Highly Fluorinated Low-Molecular-Weight Photoresists for Optical Waveguides

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ABSTRACT: A series of highly fluorinated polymers were synthesized by copolymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and fluorinated styrene derivate monomer (FSDM). Their chemical structure were confirmed by ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra. The refractive index and crosslinking density of the polymers can be tuned and controlled by monitoring the feed ratio of comonomers. A series of negative-type low-molecular-weight fluorinated photoresists (NFPs) were prepared by composing of fluorinated polystyrene derivates (FPSDs), diphenyl iodonium salt as a photoacid generator (PAG) and solvent. The polymer films prepared

INTRODUCTION Polymer optical waveguides have attracted considerable attention for use in economical and practical optoelectronic devices and as interconnections in optical communication systems because of it is easier to fabricate these waveguides by spin casting than inorganic material waveguides.¹⁻⁵ The techniques that have been used for patterning optical waveguides in polymer films include photolithography and reactive ion etching (RIE) techniques. However, RIE process requires complex multilevel resist schemes and expensive equipment.^{6,7} Direct-write UV lithography is one of the candidates of photolithography technologies for fabricating micropatterns, even nanoscale structures.^{8,9} Therefore, it is desirable to have a deep-UV photoresist that can be used both as the core and the grating structures.^{10–13} A negative tone epoxy Novolak resin NANOTM SU-8 is a chemically amplified negative photoresist, which is widely used as the waveguide material, but the optical loss of the material at 1550 nm is above 1 dB/cm.¹³⁻¹⁵

Fluorine-containing polymers are of considerable interest for optical and electronic applications because of their low optical loss, surface energy, moisture absorption, and good thermal and chemical stability.^{17–23} It is known that the loss of polymeric materials at near-infrared wavelengths is attrib-

from NFP by photocuring exhibited excellent chemical resistance and thermal stabilities (T_d ranged from 230.5 to 258.1 °C). 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 0.25 dB/cm at 1550 nm. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 762–769, 2011

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uted mainly to absorption from vibration overtones of C—H bond, and this loss can be reduced appreciably by the substitution of hydrogen atoms with fluorine. Thus, fluorinated polymers are considered to be one of the potential candidates for optical applications.^{24–29}

The ever decreasing feature size on wafers is strongly pointing out roughness as one of the most critical issues for controlling propagation loss in optical devices: in fact line edge roughness (LER) has shown up itself as a standard topic for its possible yield impact on wafer production. The key strategy to resolve the LER problem is to reduce the molecular size comparing with that of the linear polymers to be able to print for the minimum feature size.³⁰⁻³³ As a result, one of the photoresist-material-based approaches to improve LER is the application of low-molecular-weight compounds. Lowmolecular-weight materials have several advantages as patterning features become smaller.34 The limit of resolution can be expanded to a molecular level since the building block of the image features becomes smaller. When a highmolecular-weight polymer is used as the building block of patterns, the image size never excels over the size of building block itself and small patterns on the order of a molecular can not be delineated.^{35–37}

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These findings prompted us to employ the new approach to develop a new low-molecular-weight fluorinated photoresist for optical waveguide. In this article, we introduced a series of novel epoxy-based negative-type fluorinated photoresists (NFPs) and a simple process for fabricating the low loss waveguides. With a diphenyl iodonium salt as photoinitiator, coated on a substrate and exposed to UV light (200–300 nm), the NFPs resist formed a highly cross-linked structure and it showed excellent processability.

EXPERIMENTAL

Materials

2,3,4,5,6-Pentafluorostyrene (PFS), 4,4'-(hexafluoro-isopropylidene) diphenol (6F-BPA), diphenyliodonium hexafluor-ophosphate (PI) 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.

Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 500 MHz for ¹H, 125 MHz for ¹³C, and 470 MHz for ¹⁹F. The chemical shifts relative to tetramethylsilane (TMS) for ¹H NMR, ¹³C NMR, and CFCl₃ for ¹⁹F NMR as internal reference are reported on the ppm scale. For ¹³C NMR, to yield the signal and multiplicity information for all carbon types including the signals of quaternary carbons, a pulse sequence DEPTQ (distorsionless enhancement by polarization transfer including the detection of quaternary nuclei) experiment was performed. IR spectra (KBr) were taken on an AVATAR 360 transform infrared (FT-IR) spectrophotometer. The molecular weights and molecular weight distributions were determined by gel permeation chromatography-refractive index-multi-angle laser light scattering (GPC-RI-MALLS) detection 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. The glass transition temperatures (T_g) of the polymers were determined by using differential scanning calorimetry (DSC) measurements performed on NETZSCH 4 instrument at a scan rate of 10 °C /min in the temperature range of 20-300 °C under nitrogen. Thermal stability of the polymer samples was analyzed using Perkin-Elmer thermogravimetry (TGA)-7 analyzer from 100 to 700 °C at a heating rate of 10 °C /min under nitrogen atmosphere. 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 a M-2000VI ellipsometer (J.A.Woolam Co.). 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. Elemental analysis was performed by Shanghai Institute Organic Chemistry.

