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$T_d$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	Gel fraction (%) <sup>d</sup>
PA-AE Me 1	0	139.6	—	—
PA-AE Me 2	25	131.4	—	—
PA-AE Me 3	50	119.6	—	—
PA-AE Me 4	75	100.3	—	—
PA-AE OH 1	0	140.3	—	—
PA-AE OH 2	25	136.5	—	—
PA-AE OH 3	50	131.7	—	—
PA-AE OH 4	75	117.6	—	—
PA-AE EP 1	0	136.5	278.8	99.83
PA-AE EP 2	25	130.2	270.5	99.58
PA-AE EP 3	50	128.8	238.7	99.52
PA-AE EP 4	75	108.1	230.4	99.47

<sup>a</sup> Molar ratio of [12F-diol]/[Me-HQ + 12F-diol].

<sup>b</sup> Glass transition temperature of uncross-linked polymer measured by DSC with a heating rate of  $10^{\circ}\text{C}/\text{min}$  in nitrogen.

<sup>c</sup> Onset temperature for 5% weight loss of cross-linked PA-AE EP 1–4 measured by TGA with a heating rate of  $10^{\circ}\text{C}/\text{min}$  in nitrogen.

<sup>d</sup> Gel fraction was obtained from the ratio of the weight of cross-linked PA-AE EP 1–4 from chloroform and their correspondingly initial weight.

signals at  $-124.0$ ,  $-123.0$ ,  $-121.7$  ppm were ascribed to the fluorine atoms on the aliphatic main chain, and the relative peak intensities correlated well with the Me-HQ/12F-diol ratios. It is interesting that the resonance of the ortho fluorine atoms of the DFBP unit split into four peaks at  $-155.7$ ,  $-154.1$ ,  $-153.4$ , and  $-150.5$  ppm, due to the different combination of two possible adjacent units (Me-HQ or 12F-diol) at either side, which agreed well with the results reported by Ding et al.

### 3.4. Photo cross-linking

The direct UV-written aromatic-aliphatic copolyether elaborated in this study have been designed to contain photochemical amplification based on photoacid generator (PAG). Cationic rather than radical photochemistry was preferred because it is not inhibited by atmospheric oxygen. Another advantage of systems incorporating chemical amplification is the low amount of photoinitiator necessary to photopattern images, thus minimizing optical losses induced by photoinitiator [11]. The film spin-coat on a Si wafer was prebaked at  $90^{\circ}\text{C}$  for 30 min, irradiated by UV light, cured at  $100^{\circ}\text{C}$  for 1 h, and then developed in negative mode with

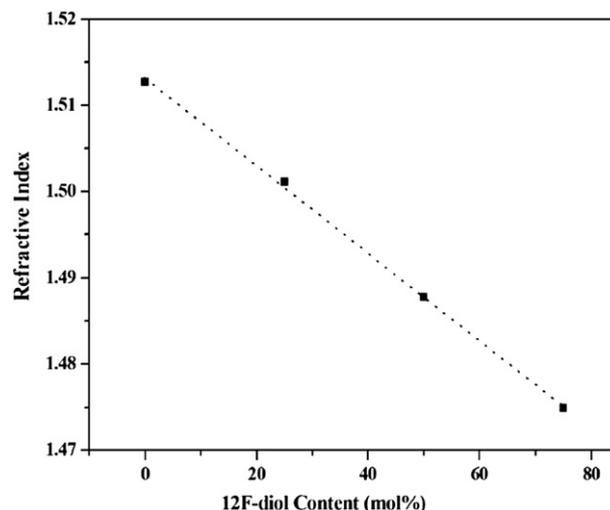


Fig. 4. Dependence of refractive index of FA-APE EP films on 12F-diol content.

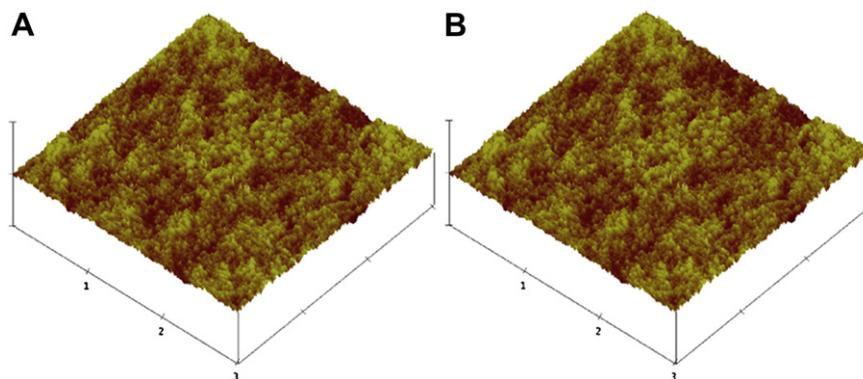


Fig. 5. AFM photograph of surface from FA-APE EP 2 (A) before cross-linking and (B) after cross-linking ( $3 \times 3 \mu\text{m}^2$ ).

