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Effect of fluoro-polycarbonates containing aliphatic/aromatic segments on the characteristics of thermo-optic waveguide devices†

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Fluorinated polycarbonates containing dodecyl groups (AF-Ali-PC EPs), biphenyl groups (AF-Ar-PC EPs), and cross-linkable epoxy groups were synthesized to investigate the effects of the flexibility of monomers on the properties of thermo-optic waveguide devices. Transparent polymer films were prepared via photocuring of a solution (FPRs) containing AF-Ali-PC EPs or AF-Ar-PC EPs, a photo initiator, and cyclopentanone. The optical films have low surface energies and roughnesses, high thermal stabilities, and tunable refractive indices. Straight optical waveguide and MZI thermo-optic waveguide switch arrays were fabricated using Ali-PR 1 and Ar-PR 1. The propagation losses of the channel waveguides, measured by the cutback method, were 0.21 dB cm⁻¹ and 0.19 dB cm⁻¹ at the monitoring light of 1550 nm for the Ali-PR 1 and Ar-PR 1, respectively. The rise and fall times of the thermo-optic switch upon application of a 200 Hz square-wave voltage were 1.822 ms and 1.364 ms, respectively, for Ali-PRs and 2.994 ms and 2.301 ms, respectively, for Ar-PRs at the square-wave voltage of 110 Hz. The insertion loss and extinction ratio were measured to be 9.2 dB and 12.0 dB for the aliphatic segment-containing photoresists and 8.9 dB and 12.3 dB for the aromatic segment-containing photoresists, respectively. The applied electric powers were 15.0 mW and 20.0 mW, which were also the switching powers. In contrast with our previous work, fluoro-polycarbonates containing aliphatic segments were more suitable for optical waveguide devices than those containing aromatic segments.

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Introduction

Optical switches, which are implemented to establish reconfigurable connections between multiple sources and multiple destinations, are essential building blocks for both long-haul optical communications and short-reach photonic networks-on-chips.¹ Nowadays, optical switches and their related arrays are widely used in optical cross connects (OXCs), optical add-drop multiplexers (OADMs), optical network monitoring, and on-chip optical interconnections.² It is desirable for these switches to have large optical bandwidths, small physical dimensions, and good performance.³ To realize these properties, various device structures such as Mach-Zehnder interferometer (MZI) switches, multimode interference (MMI) switches, and directional coupler (DC) switches have been employed.⁴

The thermo-optic MZI is a basic device in planar light-wave circuits. In optical communication systems, it is widely used in optical modulators or switches because of its low optical loss, polarization independence, and long-term stability.⁵ Polymer materials have been intensively investigated due to their potential applications in optical waveguides because of their excellent characteristics⁴ such as low optical loss, high extinction ratio, small cubage, easy integration, high thermal and environmental stability, and flexible refractive index controllability.⁶ Various organic polymers including polyimides, acrylic polymers, polycarbonates, polystyrenes, polysiloxanes, hyperbranched polymers, perfluorinated methacrylates, and bis-phenol-A novolac resin (SU-8) have been tested as optical waveguide materials.⁷

In general, glass and silicon wafers are selected as substrates for the fabrication of optical waveguides. However, Si-O or Si-OH groups on the surfaces of the substrates result in highly polar surfaces; moreover, it is difficult to obtain good adhesion with polymers. To solve this problem, polar functional groups, such as carbonate groups, can be introduced to enhance the adhesion of the polymer layer to the substrates.^{7g} Apart from this, the properties such as transparency, broad temperature resistance, inherent toughness, and high index of refraction of polycarbonates have increased their popularity in the optical waveguide field.⁸ However, polycarbonates have relatively high

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absorption losses at optical communication wavelengths (0.6 dB cm^{-1} at 1550 nm), resulting from the absorption of C–H bonds.^{7f} Replacing C–H bonds with C–F bonds in polymers can reduce the intrinsic optical loss at the key telecommunication wavelengths of 1310 and 1550 nm.¹⁰ Fluorine-containing polymers exhibit good thermal and chemical stability and decreased intermolecular attractive forces (which results in better solubility) compared to hydrocarbon polymers.^{7g,10a,11} The refractive indices of the polymers that we have synthesized⁹ (AF-Z-PC EPs) can be adjusted by controlling the content of bisphenol Z. For AF-Z-PC EPs containing epoxy groups, we utilized a simple method to fabricate the waveguide devices. Encouraged by these results, we designed another experiment for further exploration.

The crystallinity of a polymer depends on its chain flexibility. Bisphenol-A polycarbonate (BAPC) presents poor crystallization because of its rigidity.¹² In this study, a series of fluoropolycarbonates containing aliphatic segments (AF-Ali-PC EPs) and biphenyl segments (AF-Ar-PC EPs) were synthesized with the intention of investigating the effects of the flexibility of the monomers on the characteristics of thermo-optic waveguide devices. AF-Ali-PC EPs and AF-Ar-PC EPs were mixed with cyclopentanone and a photoinitiator, respectively, to prepare a series of negative-type fluorinated photoresists (Ali-PRs and Ar-PRs, respectively). Through direct UV-writing, the photoresists could be fabricated into straight optical waveguide and MZI thermo-optic waveguide switch arrays. The propagation losses of the channel waveguides, measured by the cutback method, were 0.21 dB cm^{-1} and 0.19 dB cm^{-1} at the monitoring light of 1550 nm for the Ali-PR 1 and Ar-PR 1, respectively. The rise and fall times of the thermo-optic switch upon application of a 200 Hz square-wave voltage were 1.822 ms and 1.364 ms, respectively, for Ali-PRs and 2.994 ms and 2.301 ms, respectively, for Ar-PRs at the square-wave voltage of 110 Hz. The insertion loss and extinction ratio were measured to be 9.2 dB and 12.0 dB, respectively, for the aliphatic segment-containing photoresists and 8.9 dB and 12.3 dB, respectively, for the aromatic segment-containing photoresists. The applied electric power was 15.0 mW and 20.0 mW.

Experimental

Materials

4,4'-(Hexafluoroisopropylidene) diphenol (98%), 4,4'-dihydroxydiphenyl (97%), and triphosgene (99%) were purchased from Aladdin Industrial Co. and used as received. Dodecanedioic acid (99%) (Sigma-Aldrich), thionyl chloride (99.5%) (Fuchen Chemical Co., Ltd), and triphenylsulfonium hexafluorophosphate (Sigma-Aldrich) were used as received without further purification. Epoxy chloropropane, pyridine, and dichloromethane were purchased from Beijing Chemical Co., Ltd and were used after purification.