1,1-(Hexafluoro-Isopropylidene)-1-(4-Hydroxyphenyl)-Methyl-1-Phenyl 2,3,5,6-Terafluorostyrol Ether (HPFS)

PFS (2.00 g, 0.0104 mol), 4,4'-(hexafluoro-isopropylidene) diphenol (5.00 g, 0.0154 mol), calcium hydride (1.37 g, 0.033 mol), and cesium fluoride (0.13 g, 0.9 mmol) were added into a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a water condenser. Then, N,N-Dimethylacetamide (DMAc) (25 mL) was added into the flask under the nitrogen atmosphere. The mixture was heated to 80 °C with stirring under nitrogen in the dark for 18 h. After the solution cooled to room temperature, it was filtered to remove the inorganic solids. The excess of DMAc was distilled off under reduced pressure. Column chromatography (ethyl acetate/hexane, 1/10, v/v) through silica gel was then used to obtain the pure product.

Yield: 2.40 g, 45.3%. IR (KBr, cm⁻¹): 1648.5 (C=C), 1126-1300 (C—F). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 7.39–7.37 (2H, d, 9.0 Hz), 7.27–7.25 (2H, d, 10.0 Hz), 6.98–6.96 (2H, d, 9.0 Hz), 6.85–6.84 (2H, m), 6.72–6.66 (1H, m), 6.15–6.11 (1H, d, 18.0 Hz), 5.75–5.72 (1H, d, 12.0 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): δ (ppm) 157.6, 156.5, 146.6, 144.6, 143.0, 141.0, 140.9, 132.3, 132.0, 129.3, 128.1, 125.8, 124.0, 123.5, 122.2, 121.2, 115.5, 115.4, 64.2. ¹⁹F NMR (470 MHz, CDCl₃, CFCl₃): δ (ppm) –64.66 (6F, s), –143.94 (2F, m), –155.62 (2F, m). Anal. Calcd for C₂₃H₁₂F₁₀O₂: C, 54.12; H, 2.35; F, 37.25. Found: C, 54.21; H, 2.36; F, 35.78.

Fluorinated Styrene Derivate Monomer

HPFS (2.40 g, 0.0047 mol) 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 $^{\circ}$ C with stirring, and this temperature was maintained for 6 h. During this time, sodium hydroxide (0.40 g, 0.0100 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.

Yield: 2.34 g, 90%. IR (KBr, cm⁻¹): 1648.5 (C=C), 1120-1300 (C-F), 929.3 (A). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 7.37–7.36 (2H, d, 9.0 Hz), 7.31–7.29 (2H, d, 9.0 Hz), 6.97–6.95 (2H, d, 9.0 Hz), 6.92–6.91 (2H, m), 6.71–6.65 (1H, m), 6.13–6.10 (1H, d, 18.0 Hz), 5.74–5.72 (1H, d, 12.0 Hz), 4.27–4.24 (1H, m), 3.98–3.94 (1H, m), 3.37–3.34 (1H, m), 2.90–2.87 (1H, m), 2.76–2.74 (1H, m). ¹³C NMR (125 MHz, CDCl₃, TMS): δ (ppm) 159.2, 157.6, 146.6, 144.6, 142.9, 141.0, 132.3, 131.9, 129.2, 128.0, 126.0, 124.1, 123.5, 122.2, 121.2, 115.5, 114.7, 69.2, 64.4, 50.4, 45.0. ¹⁹F NMR (470 MHz, CDCl₃, CFCl₃): δ (ppm) –64.62 (6F, s), –143.89 (2F, m), –155.57 (2F, m). Anal. Calcd for C₂₆H₁₆F₁₀O₃: C, 55.12; H, 2.83, F, 33.57. Found: C, 54.93; H, 2.79; F, 32.41.

