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Characterization of chloro-fluorinated poly(arylene ether)s for optical waveguide application

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Summary

Optical polymers which exhibit good thermal stability, controllable refractive index, and low optical loss in the optical communication wavelengths of 1.3 and 1.55 μm were synthesized from 4,4’-(hexafluoroisopropylidene)diphenol (bisphenol AF) and decafluorobiphenyl. The copolymers were prepared by the appropriate molar ratio of 4,6-dichlororesorcinol and bisphenol AF with decafluorobiphenyl. Optical properties such as refractive index and absorption behavior in the near IR region of the resulting polymers were characterized. As the content of chlorine was increased, the refractive indices of polymer were increased without causing further optical loss. Embedded optical waveguides were fabricated by using fluorinated and chloro-fluorinated poly(arylene ether)s.

Introduction

There have been a great deal of interests and researches on polymer optical waveguides (1-2). Polymers suitable for waveguide applications must have high thermal stability, good refractive index controllability, and low optical loss in the optical communication wavelengths of 1.3 and 1.55 μm. It is known that the loss at near-infrared (IR) wavelengths can be reduced appreciably by the substitution of hydrogen atoms to deuterium or fluoride (3). Fluorinated or perfluorinated polyimide has been considered for real device application due to its excellent thermal, mechanical, and optical properties (4-6). Since fluorinated poly(arylene ether) has a good thermal stability and a low dielectric constant (7), and carbon-chlorine (C-Cl) bond is expected to have low loss at 1.3 and 1.55 μm like carbon-fluorine (C-F) bond, chloro-fluorinated poly(arylene ether) can be a potential candidate for optical application. In this paper, we demonstrate a novel approach in designing optical polymers which exhibit a good thermal stability, refractive index controllability, and low optical loss in the near-infrared wavelength region by using chloro-fluorinated and fluorinated poly(arylene ether)s.

Experimental

Materials

Decafluorobiphenyl (Aldrich) and 4,4’-(hexafluoroisopropylidene)diphenol

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(bisphenol AF, Aldrich) were used as received. Dimethylacetamide (DMAc, Aldrich) was purified by distillation under reduced pressure over calcium hydride. Potassium carbonate (Aldrich) was dried at 130 ℃ before used. 4,6-dichlororesorcinol (Aldrich) was vacuum sublimated under reduced pressure. Cyclohexanone (Aldrich) and γ-butyrolactone (Aldrich) were used as received.

Preparation of Homopoly(arylene ether)

Fluorinated poly(arylene ether) was prepared according to the general reaction shown in scheme 1. To a 250 mL round bottom flask was added 7.5 g (0.0223 mole) of bisphenol AF, 7.6 g (0.0227 mole) of decafluorobiphenyl, 120 g of DMAc and 8.63 g (0.06 mole) of potassium carbonate. The mixture was heated at 80 ℃ while stirring under nitrogen overnight. The reaction mixture was then filtered hot to remove the unreacted potassium carbonate and potassium fluoride by-product. The polymer was isolated by precipitation into excess water, then filtered and dried in a vacuum oven overnight.

Preparation of Copoly(arylene ether)s

The copolymers were prepared from the two biphenols, 4,6-dichlororesorcinol and bisphenol AF, with decafluorobiphenyl as shown in Scheme 1. Both bisphenol AF and 4,6-dichlororesorcinol, which was varied to 10~25 mole% based on bisphenol AF, were reacted with decafluorobiphenyl in the presence of potassium carbonate under nitrogen for 12 hours at 110 ℃. The isolation of polymers was done by the same procedures described as above.

Film preparation

The polymer solutions were prepared from a 50/50 mixture of γ-butyrolactone and cyclohexanone. After filtering by using a 0.2 μm Teflon filter, the polymer solutions were spin-coated onto a silicon wafer, and then backed for 15 minutes at 100 ℃, 20 minutes at 180 ℃, and 45 minutes at 400 ℃. The film thickness was controlled by changing the spin speed and the solid content of polymer solution. The thick (300 μm) polymer film for near-IR measurement was prepared by casting the polymer solution onto a silicon substrate and backing to 400 ℃.

Waveguide fabrication

An embedded single mode waveguide was fabricated by spin coating an undercladding and a core polymer on an oxidized silicon substrate. Core ridges were then formed by conventional photolithography and dry etching using an inductive coupled plasma (ICP) 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. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC 7 at a heating rate of 10 ℃/min. The molecular weights and molecular weight distributions of the polymers were measured by a Waters 490 gel permeation chromatography (GPC) using polystyrene as a standard. Refractive indices of the polymer films were measured using a Metricon 2010 prism coupler using light from a 0.63 μm helium-neon laser, a 1.3 μm laser diode, and a 1.55 μm laser diode. Near infrared spectra of the samples were measured using an ATI Mattson Infinity FTIR Spectrometer. The near-field mode pattern of the waveguide was recorded at 1.55 μm using the experimental set-up as illustrated in Figure 1.