Measurements

IR spectra were obtained *via* an AVATAR 360 spectrophotometer using KBr pellets. UV-vis-NIR spectra were acquired using a SHIMADZU UV-3600 spectrometer. ¹H NMR, ¹³C NMR,

and ¹⁹F NMR spectra were obtained *via* a Bruker AVANCE NMR spectrometer, operated at 500, 125, or 300 MHz, respectively. ¹H, ¹³C, and ¹⁹F chemical shifts have been reported as values (ppm) relative to CDCl₃ (7.24). The molecular weights of the polymers were determined relative to polystyrene standards using gel permeation chromatography (GPC) in THF at room temperature. Thermal analyses were conducted *via* a NETZSCH 4 differential scanning calorimeter (DSC) and a Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA) at the heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Cross-section images of the specimens were obtained *via* a scanning electron microscope (JEOL FESEM 6700F). An M-2000VI ellipsometer was used to determine the refractive indices of the films. The surface morphologies of the films were investigated under ambient conditions using a Digital Instruments Nanoscope IIIA instrument.

Synthesis of the polymers

Synthesis of hydroxyl-terminated fluoro-polycarbonates containing aliphatic segments. The preparation procedure has been described in our previous work.^{9,13} The typical procedure is as follows: a round-bottomed flask was charged with dodecanedioic acid (DDDA) (0.96 g, 3.0 mmol) and thionyl chloride (1 mL, 14 mmol). The mixture was heated to the reflux temperature, and the temperature was maintained for 4 h. After the reaction completed, the organic phase was removed under reduced pressure, and dodecanedioyl dichloride was obtained. 4,4'-(Hexafluoroisopropylidene) diphenol (6FBPA) (2.69 g, 8.0 mmol) was dissolved in 0.48 mL of pyridine and methylene chloride and then cooled down to 0 °C; after this, dodecanedioyl dichloride was added dropwise. The reaction mixture was vigorously stirred at 0–5 °C for 10 min and at room temperature for 2 h. Finally, 6FBPA, pyridine, and methylene chloride were added to the reaction flask. The solution was cooled down to 0 °C. A solution of triphosgene in methylene chloride was then added dropwise, and the reaction mixture was stirred for another 6 h at room temperature. After this, the solution was precipitated in methanol (400 mL), and the precipitates were obtained by filtration. The products were dried under vacuum and were denoted as AF-Ali-PC OHs.

AF-Ali-PC OH 1: 6FBPA (13.44 g, 40 mmol), pyridine (6.0 mL), and triphosgene (3.71 g, 12.5 mmol). AF-Ali-PC OH 1 was obtained as a white powder (11.59 g, 65%). GPC: $M_n = 11\,892 \text{ g mol}^{-1}$; $M_w/M_n = 1.20$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1177\text{--}1239$, $\gamma(\text{aromatic}) = 1607$ and 1509 , $\gamma(\text{CO-O-Ar}) = 1777$, $\gamma(-\text{CH}_2-) = 1712$ and 732 . ¹H NMR (500 MHz, CDCl₃): δ (ppm): 7.51–7.50 (t, 1H, ArH), 7.44–7.43 (t, 1H, ArH), 7.37–7.36 (t, 11H, ArH), 7.16–7.13 (t, 1H, ArH), 2.62–2.59 (m, 1H, –CH₂), 1.82–1.75 (m, 1H, –CH₂), 1.44–1.36 (m, 3H, –CH₂). ¹³C NMR (125 MHz, CDCl₃): δ (ppm): 171.93, 151.22, 151.17, 131.69, 131.28, 123.94, 121.53, 120.77, 120.52, 115.16, 64.00, 34.37, 29.39, 29.23, 29.07, 24.86. ¹⁹F NMR (470 MHz, CDCl₃, CFCl₃): δ (ppm): –63.87 (6F, –CF₃).

AF-Ali-PC OH 2: 6FBPA (7.392 g, 22 mmol), pyridine (3.6 mL), and triphosgene (2.227 g, 7.5 mmol). AF-Ali-PC OH 2 was obtained as a white powder (7.94 g, 68%). GPC: $M_n = 11\,541 \text{ g mol}^{-1}$; $M_w/M_n = 1.31$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1174\text{--}1242$,



$\gamma(\text{aromatic}) = 1605$ and 1508 , $\gamma(\text{CO-O-Ar}) = 1777$, $\gamma(-\text{CH}_2-) = 1709$ and 736 . $^1\text{H NMR}$ (500 MHz, CDCl_3), δ (ppm): 7.51–7.50 (t, 8H, ArH), 7.44–7.43 (t, 1H, ArH), 7.37–7.35 (t, 8H, ArH), 7.16–7.14 (t, 1H, ArH), 2.62–2.59 (m, 1H, $-\text{CH}_2$), 1.81–1.75 (m, 1H, $-\text{CH}_2$), 1.44–1.36 (m, 3H, $-\text{CH}_2$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 172.01, 151.22, 131.69, 131.39, 131.28, 122.17, 121.48, 120.77, 120.52, 115.18, 64.00, 34.37, 29.39, 29.23, 29.07, 24.86. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -63.87 (6F, $-\text{CF}_3$).

AF-Ali-PC OH 3: 6FBPA (3.36 g, 10 mmol), pyridine (2.0 mL), triphosgene (1.238 g, 4.17 mmol). AF-Ali-PC OH 3 was obtained as a white powder (5.04 g, 66%). GPC: $M_n = 11\,568$ g mol $^{-1}$; $M_w/M_n = 1.35$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1163$ – 1239 , $\gamma(\text{aromatic}) = 1612$ and 1515 , $\gamma(\text{CO-O-Ar}) = 1784$, $\gamma(-\text{CH}_2) = 1715$ and 736 . $^1\text{H NMR}$ (500 MHz, CDCl_3), δ (ppm): 7.51–7.50 (t, 5H, ArH), 7.44–7.43 (t, 1H, ArH), 7.37–7.36 (t, 5H, ArH), 7.16–7.14 (t, 1H, ArH), 2.62–2.59 (m, 1H, $-\text{CH}_2$), 1.81–1.75 (m, 1H, $-\text{CH}_2$), 1.44–1.36 (m, 3H, $-\text{CH}_2$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 171.94, 151.22, 151.16, 131.70, 131.40, 130.33, 123.95, 121.54, 120.78, 115.15, 64.00, 34.37, 29.39, 29.24, 29.08, 24.86. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -63.87 (6F, $-\text{CF}_3$).

Synthesis of hydroxyl-terminated fluoro-polycarbonates containing aromatic segments. To a 250 mL three-neck flask, 6FBPA, 4,4'-dihydroxydiphenyl (DOD, 6 mmol, 1.116 g), pyridine, and tetrahydrofuran were added. The solution was cooled down to 0 °C. A solution of triphosgene in tetrahydrofuran was added dropwise, and the reaction mixture was stirred for another 6 h at room temperature. After this, the solution was precipitated in methanol (400 mL), and the precipitates were obtained by filtration. The products were dried under vacuum and were denoted as AF-Ar-PC OHs.

AF-Ar-PC OH 1: 6FBPA (16.13 g, 48 mmol), pyridine (7.3 mL), and triphosgene (4.46 g, 15 mmol). AF-Ar-PC OH 1 was obtained as a white powder (11.22 g, 61%). GPC: $M_n = 9894$ g mol $^{-1}$; $M_w/M_n = 1.32$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1173$ – 1211 , $\gamma(\text{aromatic}) = 1609$ and 1512 , $\gamma(\text{CO-O-Ar}) = 1782$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm): 7.66–7.64 (t, 3H, ArH), 7.51–7.49 (t, 17H, ArH), 7.40–7.35 (m, 20H, ArH), 7.27 (s, 1H, ArH), 6.82 (s, 1H, ArH). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 156.20, 151.33, 151.22, 150.44, 138.50, 131.69, 131.27, 128.38, 123.95, 121.26, 120.76, 120.52, 115.17, 64.01. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -63.86 (6F, $-\text{CF}_3$).

