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Synthesis and characterization of novel fluorinated polycarbonate negative-type photoresist for optical waveguide

Zhenzhen Cai [a], Huanyang Yu [b], Yingchao Zhang [a], Ming Li [a], Xiaoyan Niu [d], Zuosen Shi [a, **], Zhanchen Cui [a, c, *], Changming Chen [d], Daming Zhang [d]

[a] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, People's Republic of China
[b] College of Materials Science and Engineering, Jilin Jianzhu University, Changchun 130118, People's Republic of China
[c] Department of Chemistry and Pharmacy, Zhuhai College of Jilin University, Zhuhai 519041, People's Republic of China
[d] State Key Lab on Integrated Opto-electronics, Jilin University Region, Changchun 130012, People's Republic of China

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ABSTRACT

A kind of fluorinated and epoxy-terminated low-molecular-weight bisphenol A polycarbonate (FBPA-PC EP) was synthesized by solution polymerization of 4, 4′-(hexafluoro-isopropylidene) diphenol (6F-BPA) with triphosgene (BTC) and further reacted with epoxy chloropropane. The structure of the polymer was confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. A series of negative-type fluorinated photoresists (NTFPs) were prepared by mixing of FBPA-PC EP and FSU-8 with triphenylsulfonium hexafluorophosphate and cyclopentanone as the photoacid generator (PAG) and solvent. The polymer films prepared from NTFPs by UV-curing exhibited superior chemical resistance, excellent thermal stability (Tds ranged from 295 to 303 °C) and low surface roughness. A clear negative pattern was obtained through direct UV photo-cross-linking and then chemical development which can be used as high-quality channel waveguides (the roughness of the lateral ridge ranged from 21 to 32 nm (1 × 1 μm)). For waveguides with the polymethylmethacrylate as upper cladding, the propagation loss of the channel waveguides was measured to be 0.25 dB/cm at the monitoring light of 1550 nm.

1. Introduction

Since 90s last century, organic polymers appear to be promising candidates for optical waveguide due to their possible application in economical and practical optoelectronic devices and as optical components in interconnects and optic communication systems, because they exhibit controllable refractive indices, good thermal stability, better process ability and lower fabricating cost comparing with inorganic material waveguides [1–12]. There are many techniques to fabricate optical waveguides in the literature, such as photolithography, reactive ion etching (RIE) techniques, and direct-write UV lithography [9,11,13,14]. Among them, direct-write UV lithography has attracted considerable attention as a promising photolithography technology for fabricating micro-patterns, even nanoscale structures, exhibiting lower cost, higher yield and larger dimension [15,16]. Therefore, some deep-UV photoresists, such as the negative tone epoxy Novolak resin NANOTM SU-8 have been used in integrated optics [17–20]. It is well known that, at the telecommunication wavelengths (e.g. 1310 and 1550 nm), the vibrational overtone absorption of C—F bonds is very weak resulting in lower optical loss than that of hydrocarbon-based polymers [6,9,10,12,21–23]. In addition to the low optical loss, other properties of fluorine-containing polymers such as good thermal and chemical stability make it attractive for waveguides applications [12,24,25].

However, most of the fluorinated polymers have been limited in application because they have severe shortcomings including poor adhesion to substrates and low transparency, arising from the high surface energy and crystalline properties of fluorine compounds [24,26,27]. Usually, the substrates used for fabricating the optical waveguide including glass and silicon wafer are highly polar because of silicon oxide or silanol on the surface. So, for the sake of enhancing the adhesion of the polymer layer to the substrates, an

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[*] Corresponding author. State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, People's Republic of China. Tel.: +86 431 85168217.

[**] Corresponding author. Tel.: +86 431 85168930.

E-mail addresses: shizs@jlu.edu.cn (Z. Shi), czc@jlu.edu.cn (Z. Cui).

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effective method is to introduce the polar functional groups such as carbonate or carbamate groups to enhance the interaction between materials and substrate [24,28,29]. In optical devices, propagation loss is one of the most critical issues, and most of the propagation loss is resulted by the line edge roughness (LER). The key strategy to resolve the LER problem is to reduce the molecular size [30–33]. As a result, one of the photoresist-material-based approaches to improve LER is using low-molecular-weight compounds. If the building block of patterns is a high-molecular-weight polymer, the image size will never excels over the size of building block itself and small patterns on the order of molecular will not be delineated. As the building block of the image features becomes smaller, it can make up the drawback of resolution which can be expanded to a molecular level [34–36]. In previous works of our group's, have reported the low-molecular-weight [11] and aromatic–aliphatic copolyethers [12] photoresists for optical waveguide. In the former one, highly fluorinated polymers with the number average molecular weight between 2000 and 3500 were synthesized by copolymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and fluorinated styrene derivate monomer (FSDM). The root-mean-square (RMS) surface roughness was only 0.238 nm for cross-linked film. In the latter one, (4-methoxy) phenylhydroquinone (Me-HQ), 2,2,3,3,4,4,5,5,6,6,7,7-dodeca-fluoro-1,8-octanediol (12F-diol) and decafluorobiphenyl (DFBP) were polymerized and further reaction with epoxy chloropropane to obtain highly fluorinated aromatic-aliphatic copolyethers containing epoxy groups (FA-APE EP).