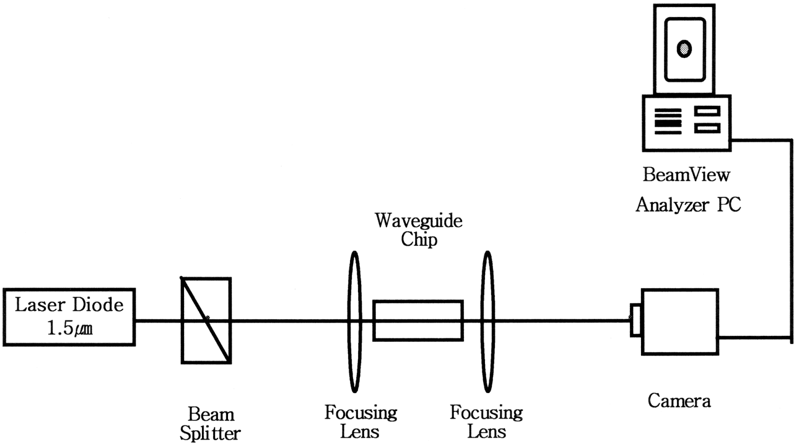


Figure 1. Experimental setup for measuring near-field mode pattern

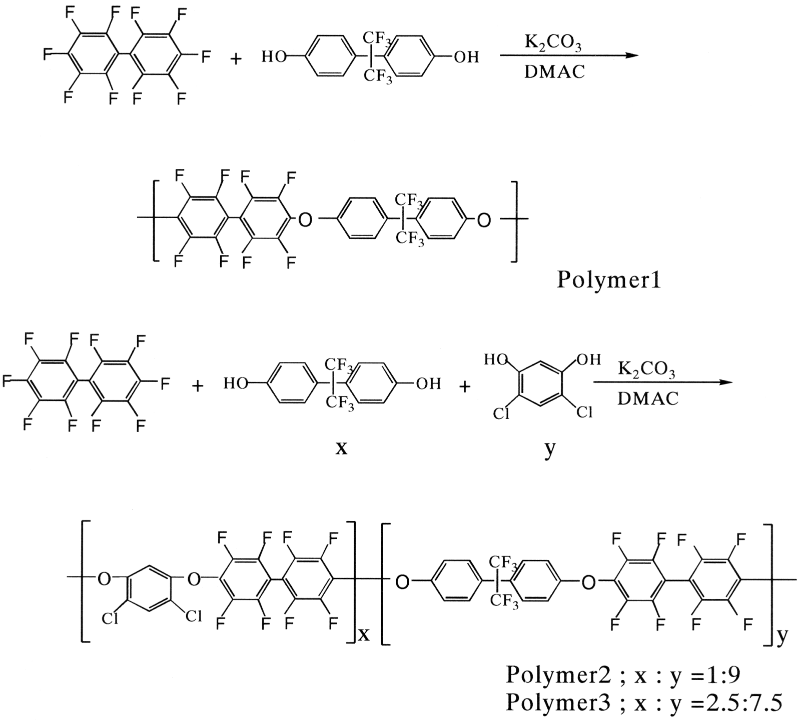
Results and Discussion

Fluorinated poly(arylene ether) was synthersized from the reaction of 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF) with decafluorobiphenyl, and the copolymers were prepared by the appropriate molar ratio of 4,6-dichlororesorcinol and bisphenol AF with decafluorobiphenyl as shown in the Scheme 1. The molecular weights, glass transition temperatures (T_g), and onset temperatures of weight loss of the polymers are summarized in Table 1. The resulting polymers have Tg values in the range of 181~186 ℃ and show no appreciable weight loss up to 540 ℃ in the TGA thermograms indicating good thermal stabilities.

Table1. Characterizations of polymers

Polymer	M_nx10^{-4} (g/mole)^a	T_g (^{o}C)^b	Onset temperature of weight loss ^{c}
1	3.0	182	521
2	3.6	181	524
3	3.2	186	541

a : determined by GPC using polystyrene as a standard. b : determined by DSC at a heating rate of 10 ^{o}C/min in nitrogen. c : determined by TGA at a heating rate of 10 ^{o}C/min in nitrogen.



Scheme 1. Synthesis of poly(arylene ether)s

The effect of the chlorine moiety on optical loss of the polymer was investigated by comparing the near-IR spectra of poly(methyl methacrylate) (PMMA) and carbon tetrachloride (CCl_4). The spectra of PMMA and CCl_4 were obtained by using 300 μm thick film and 5 cm path quartz cell, respectively. As shown in Figure 2, there are strong absorption bands around 1.1 and 1.4 μm in PMMA whereas these bands are not observed in carbon tetrachloride. It is known that the absorption bands around 1.1 and 1.4 μm are results from absorption of these wavelengths by carbon-hydrogen bonds (C-H) in the polymer backbone (3). 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 polymer waveguide. These absorption bands can be shifted to longer wavelengths than those of C-H bond when hydrogen is replaced to heavier atom such as fluorine (F) and deuterium (D) (8). The chlorine (Cl) shows the same effect as fluorine or deuterium. Calculations represent that the wavelengths for the fundamental stretching vibrations of the C-Cl bond are about 3.1 times longer than those of the C-H bonds (9). This was confirmed by observing no absorption bands in the near-IR region in the spectra of carbon tetrachloride as shown in Figure 2.