DMF at room temperature. The cured copolymers were insoluble in common organic solvents such as acetone, dichloromethane, chloroform, tetrahydrofuran, and DMF. To examine the gel fraction of the cured polymers, the cured films were extracted with chloroform for 3 days and then dried for 3 days at  $60^\circ\text{C}$  under vacuum. Gel fraction was obtained from the ratio of the weight of the cross-linked polymers after extraction from chloroform and the initial weight. From Table 2, gel fraction decreased with increasing the content of 12F-diol, and there were all only less than 1% weight loss.

Optical materials with different refractive indices are required as core and a cladding part of an optical waveguide. The core material must have a higher refractive index than cladding material [2]. Therefore, precise control of refractive index is extremely important for making polymer-based optical waveguide devices. The refractive index of the FA-APE EP 1–4 films were measured at 1550 nm by ellipsometry. As shown in Fig. 4, the refractive indices of FA-APE EP 1–4 could be controlled by varying the molar ratio of the bisphenol and diol. The values of the refractive indices decreased from 1.5230 to 1.5043 as the amount of the 12F-diol content in the copolymer increased. Meanwhile, a nearly linear relationship was found between the refractive index of the film and 12F-diol content.

The AFM images of the spin-coated FA-APE EP 2 film before and after cross-linking are shown in Fig. 5, respectively. The image ( $3 \times 3 \mu\text{m}^2$ ) obtained was representative of the sample surface. The root-mean-square surface roughness were both small and similar, 0.231 nm for uncross-linked film and 0.267 nm for cross-linked

film. The surfaces of the spin-coated films exhibited uniform fractal morphology, which was characteristic for glassy polymers. The obtained AFM images also showed no phase separation happened in the films.

### 3.5. Thermal properties

The thermal properties of the copolymers were investigated by DSC and TGA. Table 2 shows the  $T_g$ s of uncross-linked copolymers. FA-APE OH series of copolymers showed higher  $T_g$ s than the corresponding FA-APE Me and FA-APE EP copolymers, due to the polar nature of hydroxyl group. No glass transition temperature for FA-APE EP was observed after cross-linking. The results of TGA are shown in Fig. 6. The cross-linked FA-APE EPs exhibited satisfactory thermal stability, and the 5% weight loss ( $T_d$ ) for all the cross-linked FA-APE EPs were in range of  $230$ – $279^\circ\text{C}$ , as listed in Table 2, and  $T_d$  increased with increasing cross-linking density. These results indicate that the epoxy groups have reacted with each other resulting in cross-linked network structure, which improves the thermal stability of the copolymers.

### 3.6. Optical waveguide fabrication and propagation loss measurement

The key requirement imposed on polymeric materials is low optical transmission loss at the telecommunication waveguide region ( $1.3$  and  $1.55 \mu\text{m}$ ). In polymers, optical propagation losses at

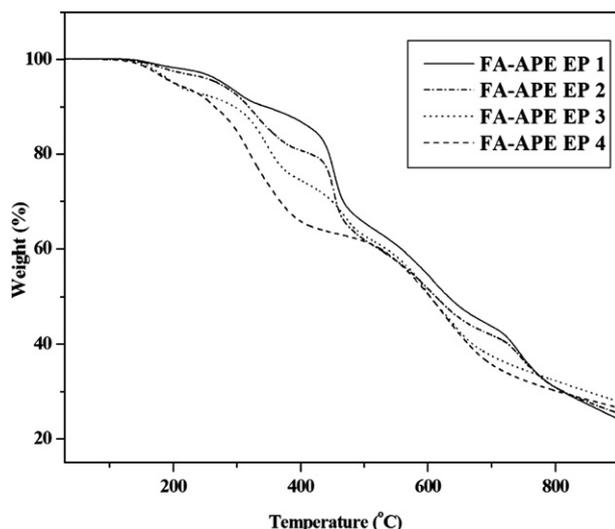


Fig. 6. TGA thermograms of cross-linked FA-APE EP 1–4.

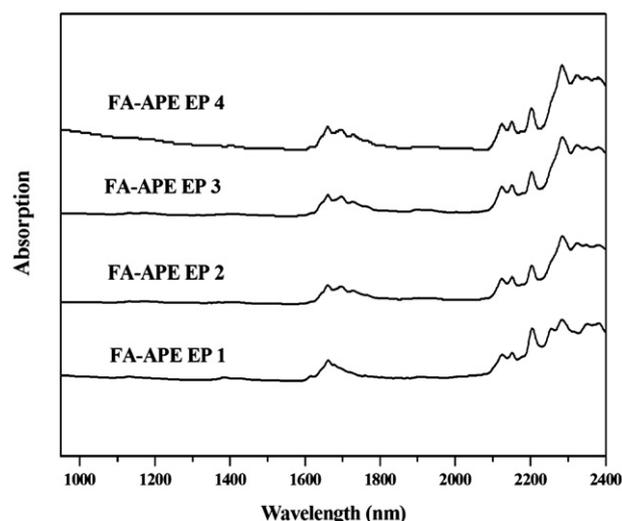


Fig. 7. Near-infrared absorption spectra of FA-APE EP 1–4.

