Low-Loss Passive Polymer Waveguides by Using Chlorofluorinated Polyimides

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ABSTRACT: Chlorofluorinated polyimides were prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB), and 2,2′-dichloro-4,4′-diaminobiphenyl (DCB) for optical waveguide applications. The resulting optical polymers exhibited good thermal stability, controllable refractive index, and low optical loss in the optical communication wavelengths of 1.3 and 1.55 μm. The control of refractive indices of the polymers was achieved by copolymerization of 6FDA/PFMB and 6FDA/DCB. As the amount of DCB was increased, the refractive indices of polymer were increased. The effect of addition of chlorine on optical properties of polymers such as absorption loss in the near-IR region were also investigated. Rib-type optical waveguides were fabricated using these chlorofluorinated polyimides. These waveguides exhibited low loss of less than 0.4 dB/cm for both TE and TM polarizations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 107–112, 1999

Key words: chlorofluorinated polyimides; refractive index; low optical loss; optical telecommunication; optical waveguide; low birefringence; low polarization dependence loss (PDL)

INTRODUCTION

There have been many researches on polymer-based optical waveguides due to their ease of processing compared to silica based materials.[1–3] One of the critical considerations for an optical polymer is low optical loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm. It is known that loss at near-infrared (IR) wavelengths is mainly attributed to absorption from vibrational overtones of the carbon–hydrogen (C—H) bond, and this loss can be reduced appreciably by the substitution of hydrogen atoms to deuterium or fluoride.[4–7] Because the optical waveguides consist of a light carrying core and a cladding, another important requirement for the optical polymer is precise control

of the refractive indices of polymers. It is reported that the copolymerization of fluorinated and nonfluorinated monomers provides good methodology to control the refractive indices of polymers.[8,9] Recently, Kobayashi et al. reported low-loss optical waveguides using fluorinated polyimides based on 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB).[10] They controlled the refractive indices of the polymers for core and cladding by copolymerization of 6FDA with PFMB and nonfluorinated diamine, 4,4′-oxydianiline (ODA). Although the refractive indices of the polymers were increased as the amounts of nonfluorinated diamine were increased, it is expected that the increased amount of nonfluorinated diamine can cause additional optical loss of these polymers due to the increment of C—H bond number density. Because the carbon–chlorine (C—Cl) bond is reported to have low loss at 1.3 and 1.55 μm like the

carbon–fluorine (C—F) bond based on the calculation,[11] and has larger polarizability than the C—F bond, incorporation of the C—Cl bond into the polymer backbone may yield good refractive index controllability without additional optical loss. Thus, chlorofluorinated polyimides can be a potential candidate for optical application. In this article we demonstrate a novel approach in designing optical polymers that exhibit a good thermal stability, refractive index controllability, and low optical loss in the near-infrared wavelength region by using chlorofluorinated and fluorinated polyimides.

EXPERIMENTAL

Materials

1-Chloro-3-nitrobenzene (Aldrich), ethanol (Aldrich), ethylene glycol (Aldrich), sodium hydroxide (Fisher), zinc dust (Aldrich), and phosphoric acid (Fisher) were used as received. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Chriskev) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB, Fluoro Chem.) were dried at 150°C under reduced pressure and sublimated prior to use. N,N′-dimethylacetamide (DMAc, Aldrich) was purified by distillation under reduced pressure over calcium hydride.

Monomer Synthesis[12]

3,3′-Dichloroazoxybenzene

A mixture of 60 g (1.50 mol) of sodium hydroxide, and 175 mL of ethanol contained in a 1-L, three-neck, round-bottom flask, which was fitted with a nitrogen inlet, a condenser, and a mechanical stirrer, was heated to 70°C until most of the sodium hydroxide dissolved. After ethylene glycol (210 mL, 3.76 mol) and 1-chloro-3-nitrobenzene (22.06, 0.140 mol) were added, the reaction mixture was heated at reflux for 2 h. The warm mixture was added to 2 L of ice water and stirred for 30 min. The resulting precipitate was collected by filtration and washed with 2.5 L of distilled water. After the precipitate was dissolved in acetone, the solution was dried over magnesium sulfate and decolorized with charcoal. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol and dried at 50°C under reduced pressure. ^{1}H-NMR (DMSO-d_6) δ 7.45–8.38 ppm (m, 8H, aromatic).