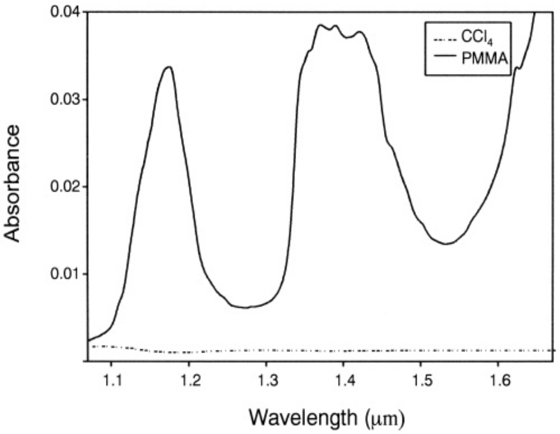


Figure 2. Near IR spectra of PMMA film and CCl_4

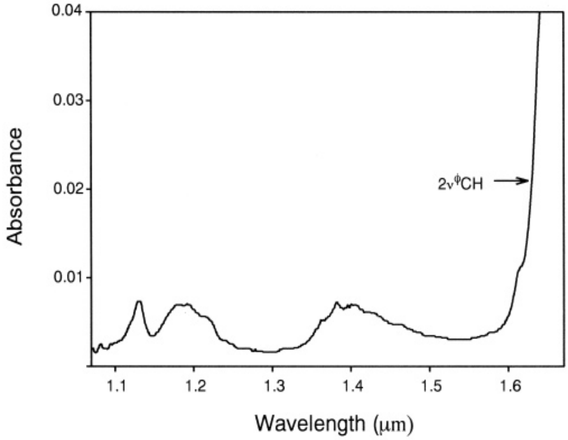


Figure 3. Near IR spectra of fluorinated poly(arylene ether) film

Figure 3 shows a near IR spectrum of the 300 μm thick fluorinated poly(arylene ether) film. As shown in this spectrum, this polymer has small light absorption at the wavelengths of 1.3 and 1.55 μm due to higher fluorine content. This polymer, thus, is expected to be applicable to waveguide application.

The effect of the chlorine moiety on refractive index of a polymer was monitored using the prism coupler. As shown in Figure 4, the refractive index of the polymer increased linearly with increasing the chlorine moiety at three wavelengths. This may result from the larger electronic polarizability of the C-Cl than that of the C-F (10). Above results show that the refractive indices of the optical polymers can be controlled by the appropriate combination of chlorine and fluorine contents in the polymer, without causing further optical loss.

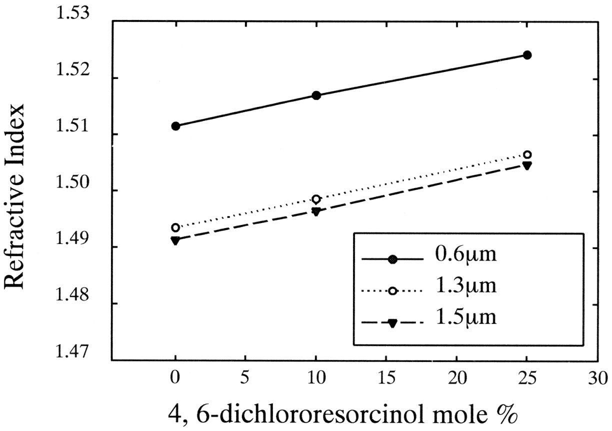


Figure 4. Refractive indices of poly(arylene ether)s at TE mode

Embedded single mode waveguides were fabricated by using fluorinated and chlorofluorinated poly(arylene ether)s. An undercladding layer (polymer 1) and a core layer (polymer 2) were spin-coated on an oxidized silicon substrate. Core ridges were then formed by conventional photolithography and dry etching using an inductive coupled plasma (ICP) etcher. Waveguides were fabricated by covering the core ridges with an overcladding polymer by spin-coating. The core size of the waveguide is 7 x 6 μm^2, and the refractive index difference between the core and cladding polymer is 0.3 %, achieving single mode operation. The near-field mode pattern of the waveguide for TE polarised light at 1.55 μm was shown in Figure 5.

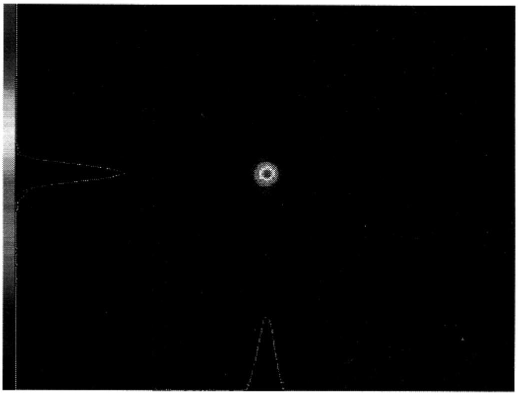


Figure 5. Near-field mode pattern for TE polarised light at 1.55 μm

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