TABLE 1	Characterization	of the	Fluorinated	Polymers	(FPSD 1-4	4)
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Polymer	PFS in Feed (mol %) ^a	Conversion (%)	PFS Composition (mol %)	<i>M</i> _n ^b	$M_{\rm w}/M_{\rm n}$	<i>T</i> _g (°C) ^c	7 _d (°C) ^d	Gel Fraction (%) ^e
FPSD 1	0	93.5	0	2436	2.01	102.3	258.1	99.53
FPSD 2	25	92.3	24.6	3574	1.88	110.5	251.2	99.26
FPSD 3	50	94.6	50.7	3087	2.13	105.2	236.1	99.14
FPSD 4	75	93.4	76.5	2679	1.98	112.6	230.5	99.11

^a Molar ratio of [PFS] / [PFS+PFDM].

^b Number average molecular weight determined by GPC.

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

Fluorinated Polystyrene Derivates (FPSD 1-4) FPSD 1

FSDM (2 g, 3.53 mmol), 10 mL of toluene, and azobisisobutyronitrile (AIBN) (0.02 g, 0.12 mmol) were introduced to a round-bottom flask fitted with a condenser. The mixture was swept by nitrogen, and then heated to 70 °C. After 6 h, the obtained mixture was poured into a large excess of methanol (20 mL). The resulting white precipitate was collected by filtration, washed thoroughly with methanol, and dried at room temperature under vacuum.

Yield: 1.87 g, 93.5%. $M_n = 2436$; $M_w/M_n = 2.01$. IR (KBr, cm⁻¹): 1120–1300 (C—F), 928.9 (A). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 7.29 (2H, s), 7.19 (2H, s), 6.80 (4H, s), 4.18–4.16 (1H, d, 10.5Hz), 3.87 (1H, s), 3.28 (1H, s), 2.83 (1H, s), 2.68 (1H, s), 2.60–2.56 (1H, m), 2.16–2.07 (2H,m). ¹³C NMR (500 MHz, CDCl₃, TMS): δ (ppm) 159.1, 157.3, 143.6, 142.6, 142.0, 140.4, 132.3, 131.8, 129.4, 128.6, 127.9, 125.8, 124.1, 123.4, 122.2, 121.1, 115.5, 114.6, 69.1, 64.1, 50.3, 45.0, 44.8, 21.9. ¹⁹F NMR (500 MHz, CDCl₃, CFCl₃): δ (ppm) –64.57 (6F, d), –143.81 (2F,m), –155.48 (2F, m). Anal. Calcd for C₂₆H₁₆F₁₀O₃: C, 55.12; H, 2.83, F, 33.57. Found: C, 55.75; H, 2.88; F, 31.29

The other polymers from both FSDM and PFS with the corresponding feed ratio of [PFS]/[PFS+PSDM] were prepared using the same procedure outlined above listed in Table 1. Their characterizations are as follows.

FPSD 2

Yield: 92.3%. $M_n = 3574$; $M_w/M_n = 1.88$. IR (KBr, cm⁻¹): 1120–1300 (C—F), 928.9 (A). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 7.31 (6H, s), 7.24 (6H, s), 6.82 (12H, s), 4.19 (3H, s), 3.89 (3H, s), 3.29 (3H, s), 2.85 (3H, s), 2.69 (3H, s), 2.60–2.57 (4H, m), 2.09–2.05 (8H, m). ¹³C NMR (500 MHz, CDCl₃, TMS): δ (ppm) 159.2, 157.3, 142.9, 140.8, 139.5, 136.8, 132.3, 131.8, 129.5, 128.0, 125.9, 123.4, 121.1, 115.2, 114.6, 69.2, 64.2, 50.3, 44.9, 44.6, 21.6. ¹⁹F NMR (500 MHz, CDCl₃, CFCl₃): δ (ppm) –64.57 (18F, d), –143.85 (8F, m), –155.52 (8F, m), –161.26 (1F, m). Anal. Calcd for C₈₆H₅₁F₃₅O₉: C, 54.55; H, 2.70, F, 35.15. Found: C, 55.37; H, 2.38; F, 33.41.

FPSD 3

Yield: 94.6%. $M_n = 3087$; $M_w/M_n = 2.13$. IR (KBr, cm⁻¹): 1120–1300 (C–F), 929.9 (A). ¹H NMR (500 MHz, CDCl₃,

 $^{\rm d}$ Onset temperature for 5% weight loss measured by TGA with a heating rate of 10 $^{\circ}{\rm C/min}$ in nitrogen.