2,2′-Dichloro-4,4′-diaminobipheny (DCB)

After 3,3′-dichloroazoxybenzene (18 g, 0.0667 mol) was dissolved in 150 mL of tetrahydrofuran,

210 mL of glacial acetic acid was added. Zinc dust (16.8 g) was then slowly added. After addition was complete, 30 mL of 85% phosphoric acid was added slowly over 20 min so that the reaction remained below 55°C. After stirring for 30 min, the solution was diluted with 450 mL of distilled water and then extracted with 225 mL methylene chloride. After the zinc solids in the organic phase were removed by filtration, the liquid was added dropwise to 90 mL of concentrated hydrochloric acid at −5°C. The white paste was collected by filtration, washed with methylene chloride, and then dissolved in warm water. It was neutralized with sodium hydroxide to precipitate the product. The crude product was purified by recrystallization from toluene. ^{1}H-NMR (DMSO-d_6) δ 5.38 (s, 4H, ArNH$_2$), 6.50 (d, 2H, aromatic), 6.65 (s, 2H, aromatic), and 6.85 ppm (d, 2H, aromatic).

Polymerization and Film Preparation

Chlorine and fluorine-containing polyimides were prepared according to the general reaction shown in Scheme 2. Polymerizations were carried out under nitrogen atmosphere by adding a stoichiometric amount of diamine and dianhydride in DMAc at room temperature. The copolyimides were prepared from the two amines, PFMB and DCB, with 6FDA. The content of DCB was varied (20–80 mol % based on PFMB). The resulting poly(amic acid) solutions were filtered through 0.2-μm Teflon filter and then spun coated on a Silicon wafer, followed by curing at 80°C/2 h, 160°C/1 h, 250°C/0.5 h, 300°C/0.5 h, and 350°C/0.5 h.

Waveguide Fabrication

Rib-type optical waveguides were fabricated by spin coating an undercladding and a core polymer of an oxidized silicon substrate. Core ridges were then formed by conventional photolithography and dry etching using a plasma etcher. The waveguides were fabricated by covering the core ridges with overcladding polymer by spin coating.

Measurements

A Varian Gemini 200 was used for ^{1}H-NMR measurements. TA TMA 2940 thermal mechanical analyzer was used to obtain the glass transition temperatures (T_g) of the polymers at a heating rate of 10°C/min. The internal stresses of thin polymer films (10 μm) were recorded by using a Tencor FLX-2908 thin-film stress-measurement

Figure 1 Experimental setup for measuring near-field mode pattern and loss of waveguides.

Scheme 1

instrument. The degrees of warping of polyimide-coated wafers were converted to the internal stress of polyimide films. Refractive indices of the polymer films were measured using a Metricon 2010 prism coupler using light from a 1.3-μm laser diode, and a 1.55-μm laser diode. Near-infrared spectra of the samples were recorded on a ATI Mattson Infinity FTIR Spectrometer using a 5-cm path quartz cell. The near-field mode pattern and loss of the waveguides were recorded at 1.55 μm using the experimental setup, as illustrated in Figure 1. The incident light beam was introduced to the waveguides through single mode fibers with a mode-field diameter of 10 μm. The propagation losses of the straight waveguides were measured by the cutback method.[13] The output beam power intensity was measured with an Anritsu optical power meter.

RESULTS AND DISCUSSION

Synthesis of Monomer

To incorporate chlorine moiety into the polymer backbone, a chlorinated monomer is needed. We chose 2,2′-dichloro-4,4′-diaminobiphenyl (DCB) because its structure is the same as 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) except it has two chlorines on the benzene ring instead of trifluoromethyl groups. 1-Chloro-3-nitrobenzene was reduced with sodium hydroxide and ethanol to the 3,3′-dichloroazoxybenzene (compound 1) in the presence of ethylene glycol. This azoxy compound was then reduced further to 3,3′-dichlorohydrazobenzene with zinc dust. This compound was treated with hydrochloric acid to catalyze the benzidine rearrangement that afforded 40% yield of the 2,2′-dichloro-4,4′-diami-

nobiphenyl (DCB, compound 2) as shown in Scheme 1.

