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Sul-containing fluorinated polyimides for optical waveguide device

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Abstract

Novel sul-containing fluorinated polyimides have been synthesized by the reaction of 2,2′-bis-(trifluoromethyl)-4,4′-diaminodiphenyl sulfide (TFDAS) with 1,4-bis-(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA), 2,2′-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 4,4′-oxydiphthalicanhydride (ODPA) or 3,4,3′,4′-biphenyl-tetracarboxylic acid dianhydride (*s*-BPDA). The fluorinated polyimides, prepared by a one-step polycondensation procedure, have good solubility in many solvents, such as *N*-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), cyclohexanone, tetrahydrofuran (THF) and *m*-cresol. The molecular weights (M_n's) and polydispersities (M_n/M_w's) of polyimides were in the range of 1.24×10^5 to 3.21×10^5 and 1.59–2.20, respectively. The polymers exhibit excellent thermal stabilities, with glass-transition temperatures (T_g) at 221–275 °C and the 5% weight-loss temperature are above 531 °C. After crosslinking, these polymers show higher thermal stability. The films of polymers have high optical transparency. The novel sul-containing fluorinated polyimides also have low absorption at both 1310 and 1550 nm wavelength windows. Rib-type optical waveguide device was fabricated using the fluorinated polyimides and the near-field mode pattern of the waveguide was demonstrated.

Keywords: Optical waveguide; Fluorinated polyimide; Sulfur

1. Introduction

Polymer optical waveguides have attracted considerable attention for their possible application as optical components in optical interconnects and optical communication systems because of their potential ease of manufacture at low temperature, and the low cost of processing [1].

The key issues on the polymer waveguide materials include four aspects: (1) low propagation losses at the optical communication wavelengths, (2) high thermal stability to provide compatibility with high-performance electronic device fabrication, (3) controllability of refractive index for the easy control of the waveguide dimension to match the mode size with fibers, and (4) good adhesion to the silicon substrate [2–5]. However, hydrocarbon polymers have a high optical loss in the infrared communication region due to carbon–hydrogen (C–H) bond vibrational absorption. By modifying a molecule via the substitution of fluorine or deuterium for hydrogen in the C–H greatly reduces optical loss. Many organic polymers such as deuterated or fluorinated poly(methyl methacrylate) (PMMA) [6,7], polystyrene (PS) [8,9], and poly(carbonate) (PC) [10,11] are used as materials for a variety of optical components. However, these polymers do not have sufficient thermal stability at high temperature, for the fabrication temperature of the optical devices is 260 °C, and the short time temperature is up to 400 °C. Fluorinated polyimides are more accessible than these polymers because of their molecular structure. In addition, they have good thermooxidative stability, outstanding mechanical properties, fire resistance and so on [12–15]. However, polyimides due to their stiff backbone need improvements to lower the birefringence.

Moreover, sul-containing aromatic polymers such as polysulfide and polysulfone are key polymers for optical materials because of their high atomic refraction of the sulfur atom [16–18]. Further sul-containing aromatic polymers have great thermal stability for the existence of 3d orbit sulfur atom.

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In this study, we introduced the sulfur atom to the famous fluorinated polyimide monomer 2,2′-bis-(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) [19,20], and hope the new material can keep the advantage of the famous polyimide. The sulfide groups in polymers were introduced to improve adhesion to the Si substrates [5]. Furthermore, sulfur atom can act as a potential crosslinking group while fabricating optical waveguide devices. It can be heated or irradiated to crosslink to satisfy the need of the interbedded technology of the devices [21–24]. After crosslinking, these polymers show higher thermal stability. The sulfide crosslinking will not introduce C–H bond compared to the other common crosslinking groups [5,25], thus it can decrease the C–H bond vibrational absorption and lower optical loss will be expected. The novel polyimides were charactered in detail for properties and also applied to fabricate optical waveguide devices. The optical properties of the device are also demonstrated.