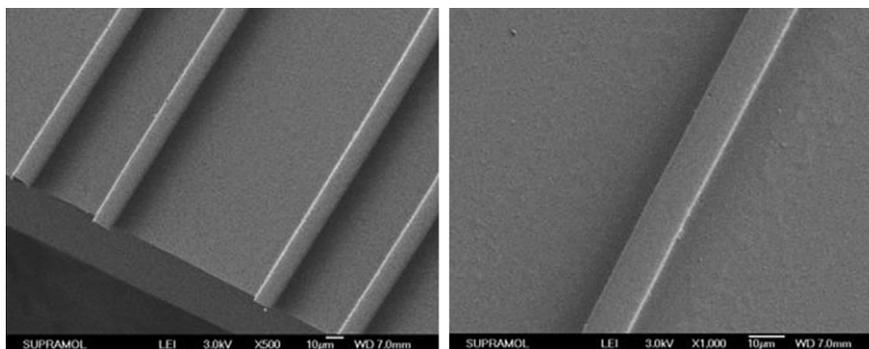


Fig. 8. SEM images of straight waveguide fabricated with FA-APE EP 2.

around that region are caused by the vibration absorption of Carbon-hydrogen (C–H) and oxygen-hydrogen (O–H) bonds. Highly fluorinated polymers containing the minimum amount of absorptive bonds can significantly reduce the optical loss in near-IR region [18,21]. To make low loss optical waveguide, it is very important to know the absorbance of FA-APE EP films. So, we evaluated the absorption spectra in the near-IR region of FA-APE EP 1–4 films. It was found that the FA-APE EP 1–4 films exhibited colorless low absorption at the optical communication wavelength Fig. 7).

Direct-write UV lithography is advantageous over other techniques because fewer steps are involved. Furthermore, this technique is capable of patterning features with long and linear dimensions over comparatively large planar areas. Nanometer patterns with flexibility in writing complex structures are possible [9,13]. In this study, the channel waveguides were fabricated by first spin-coated FA-APE EP solution with 5–7 μm in thickness on a Si substrate with a 2-μm SiO<sub>2</sub> layer, and the films were dried at 90 °C for 30 min to remove all the solvent. Finally, photopatterning of the film was performed by exposing the film to the UV light through a mask for 8 min, followed by a post-baking at 100 °C for 1 h and developing with DMF. In this case, the ridge heights and widths of the straight waveguide were in the range of 5–15 μm. The scanning electron microscope (SEM) images to the typical ridge structure from FA-APE EP 2 in Fig. 8 indicated that well-defined waveguide structure with very smooth ridge walls were easily prepared using direct-write UV technique. The spectral-transmission characteristics of waveguide device were measured by tuneable laser with

a center wavelength a 1550 nm and a spectrum analyzer. Light from a tuneable semiconductor laser was coupled into the input waveguide through a single-mode fiber. The near-field mode pattern at the out channels shown in Fig. 9 was observed with an infrared vidicon after being magnified by an objective lens. The propagation loss in the waveguides was calculated from the slope of the total loss versus length curves. The obtained data demonstrated very low propagation loss at 1550 nm. For example, a 6 × 6 μm<sup>2</sup> straight waveguide fabricated from FA-APE EP 2 had a propagation loss of 0.18 dB/cm by cut-back method.

#### 4. Conclusions

Highly fluorinated aromatic-aliphatic copolyethers had been prepared by copolycondensation reactions of decafluorobiphenyl (DFBP) with (4-methoxy) phenylhydroquinone (Me-HQ) and 2,2,3,3,4,4,5,5,6,6,7,7-dodeca-fluoro-1,8-octanediol (12F-diol). Then a series of direct UV-written fluorinated aromatic-aliphatic copolymer mixtures based on fluorinated aromatic-aliphatic copolyethers and photoinitiator were prepared. The cross-linked materials had good film-forming capability, chemical resistance, thermal stability and tuneable refractive index. The propagation loss through channel optical waveguides fabricated by direct photolithography technique was measured to be 0.18 dB/cm at 1550 nm by the cut-back method fabricated with FA-APE EP 2.

#### Acknowledgments

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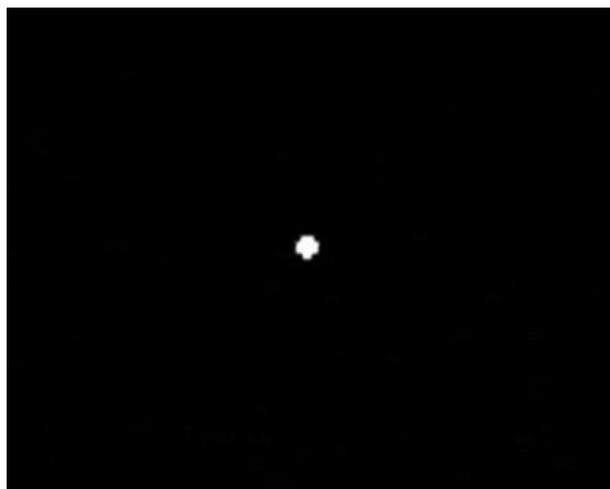


Fig. 9. Near-field pattern of waveguide mode at 1550 nm obtained with FA-APE EP 2.

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