AF-Ar-PC OH 2: 6FBPA (12.10 g, 36 mmol), pyridine (5.65 mL), and triphosgene (3.47 g, 11.7 mmol). AF-Ar-PC OH 2 was obtained as a white powder (8.33 g, 59%). GPC: $M_n = 8057$ g mol $^{-1}$; $M_w/M_n = 1.29$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1176$ – 1215 , $\gamma(\text{aromatic}) = 1612$ and 1512 , $\gamma(\text{CO-O-Ar}) = 1776$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm): 7.66–7.64 (t, 3H, ArH), 7.51–7.50 (t, 12H, ArH), 7.40–7.36 (m, 15H, ArH), 7.27 (s, 1H, ArH), 6.81 (s, 1H, ArH). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 156.25, 151.34, 151.22, 150.46, 138.50, 131.69, 131.29, 128.38, 123.94, 121.33, 121.26, 120.76, 115.17, 63.97. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -63.87 (6F, $-\text{CF}_3$).

AF-Ar-PC OH 3: 6FBPA (8.06 g, 24 mmol), pyridine (4.02 mL), triphosgene (2.48 g, 8.33 mmol). AF-Ar-PC OH 3 was obtained as a white powder (5.50 g, 55%). GPC: $M_n = 7900$ g mol $^{-1}$; $M_w/M_n = 1.34$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1173$ – 1211 , $\gamma(\text{aromatic}) = 1612$ and 1512 , $\gamma(\text{CO-O-Ar}) = 1782$. $^1\text{H NMR}$ (500 MHz, CDCl_3):

δ (ppm): 7.66–7.64 (t, 4H, ArH), 7.51–7.50 (t, 10H, ArH), 7.40–7.36 (m, 14H, ArH), 7.27 (s, 1H, ArH), 6.80 (s, 1H, ArH). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 156.22, 151.34, 151.23, 150.47, 138.51, 131.69, 131.28, 128.38, 123.95, 121.36, 120.83, 120.77, 115.16, 64.01. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -63.86 (6F, $-\text{CF}_3$).

Preparation of epoxy-terminated fluoro-polycarbonates containing aliphatic segments. A round-bottomed flask was charged with PEC-OH and epoxy chloropropane. The reaction mixture was mechanically and vigorously stirred at 55 °C. Then, sodium hydroxide was added every 30 min. The reaction mixture was heated to 60 °C and stirred for a further 6 h. After the reaction completed, epoxy chloropropane was completely removed under reduced pressure. Then, the residue was dissolved in dichloromethane, followed by removal of sodium chloride by filtration. The products, light yellow viscous liquids, were dried under vacuum for 24 h and were denoted as AF-Ali-PC EPs.

AF-Ali-PC EP 1: AF-Ali-PC OH 1 (11.59 g, 0.97 mmol), epoxy chloropropane (40 g, 0.432 mol), and sodium hydroxide (0.2 g, 5 mmol). PEC-EP-1 was obtained as a light yellow viscous liquid (11.03 g, 96%). GPC: $M_n = 12\,001$ g mol $^{-1}$; $M_w/M_n = 1.19$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1170$ – 1251 , $\gamma(\text{aromatic}) = 1612$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1750$, $\gamma(-\text{CH}_2) = 1715$ and 736 , $\gamma(\text{epoxy group}) = 826$. $^1\text{H NMR}$ (500 MHz, CDCl_3), δ (ppm): 7.34–7.32 (t, 34H, ArH), 6.94–6.92 (t, 34H, ArH), 4.30–4.29 (m, 1H, $-\text{CH}_2$), 4.00–3.96 (m, 1H, $-\text{CH}_2$), 3.40–3.37 (m, 1H, $-\text{CH}$), 2.95–2.93 (m, 1H, $-\text{CH}_2$), 2.79–2.78 (m, 1H, $-\text{CH}_2$), 2.41–2.38 (m, 2H, $-\text{CH}_2$), 1.70–1.64 (m, 2H, $-\text{CH}_2$), 1.32–1.29 (m, 6H, $-\text{CH}_2$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 171.93, 158.65, 158.15, 153.64, 131.59, 131.51, 126.46, 125.96, 124.35, 114.15, 68.80, 63.55, 50.01, 44.64, 34.17, 29.34, 29.17, 29.01, 24.88. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.16 (6F, $-\text{CF}_3$).

AF-Ali-PC EP 2: AF-Ali-PC OH 2 (7.94 g, 0.69 mmol), epoxy chloropropane (27 g, 0.276 mol), and sodium hydroxide (0.138 g, 3.45 mmol). PEC-EP-2 was obtained as a light yellow viscous liquid (7.78 g, 96.8%). GPC: $M_n = 11\,655$ g mol $^{-1}$; $M_w/M_n = 1.29$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1170$ – 1256 , $\gamma(\text{aromatic}) = 1605$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1753$, $\gamma(-\text{CH}_2) = 736$, $\gamma(\text{epoxy group}) = 826$. $^1\text{H NMR}$ (500 MHz, CDCl_3), δ (ppm): 7.34–7.32 (t, 20H, ArH), 6.94–6.92 (t, 20H, ArH), 4.29–4.28 (m, 1H, $-\text{CH}_2$), 3.99–3.96 (m, 1H, $-\text{CH}_2$), 3.39 (s, 1H, $-\text{CH}$), 2.94 (s, 1H, $-\text{CH}_2$), 2.79 (s, 1H, $-\text{CH}_2$), 2.39 (s, 2H, $-\text{CH}_2$), 1.67–1.66 (m, 2H, $-\text{CH}_2$), 1.29 (s, 6H, $-\text{CH}_2$). $^{13}\text{C NMR}$ (125 MHz, CDCl_3), δ (ppm): 173.03, 158.65, 158.40, 158.15, 153.64, 131.51, 127.78, 125.96, 124.35, 114.15, 68.49, 63.55, 50.01, 44.63, 34.17, 29.34, 29.17, 29.01, 24.87. $^{19}\text{F NMR}$ (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.16 (6F, $-\text{CF}_3$).