2. Experimental

2.1. Materials

1,4-Bis-(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) was purchased from Changchun Institute of Applied Chemistry, Chinese Academy of Science and recrystallized from acetic anhydride before used. 4,4′-(Hexafluoroisopyrilidene)diphthalic anhydride (6FDA) was purchased from Aldrich Chemical Co. and baked at 160 °C in vacuo overnight before use. 4,4′-Oxydiphthalicanhydride (ODPA) and 3,4,3′,4′-biphenyl-tetracarboxylic acid dianhydride (*s*-BPDA) were purchased from Aldrich Chemical Co. and recrystallized from acetic anhydride before use. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves. Other chemicals were used as received.

2.2. Measurements

The differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC821e at a rate of 20 °C/min under a nitrogen atmosphere. The thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA-7 thermal analyzer system at the heating rate of 10 °C/min under nitrogen. The FTIR spectra (KBr or film) were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. Gel permeation chromatograms (GPC) were obtained by a Waters 410 instrument with tetrahydrofuran (THF) as the eluent and polystyrene as the standard. The ^{1}H NMR (500 MHz) spectra were recorded using a Bruker 510 NMR spectrometer with tetramethylsilane as the reference. The birefringence of the polymer films, at the 650 nm wavelength, were determined from coupling angles of TE (transverse electric) or TM (transverse magnetic) optical guided modes with a gadolinium gallium garnet (GGG) prism. The UV–vis absorption spectra were recorded on a UV2501-PC spectrophotometer. The SEM measurement was performed on a SHIMADZU SSX-550 microscope. Near-infrared spectra (near-IR) were performed on a Varian Kera 500 spectrometer. Refractive indices of polymer films were measured by M-2000UI spectroscopic ellipsometer (J.A. Woollam, Lincoln, USA). The atomic force microscopy (AFM) observations of the surface were carried out with the commercial instrument (Digital Instrument, Nanoscope IIIa, Multimode). All the tapping mode images were taken 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.

2.3. Synthesis of monomer

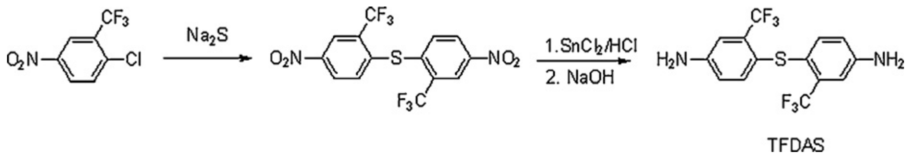
The monomer, TFDAS was synthesized several years ago [26]. In this paper, we used a different method to obtain the final monomer, and the procedure is described in Scheme 1.

A mixture of 2-chloro-5-nitrobenzotrifluoride (11.75 g, 50 mmol), sodium sulfide 9-hydrate (6 g, 25 mmol) and 50 mL DMAc was placed in a 100-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen purge. The mixture was refluxed with stirring for 8–12 h and then cooled to room temperature. The mixture was poured into an ethanol/water (1:5, v/v) mixture to give a yellow solid material, which was collected and washed with cold ethanol and water then dried at 100 °C in vacuo.

m.p.: 136 °C. FTIR (KBr): 1533, 1350, 1303, 1128, 1030, 740 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.66 (s, 2H), 8.32 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 9.0$ Hz, 2H).

A slurry of 2,2′-bis-(trifluoromethyl)-4,4′-dinitrodiphenyl sulfide (31.724 g, 77 mmol), stannous chloride ($SnCl_2$) (59.75 g, 315 mmol) and 280 mL of anhydrous EtOH was stirred while 208 mL of concentrated HCl was added slowly. After addition of HCl was over, the mixture was refluxed for 8 h. Excess EtOH was evaporated and the remaining solution was poured into 280 mL ice–water mixture. The solution was basified with 10% NaOH solution and the pale yellow precipitate was filtered off, washed repeatedly with hot water and dried in vacuo. The sample was recrystallized from aqueous alcohol.

m.p.: 74 °C. FTIR (KBr): 3500, 3544, 3361, 3224, 1347, 1029 cm^{-1}. ^{1}H NMR (500 MHz, DMSO, δ, ppm): 6.96 (s, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.71 (d, $J = 8.5$ Hz, 2H), 5.76 (s, 4H).



Scheme 1. Synthesis of 2,2′-bis-(trifluoromethyl)-4,4′-diaminodiphenyl sulfide.