^e Gel fraction was obtained from the ratio of the weight of samples from chloroform and the initial weight.

TMS): δ (ppm) 7.31 (2H, s), 7.21 (2H, s), 6.85 (4H, s), 4.21 (1H, s), 3.92 (1H, s), 3.32 (1H, s), 2.87 (1H, s), 2.71 (1H, s), 2.46–2.44 (2H, m), 2.04–2.02 (4H, m). ¹³C NMR (500 MHz, CDCl₃, TMS): δ (ppm) 159.3, 157.3, 143.0, 140.9, 139.7, 136.8, 132.5, 131.7, 129.6, 128.3, 126.1, 123.4, 121.4, 115.3, 114.7, 69.1, 64.4, 50.4, 44.7, 44.5, 21.9. ¹⁹F NMR (500 MHz, CDCl₃, CFCl₃): δ (ppm) –64.70 (6F, d), –143.85 (4F, m), –155.51 (4F, m), –161.36 (1F, m). Anal. Calcd for C₃₄H₁₉F₁₅O₃: C, 53.68; H, 2.50, F, 37.50. Found: C, 54.96; H, 2.58; F, 35.69.

FPSD 4

Yield: 93.4%. $M_n = 2679$; $M_w/M_n = 1.98$. IR (KBr, cm⁻¹): 1120–1300 (C—F), 928.2 (A). ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 7.30 (2H, s), 7.17 (2H, s), 6.84 (4H, s), 4.26 (1H, s), 3.96 (1H, s), 3.35 (1H, s), 2.90 (1H, s), 2.76 (1H, s), 2.41–2.39 (4H, m), 2.01–2.00 (8H, m). ¹³C NMR (500 MHz, CDCl₃, TMS): δ (ppm) 159.2, 157.3, 142.9, 141.5, 139.5, 138.9, 136.9, 132.4, 131.9, 129.6, 128.6, 128.0, 125.9, 124.1, 123.5, 122.5, 121.2, 115.2, 114.6, 69.2, 64.0, 50.3, 45.2, 45.0, 21.8. ¹⁹F NMR (500 MHz, CDCl₃, CFCl₃): δ (ppm) –64.58 (6F, d), –143.85 (8F, m), –155.52 (8F, m), –161.43 (3F, m). Anal. Calcd for C₅₀H₂₅F₂₅O₃: C, 52.26; H, 2.18, F, 41.38. Found: C, 53.24; H, 2.43; F, 40.24.

Film Preparation for the Measurement of Refractive Index

To prepare negative-type fluorinated photoresists 1-4 (NFP 1-4), the FPSD 1-4 solution were prepared in cyclopentanone (60–80 wt %), PI was added as the initiator (8 wt % relative to polymer). The NFPs were filtered by a syringe through a 0.22 μ m Teflon membrane filter and spin-coated onto a silicon wafer substrates. The resulting films (3–7 μ m in thickness) were baked at 90 °C for 30 min, then irradiated by UV light (1000 V) for 8 min. The films were finally baked at 100 °C for 1 h.

Photopatterning

For good adherence of NFP, the Si/SiO₂ wafer was first ultrasonically cleaned in organic solvents and then soaked in an etchant consisting of H_2SO_4 : $H_2O_2 = 7:3$ at 90 °C for 30 min. Then the Si/SiO₂ wafer was rinsed in deionized water, dried using nitrogen gas, and spin-coated with NFP. The thickness of the NFP layer on the substrate was controlled by the spinning speed and solid content of NFP.



SCHEME 1 Synthesis of fluorinated styrene derivate monomer (FSDM).

To fabricate optical waveguide by direct photolithography using a contact print of a simple grating mask, a NFP layer was spin-coated onto the Si substrate with a 2 μ m SiO₂ layer. The film (about 5- μ m thick) was dried at 90 °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 8 min, followed by a postbaking at 100 °C for 1 h and developing with dimethylformamide (DMF). The development time depended on the thickness of the layer.

RESULTS AND DISCUSSION

Synthesis of Monomer

Highly fluorinated phenol monomer containing tetrafluorostyrol and epoxy units was prepared by two steps as shown in Scheme 1. To avoid serious branching or cross-linking side reactions, the reaction was therefore carried out using a very mild reaction condition. Monomer HPFS was prepared from PFS and 6F-BPA in the presence of cesium fluoride and calcium as the catalyst and base, which have been found to facilitate the formation of the phenolates, and enables the reaction temperature as low as 80 °C. Pure HPFS could be easily separated by column chromatography in a yield of



FIGURE 1 ¹H NMR spectra of HPFS and FSDM (from bottom to top).