Encouraged by excellent properties of these two photoresists, we synthesized a novel fluorinated epoxy-terminated bisphenol A polycarbonate (FBPA-PC EP) with the number-average molecular weight about 4000 and used the fluorinated SU-8 (FSU-8) to adjust the refractive index. 44 percent of C–H bonds in the polymer were displaced by C–F bands probably leading to low loss and as a molecular scale building block and the low molecular weight polymer was in favor of decreasing the edge roughness of the waveguide. The refractive index, Td, and crosslinking degree of this polymer were all superior to the previous photoresists. After a simple process to fabricate the waveguides, coated on a substrate and exposed to UV light (200–300 nm), mixture of FBPA-PC EP and FSU-8 resist formed a highly cross-linked structure with a triphenylsulfonium hexafluorophosphate as photoinitiator and it showed excellent processability. Additionally, the optical loss of the straight waveguide fabricated with the resulting photoresist was only 0.25 dB/cm at 1550 nm.

2. Experimental

2.1. Materials

Triphosgene (BTC), 4, 4′-(hexafluoro-isopropylidene) diphenol (6F-BPA), Triphenylsulfonium hexafluorophosphate 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. Instruments and measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 500 MHz for ^{1}H, 125 MHz for ^{13}C, and 470 MHz for ^{19}F. The chemical shifts relative to tetramethylsilane (TMS) for ^{1}H NMR, ^{13}C NMR, and $CFCl_3$ for ^{19}F NMR as internal reference are reported on the ppm scale. For ^{13}C NMR, in order to yield the signal and multiplicity information for all carbon types including the signals of quaternary carbons, a pulse sequence ^{13}C-DEPT 135 (distorsionless enhancement by polarization transfer to distinguish the primary, secondary and tertiary nuclei) experiment was performed cooperating with the ^{13}C NMR. IR spectra (KBr) were taken on an AVATAR 360 transform infrared (FT-IR) spectrophotometer. The molecular weights and molecular weight distributions were determined by Prominence HPLC LC-20A Shimadzu, refractive index detector, with tetrahydrofuran (THF) as the solvent at 25 °C at a flow rate of 1.0 mL/min using polystyrene as a calibration. The glass transition temperatures (Tgs) 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 25–350 °C under nitrogen. Thermal stability of the polymer samples was analyzed using Perkin–Elmer thermogravimetry (TGA)-7 analyzer from 100 to 800 °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 and NanoNavi, SPA300) 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 2 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 on Vario micro cube.

2.3. Synthesis of the polymer

2.3.1. Synthesis of fluorinated hydroxy-terminated bisphenol A polycarbonate (FBPA-PC OH)

6F-BPA (9.027 g, 0.027 mol) was dissolved in 40 mL of pyridine and the solution was cooled to 0 °C. A solution of triphosgene (2.228 g, 0.008 mol) in methylene chloride (60 mL) was added dropwise, and the reaction mixture was vigorously stirred at 0–5 °C for 30 min. The solution became viscous and saturated with pyridine-hydrochloride during this time and was subsequently allowed to warm spontaneously to room temperature. After reaching room temperature, the suspension was stirred for 6 h. A 5% aqueous hydrochloric acid solution (310 mL) was used to neutralize the reaction mixture. The polymer was extracted with methylene chloride (3 × 50 mL) and washed with water (6 × 30 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated. The viscous residue was added into methanol dropwise, whereupon the polymer precipitated and was filtered with subsequent washing with methanol. The white pure polymer

Table 1
The root-mean-square (RMS) surface roughness of the polymer films.

Mixture	Surface roughness[a] (nm)				Surface roughness[b] (nm)			
	1	2	3	Average	1	2	3	Average
EP-FSU-8 1	0.274	0.282	0.270	0.275	0.256	0.254	0.261	0.257
EP-FSU-8 2	0.284	0.250	0.319	0.284	0.263	0.262	0.256	0.260
EF-FSU-8 3	0.289	0.305	0.274	0.289	0.364	0.374	0.358	0.365
EP-FSU-8 4	0.258	0.254	0.295	0.269	0.398	0.397	0.413	0.403

[a] Root-mean-square (RMS) surface roughness of the spin coated NTFPs film before cross-linking.

[b] Root-mean-square (RMS) surface roughness of the spin coated NTFPs film after cross-linking.