AF-Ali-PC EP 3: AF-Ali-PC OH 3 (5.04 g, 0.43 mmol), epoxy chloropropane (16 g, 0.172 mol), and sodium hydroxide (0.086 g, 2.15 mmol). PEC-EP-3 was obtained as a light yellow viscous liquid (4.88 g, 97.1%). GPC: $M_n = 11\,683$ g mol $^{-1}$; $M_w/M_n = 1.34$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1170$ – 1246 , $\gamma(\text{aromatic}) = 1612$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1743$, $\gamma(-\text{CH}_2) = 743$, $\gamma(\text{epoxy group}) = 826$. $^1\text{H NMR}$ (500 MHz, CDCl_3), δ (ppm): 7.34–7.32 (t, 12H, ArH), 6.94–6.92 (t, 12H, ArH), 4.30–4.27 (m, 1H, $-\text{CH}_2$), 4.00–3.97 (m, 1H, $-\text{CH}_2$), 3.40–3.37 (m, 1H, $-\text{CH}$), 2.95–2.93 (m, 1H, $-\text{CH}_2$), 2.80–2.78 (m, 1H, $-\text{CH}_2$), 2.41–2.37 (m, 2H, $-\text{CH}_2$), 1.68–1.66 (m, 2H, $-\text{CH}_2$), 1.31–1.29 (m, 6H, $-\text{CH}_2$). $^{13}\text{C NMR}$ (125



MHz, CDCl_3), δ (ppm): 173.03, 158.64, 158.36, 158.14, 153.60, 131.51, 126.22, 125.97, 124.35, 114.14, 68.79, 63.55, 50.01, 44.65, 34.17, 29.34, 29.17, 29.01, 24.87. ^{19}F NMR (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.17 (6F, $-\text{CF}_3$).

Preparation of epoxy-terminated fluoro-polycarbonates containing aromatic segments. The epoxy-terminated fluoro-polycarbonates containing aromatic segments were prepared with epoxy chloropropane as described above. The products were denoted as AF-Ar-PC EPs.

AF-Ar-PC EP 1: AF-Ar-PC OH 1 (11.22 g, 1.13 mmol), epoxy chloropropane (46 g, 0.503 mol), and sodium hydroxide (0.23 g, 5.8 mmol). AF-Ar-PC EP 1 was obtained as a light yellow viscous liquid (10.76 g, 97%). GPC: $M_n = 9923 \text{ g mol}^{-1}$; $M_w/M_n = 1.30$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1176\text{--}1254$, $\gamma(\text{aromatic}) = 1609$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1754$, $\gamma(\text{epoxy group}) = 829$. ^1H NMR (500 MHz, CDCl_3): δ (ppm): 7.50–7.49 (t, 3H, ArH), 7.34–7.32 (t, 20H, ArH), 7.01–6.99 (t, 3H, ArH), 6.93–6.92 (t, 20H, ArH), 4.26–4.23 (m, 2H, $-\text{CH}_2$), 3.94–3.90 (m, 2H, $-\text{CH}_2$), 3.28–3.24 (m, 2H, $-\text{CH}$), 2.92–2.90 (m, 2H, $-\text{CH}_2$), 2.71–2.70 (m, 2H, $-\text{CH}_2$). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 158.64, 158.15, 157.68, 153.64, 133.84, 131.58, 131.51, 127.79, 126.39, 125.95, 124.35, 114.94, 114.15, 68.78, 63.64, 50.03, 44.66. ^{19}F NMR (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.15 (6F, $-\text{CF}_3$).

AF-Ar-PC EP 2: AF-Ar-PC OH 2 (8.33 g, 1.03 mmol), epoxy chloropropane (43 g, 0.459 mol), and sodium hydroxide (0.21 g, 5.31 mmol). AF-Ar-PC EP 2 was obtained as a light yellow viscous liquid (7.98 g, 97.2%). GPC: $M_n = 8101 \text{ g mol}^{-1}$; $M_w/M_n = 1.28$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1176\text{--}1254$, $\gamma(\text{aromatic}) = 1612$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1759$, $\gamma(\text{epoxy group}) = 829$. ^1H NMR (500 MHz, CDCl_3): δ (ppm): 7.50–7.49 (t, 9H, ArH), 7.34–7.33 (t, 43H, ArH), 7.01–6.99 (t, 9H, ArH), 6.94–6.92 (t, 43H, ArH), 4.25–4.23 (m, 2H, $-\text{CH}_2$), 3.95–3.92 (m, 2H, $-\text{CH}_2$), 3.27–3.24 (m, 2H, $-\text{CH}$), 2.93–2.89 (m, 2H, $-\text{CH}_2$), 2.71–2.69 (m, 2H, $-\text{CH}_2$). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 158.66, 158.17, 157.70, 153.64, 133.66, 133.83, 131.58, 131.51, 127.78, 125.94, 124.37, 114.96, 114.17, 114.11, 68.79, 63.56, 50.04, 44.62. ^{19}F NMR (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.16 (6F, $-\text{CF}_3$).

AF-Ar-PC EP 3: AF-Ar-PC OH 3 (5.50 g, 0.696 mmol), epoxy chloropropane (29 g, 0.310 mol), and sodium hydroxide (0.144 g, 3.59 mmol). AF-Ar-PC EP 3 was obtained as a light yellow viscous liquid (5.23 g, 96.5%). GPC: $M_n = 7954 \text{ g mol}^{-1}$; $M_w/M_n = 1.32$. IR (KBr, cm^{-1}): $\gamma(\text{C-F}) = 1176\text{--}1254$, $\gamma(\text{aromatic}) = 1612$ and 1516 , $\gamma(\text{CO-O-Ar}) = 1755$, $\gamma(\text{epoxy group}) = 829$. ^1H NMR (500 MHz, CDCl_3): δ (ppm): 7.50–7.49 (t, 11H, ArH), 7.34–7.32 (t, 27H, ArH), 7.01–6.99 (t, 11H, ArH), 6.94–6.92 (t, 27H, ArH), 4.27–4.25 (m, 2H, $-\text{CH}_2$), 3.94–3.91 (m, 2H, $-\text{CH}_2$), 3.28–3.23 (m, 2H, $-\text{CH}$), 2.95–2.94 (m, 2H, $-\text{CH}_2$), 2.72–2.69 (m, 2H, $-\text{CH}_2$). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 158.64, 158.14, 157.69, 153.63, 133.89, 131.60, 131.51, 127.80, 125.98, 125.48, 124.34, 114.95, 114.15, 68.79, 63.75, 50.01, 44.74. ^{19}F NMR (470 MHz, CDCl_3 , CFCl_3), δ (ppm): -64.16 (6F, $-\text{CF}_3$).

Preparation of the polymer films and their exposure to UV light

To determine the optical properties and fabricate the optical waveguide, photoresist solutions were prepared by dissolving

synthesized AF-Ali-PC EPs or AF-Ar-PC EPs and initiator in cyclopentanone to form 30 to 60 wt% solutions (FPRs (Ali-PR 1–3 and Ar-PR 1–3)). FPRs were filtered using a $0.2 \mu\text{m}$ PTFE membrane to remove large particulates and spin-coated onto Si/SiO₂ wafer substrates (500 r/s 9 s and 1000 r/s 30 s). The spin-coated films were dried on a hot plate for 30 min (60°C) and then in a vacuum oven for 12 h to remove the residual solvent. Then, the films were irradiated with UV light for 6 min and post-baked at 120°C for 30 min to afford highly transparent films.