Preparation of Polymers and Their Thermal Properties

Chlorofluorinated and fluorinated polyimides were synthesized from 6FDA, DCB, and PFMB. The copolyimides were prepared from the two amines, PFMB and DCB, with 6FDA. The content of DCB was varied (20–80 mol % based on PFMB) as shown in Scheme 2. The intrinsic viscosities of resulting polymers were between 1.8 and 2.2 dL/g measured at 30°C in N-methyl-2-pyrrolidinone (NMP), exhibiting high molecular weights of these polymers. The internal stresses, glass transition temperatures (T_g), and onset temperatures of weight loss of the two homopolymers, 6FDA/PFMB and 6FDA/DCB, are summarized in Table I. The resulting polymers have T_g values around 350°C and show no appreciable weight loss up to 515°C in the TGA thermograms, indicating good thermal stability. The thermal properties of these two polymers were not much different due to their similar structure. Furthermore, the internal

Scheme 2

Table I   Characterizations of Polymers

Polymer	Internal Stress (MPa)[a]	T_g (°C)[b]	Onset Temperature of Weight Loss[c]
6FDA/PFMB	38	350	515
6FDA/DCB	38	354	512

[a] Determined by Tencor FLX-2908 thin-film stress measurement instrument.
[b] Determined by TMA at a heating rate of 10°C/min.
[c] Determined by TGA at a heating rate of 10°C/min in nitrogen.

stress of 6FDA/DCB is the same as that of 6FDA/PFMB, indicating that pendant Cl groups in DCB does not affect stress compared with pendant CF_3 groups in PFMB. This is beneficial for preventing problems that come from the internal stress caused by the CTE differences in the multilevel structure for waveguide applications.

Effect of Carbon–Chlorine (C—Cl) Bond on Optical Loss

The effect of the carbon–chlorine (C—Cl) bond in the optical loss of compounds at the near-infrared region was investigated by comparing the near-IR spectra of n-hexane (C_6H_{14}) and carbon tetrachloride (CCl_4). These spectra were measured by using a 5-cm quartz cell. As shown in Figure 2, there are strong absorption bands around 1.1 and 1.4 μm in n-hexane (C_6H_{14}), whereas these bands are not observed in carbon tetrachloride (CCl_4). It is known that the absorption bands around 1.1 and 1.4 μm are results from absorption of these wavelengths by stretching vibrations, and combination tones with deformation vibrations of carbon–hydrogen bonds (C—H).[14] Although the 1.3- and 1.55-μm wavelengths, which are used in optical telecommunications, are located in the valleys in the spectrum, the neighboring absorption bands are strong enough to increase optical loss. The low absorption at these wavelengths is one of the critical considerations for a polymeric optical waveguide. It is reported that absorption due to C—H bonds can be reduced by replacement of hydrogen in the C—H bonds to heavier atoms such as fluorine (F) and deuterium (D).[15] Groh introduced a quantum mechanical method to predict the frequency of the higher overtones from their fundamental frequency of various chemical bonds.[11] Calculations show that the wavelengths

for the fundamental stretching vibrations of the C—D and C—F bond are about 1.4 and 2.8 times longer than those of the C—H bonds, respectively. Furthermore, the corresponding wavelength for the C—Cl bonds are about 3.1 times longer than those of the C—H bonds. Thus, absorption due to C—H bond can also be effectively avoided when hydrogen is replaced to chlorine (Cl) at 1.3 and 1.55 μm. This was confirmed by observing no absorption bands in the near-IR region in the spectra of carbon tetrachloride (CCl_4).