FIGURE 2 ¹³C NMR spectra of HPFS and FSDM (from bottom to top).

45.3%. Figure 1 shows the ¹H NMR spectrum of HPFS. The signals around 6.91–7.37 ppm were attributed to the hydrogen atoms in phenyl of 6F-BPA, and the characteristic peaks around 5.74 and 6.14 ppm were assigned to the protons on the double bond. Because the proton of hydroxyl group is very reactive, its signal can not be observed in the ¹H NMR spectrum. To confirm the structure of HPFS further, ¹³C NMR measurement was also carried out. In the ¹³C NMR spectrum of HPFS (Fig. 2), two signals at 132.3 and 132.1 ppm were attributed to the carbon atoms of aliphatic double bond. The characteristic peaks of -CF₃ in 6F-BPA were observed at 129.3, 125.8, 123.5 ppm.

We prepared fluorinated styrene derivate monomer (FSDM) bearing epoxy group from HPFS and epoxy chloropropane. Monomer FSDM was isolated as colorless transparent liquid material in high yield, and its structure was also confirmed by IR, NMR, and elemental analysis. In the IR spectra, FSDM



FIGURE 3 ¹⁹F NMR spectra of HPFS and FSDM (from bottom to top).



SCHEME 2 Synthesis of fluorinated polystyrene derivate (FPSD).

showed an absorption at 929.3 cm⁻¹ attributed to the characteristic band of epoxy group, which could not be observed in the spectrum of HPFS. ¹H NMR spectrum of FSDM is shown in Figure 1. In comparison with HPFS, several new signals appeared in the 2.74–4.27 ppm region in the ¹H NMR spectrum of FSDM, which corresponded to the hydrogen atoms of epoxy group. Similarly, in the ¹³C NMR spectrum of FSDM, the characteristic peaks of epoxy group were observed at 69.2, 50.4, and 45.0 ppm as shown in Figure 2. Figure 3 shows the ¹⁹F NMR of HPFS and FSDM, respectively. The signals at -155.57 and -143.89 ppm corresponded to the aromatic fluorine atoms, and the peak at -64.62 ppm was assigned to the fluorine atoms of $-CF_3$. These results indicate that we have successfully introduced epoxy group into fluorinated styrene derivate system.

Synthesis of Polymers

Polymerizations of PFS have been reported by many groups.^{38–40} In this article, FPSD 1-4 have been prepared via free radical polymerization with AIBN as an initiator as shown in Scheme 2. FPSD 1-4 showed a low-molecular-weight (M_n) ranged from 2400 to 3600 as shown in Table 1. Low-molecular-weight polymer could have advantages in decreasing LER at very small feature sizes and it is helpful to dissolve more uniformly during development. The molecular-







lar structure of FPSD 1-4 was confirmed by ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra. Figure 4 shows the ¹H NMR spectrum of FPSD-2. The peaks at 7.29, 7.10, and 6.80 ppm were ascribed to the proton in the 6F-BPA units, and the signals in higher frequencies region corresponded to the hydrogen atoms of epoxy group and aliphatic backbone. In the ¹⁹F NMR spectrum, four resonances were observed, attributable to -CF₃ at -64.7 ppm and five fluorine atoms associate with tetrafluorostyrol unit at -143.9, -155.6, and -161.43 ppm, respectively (Fig. 5). The relative peak intensities correlate well with the ratios of PFS contents. The results of the copolymerization reaction are summarized in Table 1. Generally, composition of copolymer was well matched to the ratios of monomers used as determined by ¹⁹F NMR spectra.

Photo Cross-Linking

The NFP elaborated in this study was based on photoacid generator (PAG). Cationic rather than radical photochemistry



FIGURE 6 Dependence of refractive index of NFP films on pentafluorostyrene content.



FIGURE 7 AFM photograph of surface from NFP 2 (A) before cross-linking and (B) after cross-linking $(3 \times 3 \mu m^2)$.

was preferred because it is not inhibited by atmospheric oxygen.² The film spin-coat on a Si wafer was prebaked at 90 °C for 30 min, irradiated by UV light, cured at 100 °C for 1 h, and then developed in negative mode with DMF at room temperature.