Fabrication of the straight waveguide

To study the applications of Ali-PRs and Ar-PRs in optical waveguides, a straight waveguide was fabricated according to a previously reported method.¹⁴ To determine the propagation loss of the FPRs, a straight waveguide structure was fabricated on a Si/SiO₂ substrate *via* direct UV-writing, as shown in Fig. 1(a). After spinning the core solution (FPRs) onto a Si/SiO₂ wafer at 1000 r/s for 30 s, the coated layers (3–4 μm in thickness) were dried at 110°C for 90 min to remove the residual solvent. Then, the films were exposed to UV light for 6 min through a contact chromium mask and post-baked at 120°C for 30 min. After this, the non-cross-linked FPRs were removed by development in propylene glycol methyl ether acetate (PGMEA) for 5 s at room temperature, followed by rinsing the wafer in isopropanol. For the upper cladding layer, PMMA was selected. PMMA was spin-coated onto the core layer and baked at 125°C for 1 h to form the cladding film.

Fabrication of the MZI thermo-optic waveguide switch arrays

The MZI thermo-optic waveguide switch array device was fabricated, as described in Fig. 1(b). First, the gold stripes were patterned by photolithography and wet etching. Second, as described in the “fabrication of the straight waveguide” section in this article, the FPRs were spin-coated onto the gold electrode to form the core layer. Then, a PMMA thin film was formed as the upper cladding layer and was then baked at 125°C for 1 h.

Results and discussion

Synthesis of the polymers

Epoxy-terminated fluoro-polycarbonates containing aliphatic segments (AF-Ali-PC EPs) and epoxy-terminated fluoro-polycarbonates containing aromatic segments (AF-Ar-PC EPs) were synthesized according to Scheme 1 and 2, respectively. The purpose of the functionalization was to incorporate functional groups, such as aliphatic segments, and aromatic segments,

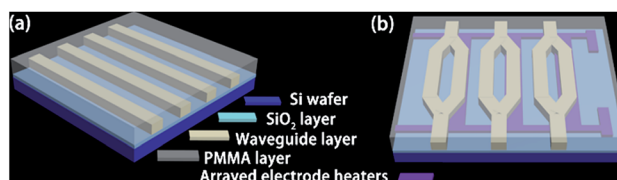
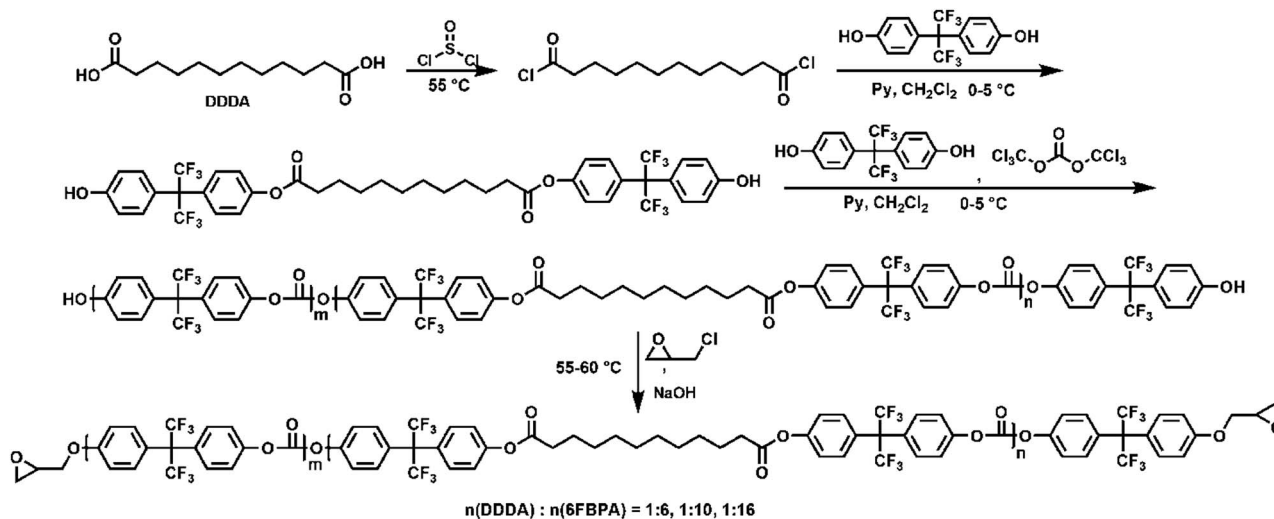


Fig. 1 Schematic of waveguide devices: (a) channel waveguide and (b) MZI thermo-optic waveguide switch arrays.





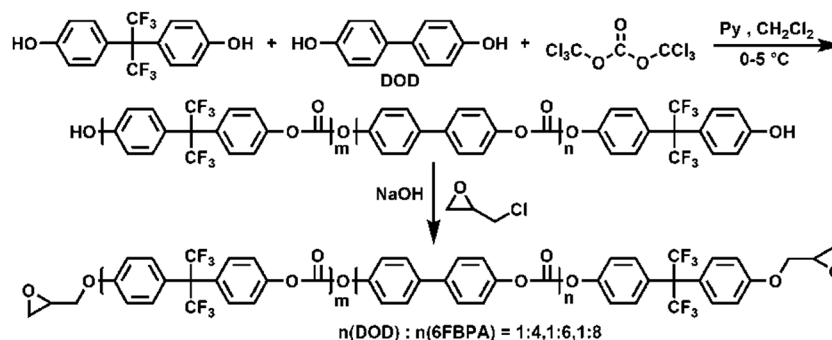
Scheme 1 The preparation of epoxy-terminated fluoro-polycarbonates containing aliphatic segments (AF-Ali-PC EPs).

into fluoro-polycarbonates chain bearing epoxy units as cross-linking sites.

To acquire AF-Ali-PC EPs, we first synthesized hydroxyl-terminated fluoro-polycarbonates containing aliphatic segments (AF-Ali-PC OHs). For the purpose of obtaining AF-Ali-PC OHs, we controlled the molar feed ratio of (6FBPA + DDDA) : BTC at 18 : 5. The structure of AF-Ali-PC OHs was determined by ^1H NMR, ^{13}C , and DEPT 135 NMR spectroscopy. In the ^1H NMR spectra (Fig. S1[†]), the signals of dodecyl in AF-Ali-PC OHs were observed at 2.62–2.59, 1.82–1.75, and 1.44–1.36 ppm. In the ^{13}C and DEPT 135 NMR spectra (Fig. S2[†]), the characteristic peaks of dodecyl in AF-Ali-PC OHs were observed at 34.37, 29.39, 29.24, 29.08, and 24.86 ppm; the $-\text{CF}_3$ peaks were observed at 127.37, 125.10, 122.80, and 120.81 ppm; and the $-\text{C}=\text{O}$ peak was observed at 151.2 ppm. The compositions of the copolymers (AF-Ali-PC OHs), calculated from their ^1H NMR spectra, were 6FBPA/DDDA = 12 : 1, 8 : 1, and 6 : 1 according to the feed ratios. In the next step, we synthesized AF-Ali-PC EPs with the AF-Ali-PC OHs and epoxy chloropropane. In the ^1H NMR spectra (Fig. S1[†]), the signals of the epoxy group in AF-Ali-PC EPs were observed at 4.30–4.27, 3.97–4.00, 3.37–3.40, 2.93–2.95, and 2.78–2.80 ppm; in the ^{13}C and DEPT 135 NMR spectra (Fig. S2[†]), the characteristic peaks of the epoxy group

were observed at 68.79, 50.01, and 44.65 ppm. These results suggest that the DDDA content of the fluoro-polycarbonates containing aliphatic segments could be readily controlled by adjusting the (6FBPA + DDDA) : BTC feed ratios.