Effect of Carbon–Chlorine (C—Cl) Bond on the Refractive Indices of Polymers

The effect of the chlorine on refractive indices of the polymers was monitored using a prism coupler. As shown in Figure 3, the refractive indices of the polymer increased linearly as the amount of chlorine containing monomer, DCB, increased at 1.55 μm for both in-plane (TE) and out-of-plane (TM) polarizations. This may result from the larger electronic polarizability of the chlorine than that of the fluorine atom.[16] The precise control of the refractive indices of the core and cladding for optical waveguides is another important issue, and this can be achieved by using these chlorofluorinated polyimides. We were able to control the refractive indices of polymers in the range of 1.5176–1.5714 for TE polarization and 1.5076–1.5590 for TM polarization at 1.55 μm by copolymerization of 6FDA/PFMB and 6FDA/DCB. Furthermore, the birefringences, the refractive indices difference between in-plane (n_{TE}) and out-of-plane (n_{TM}), of the copolyimides were not

Figure 2   Near-IR spectra of n-hexane (C_6H_{14}) and carbon tetrachloride (CCl_4).

Figure 3 Refractive indices of fluorinated and chlorofluorinated polyimides at 1.55 μm.

changed much (0.010–0.012) as the amount of 6FDA/DCB increased. This means that the difference between the refractive indices of the cladding and core for the TE polarization (Δn_{TE}) is not very different from that for TM polarization (Δn_{TE}). This is very advantageous for reducing the polarization-dependent optical loss (PDL) of

the waveguides that is caused by large difference between (Δn_{TE}) and (Δn_{TM}). The above results indicate that the refractive indices of the optical polymers can be controlled by the copolymerization of 6FDA/PFMB and 6FDA/DCB, without causing either further optical loss or changing the birefringence and internal stress.

Fabrication and Characterization of Rib-Type Waveguides

Rib-type optical waveguides were fabricated by using fluorinated and chlorofluorinated polyimides, as shown in Figure 4. An undercladding layer (6FDA/PFMB, n_{TE} = 1.5176, n_{TM} = 1.5076, and 14 μm thick) and a core layer (6FDA/PFMB: 6FDA/DCB = 6 : 4, n_{TE} = 1.5370, n_{TM} = 1.5272, and 5.5 μm thick) were spin coated on an oxidized silicon substrate. Core ridges (2.1 μm depth and 9 μm width) were then formed by conventional photolithography and dry etching. Waveguides were fabricated by covering the core ridges with an overcladding polymer by spin coating. The propagation loss of the straight waveguides at 1.55 μm was measured by the cut-back method.[13,17] The 28.5-mm long straight waveguide was shortened by 8 mm with each cut, and the transmission loss was measured from the difference between input and output light intensities by an optical power meter. The incident light beam was introduced to the waveguides through single mode fibers with a mode-field diameter of 10 μm. The horizontal axis is the length of the waveguides in cm and the vertical axis is the loss in dB. Plotting the data to a straight line gives the propagation loss from the slope. Less than 0.4 dB/cm of propagation losses were measured in a 9-μm width waveguide at 1.55 μm for both TE and

Figure 4 Schematic diagram of fabrication of polymeric waveguides.

Figure 5 Propagation losses of the waveguides.

Figure 6 Near-field mode pattern for TE polarized light at 1.55 μm.

TM polarizations, as shown in Figure 5. The polarization dependence loss (PDL), the loss difference between TE and TM, was estimated to be very small. Thus, waveguides prepared from fluorinated and chlorofluorinated polyimides are potential candidates for a real device application at a telecommunications wavelength of 1.55 μm. The near-field mode pattern of the waveguide (9 μm width) for TE polarized light at 1.55 μm is shown in Figure 6.

CONCLUSION

Chlorofluorinated polyimides with good thermal stability, refractive index controllability, and low optical loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm were synthesized. Chlorine can be used like fluorine and deuterium to control refractive indices of polymers without causing optical loss. Rib-type polymeric waveguides were prepared by using these chlorofluorinated polyimides. These waveguides exhibited low optical loss of less than 0.4 dB/cm for both TE and TM polarizations. Less than 0.1 dB/cm of the polarization dependence loss (PDL) was measured.

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