Many optical devices, such as waveguides, consist of a core and cladding assembly with small differences in refractive index between layers, the ability to turn refractive indices is extremely useful. The refractive index of the NFP 1-4 films were measured at 1550 nm by ellipsometry. As shown in Figure 6, the refractive index varied between 1.5230 and 1.5043, as PFS content varied from 0 to 75 mol %. A linear relationship was observed between the refractive index of the NFP films and the PFS content in the FPSD, for the incorporation of fluorine atoms or fluorinated side groups decreases the refractive indices of similar polymers.^{5,41}

AFM was employed to study the morphology and surface properties of the materials (Fig. 7). The images of the spincoated NFP 2 film before and after cross-linking were studied in tapping mode. The root-mean-square (RMS) surface roughness were both small and similar, 0.223 nm for uncross-linked film and 0.283 nm for cross-linked film. The surface of the spin-coated films exhibits uniform fractal morphology, which is characteristic for glassy polymers. These AFM images show that the films are fairly uniform, and no phase separation is observed.

It was found that the cross-linked polymers were insoluble in common organic solvents such as acetone, dichloromethane, chloroform, THF, and DMF. 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 1, gel fraction decreased with increasing the content of PFS, and there were all only <1% weight loss. These indicated that the cross-linked polymer films possess good resistance to organic solvents.

Thermal Properties

The glass transition temperature (T_g) of the polymers was determined by DSC measurements and the data are listed in Table 1. The T_g of uncross-linked NFPs were in the range of 102.3–112.6 °C, and no T_g were observed after cross-linking. This result can be contributed to the decreased flexibility of the polymer chains by formation of cross-linking network structure through thermal curing. Figure 8 shows the TGA



FIGURE 8 TGA thermograms of cross-linked NFP 1-3.



FIGURE 9 Near-infared absorption spectrums of NFP 1-4.



FIGURE 10 SEM images of straight waveguide fabricated with NFP 2.

curves of the cross-linked NFPs. The cross-linked NFPs exhibited satisfactory thermal stability. The 5% weight loss (T_d) for all the cross-linked NFPs were in range of 230.5–258.1 °C, as listed in Table 1, and T_d increased with increasing cross-linking density. These results indicate that the epoxy groups have reacted with each other resulting into cross-linking network structure, which improves the thermal stability of the polymer.

Optical Waveguide Fabrication and Propagation Loss Measurement

Optical waveguide devices need to have low optical loss, especially at the major telecommunication wavelengths (1310 nm and 1550 nm). Where as the harmonics and their coupling of stretching vibration of chemical bonds cause the absorption in the near-IR region. Carbon-hydrogen (C—H) and oxygen-hydrogen (O—H) bonds strongly affect the absorption in this region.^{23,25} Lower C—H bonds can significantly reduce the optical loss in near-IR region. Figure 9 shows the near-IR absorption spectra of NFP 1-4. As expected, the absorption of NFP 1-4 at 1310 and 1550 nm wavelength was very low.

Direct-write UV lithography is advantageous over other techniques because fewer steps are involved. This technique is capable of patterning features with long and linear dimensions over comparatively large planer areas.¹⁵ Figure 10 shows a typical SEM image about the core structure of straight waveguides fabricated with NFP 2. The channel waveguides were fabricated by first spin-coated NFP with 5 to 7 μm in thickness on a Si substrate with a 2- μm SiO_2 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 postbaking at 100 $^\circ\text{C}$ 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 μ m. The spectral-transmission characteristics of waveguide device were measured by tunable laser with a center wavelength a 1550 nm and a spectrum analyzer. Light from a tunable semiconductor laser was coupled into the input waveguide through a single-mode fiber. The near-field mode pattern at the out channels shown in Figure 11 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 $6 \times 6 \mu m^2$ straight waveguide fabricated from NFP 2 had a propagation loss of 0.25 dB/cm by cut-back method.

CONCLUSIONS

We had prepared a series of direct-UV-written NFPs based on FPSDs and photoinitiator. The cross-linked material had good chemical resistance, thermal stability, good adhesion on substrate, and tunable refractive index. Low-loss channel optical waveguides had been fabricated for 1310 and 1550 nm that the propagation loss was measured to be 0.25 dB/cm at 1550 nm by the cut-back method fabricated with NFP 2. These unique features will make attractive approach for lowloss waveguide devices.



FIGURE 11 Near-field pattern of waveguide mode at 1550 nm obtained with NFP 2.

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