Epoxy-terminated fluoro-polycarbonates containing aromatic segments (AF-Ar-PC EPs) were synthesized according to Scheme 2. The intermediate hydroxyl-terminated fluoro-polycarbonates containing aromatic segments (AF-Ar-PC OHs) were synthesized by controlling the molar feed ratio of DOD : BTC at 18 : 5; the structures were determined by ^1H NMR, ^{13}C , and DEPT 135 NMR spectroscopy. In the ^1H NMR spectra (Fig. S7[†]), the signals of diphenyl in AF-Ar-PC OHs were observed at 7.66–7.64 and 7.40–7.36 ppm. In the ^{13}C and DEPT 135 NMR spectra (Fig. S8[†]), the characteristic peaks of diphenyl in AF-Ar-PC OHs were observed at 121.26 and 131.27 ppm; the $-\text{CF}_3$ peaks were observed at 127.36, 125.09, 122.81, and 120.80 ppm; and the $-\text{C}=\text{O}$ peak was observed at 151.22 ppm. The compositions of the copolymers (AF-Ar-PC OHs), calculated from their ^1H NMR spectra, were 6FBPA/DOD = 6 : 1, 4.33 : 1, and 2.75 : 1 according to the feed ratios. The end products AF-Ali-PC EPs were synthesized using AF-Ali-PC OHs and epoxy chloropropane. In the ^1H NMR spectra (Fig. S7[†]), the signals of the epoxy groups in AF-Ar-PC EPs were observed at 4.26–4.23,



Scheme 2 The preparation of epoxy-terminated fluoro-polycarbonates containing aromatic segments (AF-Ar-PC EPs).



3.94–3.90, 3.28–3.24, 2.92–2.90, and 2.718–2.70 ppm; in the ^{13}C and DEPT 135 NMR spectra (Fig. S8[†]), the characteristic peaks of the epoxy group were observed at 68.79, 50.04, and 44.62 ppm. These results suggest that the DOD content of the fluoro-polycarbonates containing aromatic segments could be readily controlled by adjusting the (6FBPA + DOD) : BTC feed ratio.

The properties of the cross-linking films

Refractive index. As is known, the theoretical basis of guided-wave optics depends on the phenomenon of total internal reflection (TIR), which can confine light in the optical waveguide. Based on the device design and geometry of the waveguide, the refractive index of the core material that is being used to fabricate the waveguide must be greater than that of the cladding polymer. The controllability of the refractive-index contrast is an important feature of the polymers, which can enable high-density compact waveguiding structures with small radii of curvature. Moreover, a compact structure is critical for achieving large-scale photonic integration.⁷ As shown in Fig. 2, we synthesized six types of fluoro-polycarbonates; the refractive indices varied from 1.51 to 1.495 (at 1550 nm) for AF-Ali-PC EPs as the content of DDDA was varied from 8 to 14 mol%, and the refractive indices varied from 1.60 to 1.54 for AF-Ar-PC EPs as the content of DOD was varied from 27 to 14 mol%. The refractive indices of the polymer films and the DDDA content in AF-Ali-PC EPs or the DOD content in AF-Ar-PC EPs showed linear relationships. For the AF-Ali-PC EPs, the incorporation of flexible segments decreased the refractive indices of similar polymers, whereas for the AF-Ar-PC EPs, the rigid segments increased the refractive indices of similar polymers.¹⁵ We could obtain any refractive index between 1.60 and 1.495 by mixing the six types of fluoro-polycarbonates in appropriate proportions.

UV-near infrared spectra. Fig. 3(A) shows the near infrared spectra of the FPR films, and it can be seen that there is almost no absorption between 500 and 2000 nm compared to that of commercial photoresist SU-8. This result was due to the existence of C–F bonds in the FPRs. As is known, C–H, O–H, and N–H bonds can cause absorption in the near-IR region. When H

atoms are replaced with F atoms, the absorption in the near-IR region can be significantly reduced. For Ali-PR 1–3, the absorbance values at 1550 nm increased with the increasing DDDA content in AF-Ali-PC EP 1–3 (Fig. 3(A)(1)–(3) and (B)). Moreover, for Ar-PR 1–3, the absorbance values at 1550 nm increased with the increasing content of DOD in AF-Ar-PC EP 1–3 (Fig. 3(A)(4)–(6) and (B)). This result was mainly due to the different contents of fluorine (31.12 wt%, 30.03 wt%, and 28.16 wt% for AF-Ar-PC EP 1–3, respectively) since the absorbance values decreased with the decreasing content of F, which corresponds with the abovementioned conclusion. Due to their lower absorptions at telecommunication wavelengths (1310 nm and 1550 nm), FPRs are more suitable for application in optical waveguide devices.

Surface morphology. The surface morphologies of the FPR films were determined by atomic force microscopy (AFM). As presented in Fig. 4(A) and (B), the surface morphologies of the non-cross-linked (A) and cross-linked (B) films on the surface of Ali-PR 1 were very homogeneous, and we could not observe apparent defects, and the surface roughnesses were only 0.335 nm and 0.371 nm, respectively. This result indicates that the quality of the films, which were formed from Ali-PRs, was good. In addition, it can be suggested that the waveguide devices fabricated with Ali-PRs will have a smaller scattered light loss. Fig. 4(C) and (D) show the surface morphologies of the non-cross-linked (C) and cross-linked (D) films on the surface of Ar-PR 1, and the surface roughnesses were 0.293 nm and 2.593 nm, respectively. Owing to the presence of biphenyl structures in the polycarbonate chains, the typical droplet-like morphology with an average size of 1 μm was formed during the process of preparation of the polymer films and UV exposure.¹⁶

Solubility and thermal properties. The introduction of an aliphatic segment (AF-Ali-PC EPs) would increase the mobility and thus the flexibility of the polycarbonate chains,¹⁷ which could effectively improve their solubility compared to that of polycarbonates containing aromatic segments (AF-Ar-PC EPs). However, the cross-linked films of both polymers were all insoluble due to the formation of crosslinking network structures. We soaked the cross-linked polymer films in chloroform for a week. Then, we obtained the weights of the films before and after soaking. The results are given in Table 1. After soaking, there was less than 0.05% weight loss, which indicates that the cross-linked polymers have good resistance to organic solvents.

The thermal properties of the FPRs were evaluated by TGA and DSC measurements (Fig. S5, S6, S11 and S12[†]). The thermal decomposition behaviors and glass transition temperatures were measured under nitrogen, and the relevant results are summarized in Table 1. Weight losses of less than 5% were observed up to 260 $^{\circ}\text{C}$ before cross-linking and up to 305 $^{\circ}\text{C}$ after cross-linking for Ali-PRs, whereas those for Ar-PRs were observed up to 263 $^{\circ}\text{C}$ before cross-linking and up to 299 $^{\circ}\text{C}$ after cross-linking. The T_g s of the non-cross-linked FPRs were observed in the range of 7.3–22.8 $^{\circ}\text{C}$. Since the flexibility of the polymer chains decreased through UV light curing, no T_g was observed after cross-linking. These results indicate that all the FPRs have excellent thermal stabilities, which are sufficient for practical applications in optical waveguides.

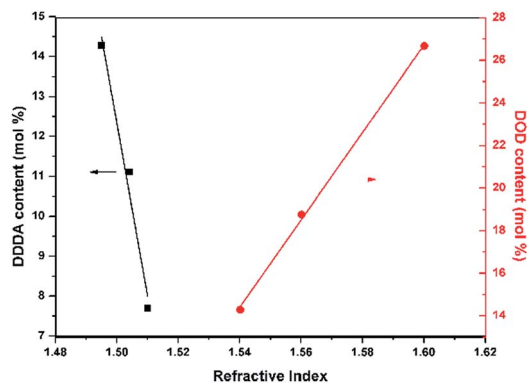


Fig. 2 Relationships between the refractive indices of the polymer films and the content of DDDA/DOD.



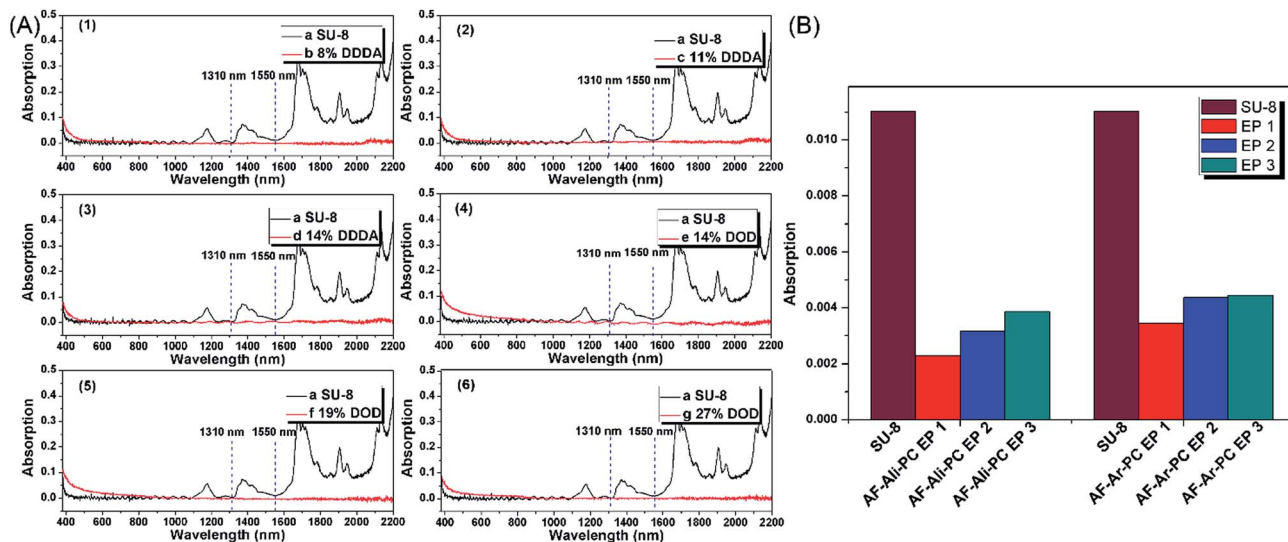


Fig. 3 (A) Near-infrared absorption spectra of Ali-PR 1–3 (b–d), Ar-PR 1–3 (e–g), and SU-8 (a). (B) The absorbance values at 1550 nm of AF-Ali-PC EP 1–3 and AF-Ar-PC EP 1–3.

Straight optical waveguide and propagation loss measurements

Typical near-field patterns of the straight waveguide at the wavelength of 1550 nm are shown in Fig. 5(A) and (B) for Ali-PR 1 and Ar-PR 1, respectively. The propagation losses at 1550 nm, which were obtained from the slope of the optical insertion loss *versus* the waveguide length

curves by the cut-back method, were 0.21 dB cm^{-1} and 0.19 dB cm^{-1} .

MZI thermo-optic waveguide switch arrays and thermo-optic characterization

Fig. 6(A) and (B) show the results of the thermo-optic switching response. The rise and fall times of the thermo-optic switch

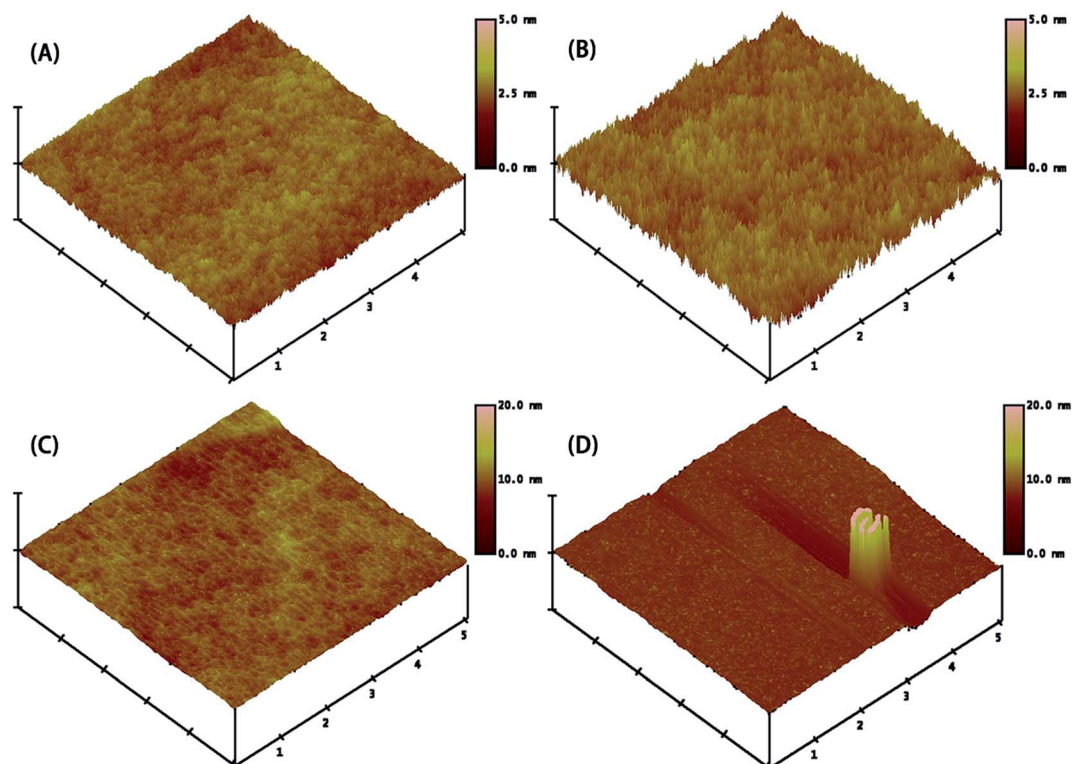


Fig. 4 AFM images of the surfaces of Ali-PR 1 (A) before cross-linking and (B) after cross-linking ($5 \times 5 \mu\text{m}$) and Ar-PR 1 (C) before cross-linking and (D) after cross-linking ($5 \times 5 \mu\text{m}$).



Table 1 Characterization and properties of the fluorinated polycarbonates

Polymer	Molar feed ratio 6FBPA to DDDA/DOD	Actual molar ratio 6FBPA to DDDA/DOD	T_g^a (°C)	T_d^b (°C)	T_d^c (°C)	Gel fraction ^d (%)
AF-Ali-PC EP 1	16 : 1	12 : 1	22.8	268	305	99.98
AF-Ali-PC EP 2	10 : 1	8 : 1	22.0	260	313	99.96
AF-Ali-PC EP 3	6 : 1	6 : 1	21.8	272	306	99.97
AF-Ar-PC EP 1	8 : 1	6 : 1	7.3	274	299	99.95
AF-Ar-PC EP 2	6 : 1	4.33 : 1	8.4	277	303	99.97
AF-Ar-PC EP 3	4 : 1	2.75 : 1	13.5	263	308	99.96

^a Determined at the heating rate of 10 °C min⁻¹ under nitrogen by DSC. ^b Defined as the weight loss of the non-cross-linked polymers at 5 wt%, which was determined at the heating rate of 10 °C min⁻¹ under nitrogen by TGA. ^c Defined as the weight loss of the cross-linked polymers at 5 wt%, which was determined at the heating rate of 10 °C min⁻¹ under nitrogen by TGA. ^d Calculated from the weight ratio of the cross-linked polymers from chloroform: initial weight.

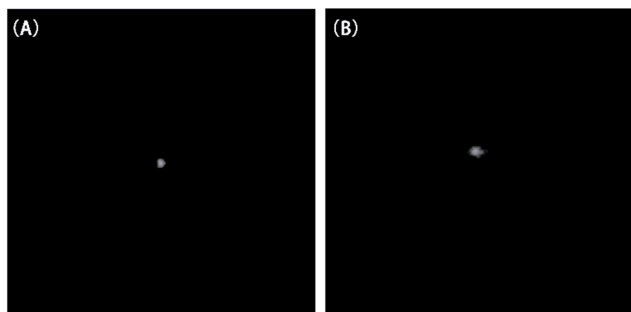


Fig. 5 Near-field patterns of the straight waveguide at 1550 nm (A) for Ali-PR 1 and (B) for Ar-PR 1.

upon application of a 200 Hz square-wave voltage were 1.822 ms and 1.364 ms, respectively, for Ali-PRs and 2.994 ms and 2.301 ms, respectively, for Ar-PRs at the square-wave voltage of 110 Hz. The insertion loss and extinction ratio were measured to be 9.2 dB and 12.0 dB for the aliphatic segment-containing photoresists and 8.9 dB and 12.3 dB for the aromatic segment-containing waveguides, respectively. The applied electric powers were 15.0 mW and 20.0 mW, which were also the switching powers. Combined with our previous work⁹ (AF-Z-PC EPs: insertion loss 9.0 dB, rise and fall times 1.546 ms and 1.226 ms (200 Hz), switching power 15.5 mW, and extinction

ratio 13.0 dB), we can predict that the fluoro-polycarbonates containing aliphatic segments are more suitable for thermo-optic waveguide switches than those containing aromatic chains.

Conclusions

In conclusion, to investigate the effects of the flexibility of the polymer chain on the characteristics of thermo-optic waveguide devices, a series of fluoro-polycarbonates were designed and successfully prepared in this study. As reported in our previous work, photocuring of solutions (Ali-PRs and Ar-PRs) containing AF-Ali-PC EPs or AF-Ar-PC EPs, a photoinitiator, and cyclopentanone yielded optical films with low surface energies and roughnesses, high thermal stabilities, and tunable refractive indices. Straight optical waveguide and MZI thermo-optic waveguide switch arrays were fabricated using Ali-PR 1 and Ar-PR 1. The propagation losses of the channel waveguide measured by the cutback method were 0.21 dB cm⁻¹ and 0.19 dB cm⁻¹ at 1550 nm. For Ali-PRs, the rise and fall times of the thermo-optic switch upon application of a 200 Hz square-wave voltage were 1.822 ms and 1.364 ms, respectively. The insertion loss and extinction ratio were measured to be 9.2 dB and 12.0 dB, respectively. The applied electric power was 15.0 mW. For Ar-PRs, the rise and fall times of the thermo-optic switch

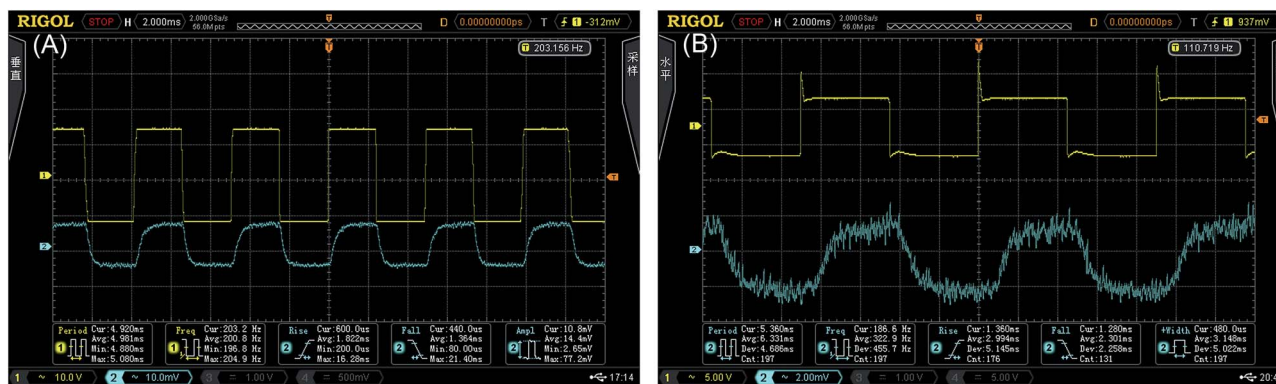


Fig. 6 Thermo-optic switch responses obtained by applying a square-wave voltage at the frequencies of 200 Hz for Ali-PR 1 (A) and at the 110 Hz for Ar-PR 1 (B).



upon application of a 110 Hz square-wave voltage were 2.994 ms and 2.301 ms, respectively. The insertion loss and extinction ratio were measured to be 8.9 dB and 12.3 dB, respectively. The applied electric power was 20.0 mW. Compared AF-Ali-PC EPs with AF-Ar-PC EPs, fluoro-polycarbonates containing aliphatic segments were more suitable for use in optical waveguide devices than those containing aromatic segments; thus, they may be more attractive for improving stabilities and realizing cross-connectors for applications in large-scale PICs such as OXC and OADM systems.

Acknowledgements

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