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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 29 Oct 2010

To cite this article: Myong-Hoon Lee, Xiangdan Li, Jink Yu Kim, Jaewook Kang, Seongho Paek & Jang Joo Kim (2002): Facile Fabrication of Polymer Waveguide by Using Photosensitive Polyimides, *Molecular Crystals and Liquid Crystals*, 377:1, 7-12

To link to this article: <http://dx.doi.org/10.1080/713738544>

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Facile Fabrication of Polymer Waveguide by Using Photosensitive Polyimides

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New soluble photosensitive poly(amide-co-imide) containing *p*-phenylenediacryloyl moiety was synthesized and its photoreactivity was characterized by UV-Vis spectroscopic methods. The copolymer was synthesized from *p*-phenylenediacryloyl chloride, bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and two equivalents of 2,2'-bis(trifluoromethyl)benzidine (BTBz) followed by chemical imidization. From the refractive index measurement by prism coupling method, it was found that the refractive index could be varied precisely with respect to the exposure time. Fabrication of passive waveguide was attempted by the photo-modulation of refractive index. Straight waveguide was easily fabricated and the single mode near-field pattern was observed by using 1.55 and 1.3 μm near-IR light.

Keywords photosensitive polyimides; polymer waveguides; fabrication; refractive index; photo-modulation

INTRODUCTION

Polymers are one of the most promising candidates for the optical materials to fabricate waveguide due to the several advantages over the inorganic materials. Optical waveguides have been produced from several polymers such as polyacrylates, polystyrene, poly(organo-silane), benzocyclobutene and so on.[1] More recently, fluorinated polyimides have been used mainly due to their high thermal stability as well as other desirable properties.[2-4] Reactive ion etching (RIE) is usually employed to fabricate optical waveguides from such polyimides because of its precise patterning characteristics. However, there are

several disadvantages in RIE, such as restriction of the processed area for less than 5 μm , the multiple and complicated processes, and longer fabrication time. To solve this problem, numerous attempts have been made. For example, electron-beam irradiation technique was reported to modulate the refractive index by bleaching the polyimide structure, and the authors successfully fabricated a channel-waveguide using electron-beam irradiation.[5] Nevertheless, complicated and expensive equipment was required and the resulting waveguide showed considerable transmission loss due to the damages in the polyimide induced by electron-beam bombardment.

Photosensitive polyimides have been widely used in electronic industry as a low-dielectric material.[6,7] Compared with ordinary polyimides, photosensitive polyimides functioned as low-dielectric interlayer, photosensitive polyimides also provide an advantage of simple processing method for micro-patterning of polyimide layer, since patterning of ordinary polyimides is achieved by an extra-processing technique that includes lithography via photoresists.

Recently, we have reported a novel photosensitive poly(amide-co-imide), **3a** (FIGURE 1), containing photosensitive *p*-phenylene-diacyryloyl moiety from copolymerization of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and *p*-phenylenediacyryloyl chloride (**1**, PDACl) with 4,4'-oxydianiline (ODA). This new photosensitive polymer showed an intrinsic photosensitivity without

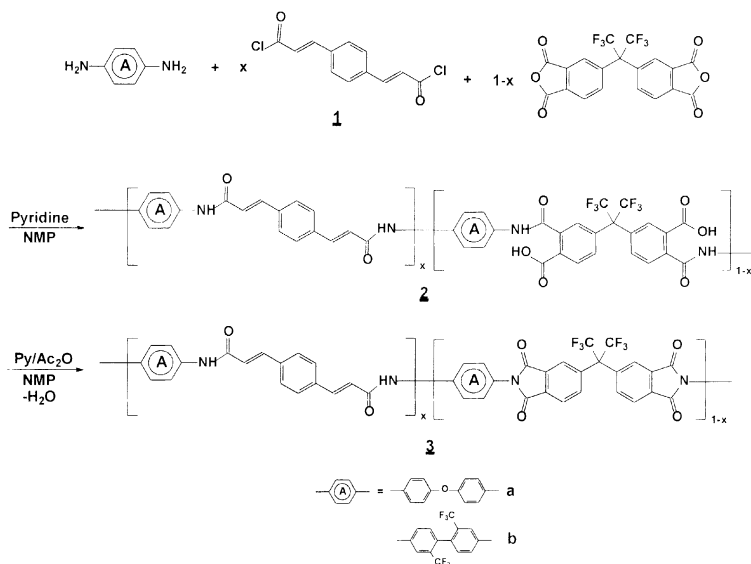


FIGURE 1. Representative synthetic scheme of photosensitive poly(amide-co-imide)

additives, low shrinkage after post-bake procedure and good processability in solution.[8] The polymer also showed photo-induced refractive index (RI) change with respect to the irradiation energy. Using this phenomenon, we successfully demonstrated a new fabrication method of polymeric passive waveguide.[9] However, the propagation loss of this device was comparably high, since the molecular structure of the polymer was not optimized and the absorption loss due to the C-H and N-H vibrational overtone was large. In this paper, we report the synthesis and characterization of a new low-loss photosensitive polyimide, **3b**, suitable for the facile fabrication of passive waveguide by using the photo-induced RI modulation technique

EXPERIMENTAL

Syntheses of Poly(amide-co-imide)

Copolymerizations were proceeded in NMP. Typically 2 mmol of **1** was reacted with 4 mmol of 2,2'-bis(trifluoromethyl)benzidine (BTBz) in the presence of pyridine at 0 °C for 2 h followed by subsequent reaction with 2 mmol of 6FDA. Chemical imidization of resulting poly(amic acid-co-amide), **2b**, was performed in the presence of pyridine-acetic anhydride at 40 °C for 2 h. The resulting mixture was precipitated into methanol for 3 times to give light yellow product (**3b**). Various copolyimides having different monomer contents were prepared and named as 6F-PD/BT-*n* where *n* denotes for the PDACl content x (%) in FIGURE 1.

Refractive Index Measurement

Polymer thin film (2 ~ 4 nm thick) was produced by spin coating a filtered (0.4 µm Millipore) NMP solution (14.5 wt.%) of **3b** at 700 rpm on a Si wafer and drying in a vacuum oven for 14 h at 60 °C. RI was measured by prism coupling method by using 1.55 µm light source while irradiating the film with UV light (365 nm, 76mW/cm²) at 150 °C.

Fabrication of Straight Waveguide

Straight waveguide was fabricated by using the photo-induced RI modulation technique. 9.5 µm of Cyclotene 3022[®] lower cladding was produced on a Si wafer as described in the literature.[10] Then, **3b** was spin-coated and dried in vacuum to produce 4.6 µm film. UV was firstly irradiated with 500 W mercury lamp at 150 °C for 250 min all over the area, and then the irradiation was continued for 120 min over the area except the core (by using 5 µm x 50 mm mask pattern). Finally, 10 µm of Cyclotene 3022[®] upper cladding was spin-coated over the core layer. The resulting waveguide was examined by observing a near

field pattern with a 1.55 μm light source and the IR camera.

RESULT AND DISCUSSIONS

Syntheses of Poly(amide-co-imide)

Recently, we reported synthesis of a photosensitive polyimide and their utilization in the fabrication of passive waveguide.[9] Although the attempted fabrication of polymer waveguide by using the photo-induced modulation of refractive index was successful, the propagation loss was comparably large due to the vibrational overtone absorption by C-H and N-H bonds at 1.3 and 1.55 μm . Since one of the simplest way to reduce the absorption loss is to incorporate a large molar mass of fluorine atom in the polymer, the photosensitive polyimide of low optical loss was synthesized from the highly fluorinated aromatic diamine, BTBz instead of ODA as shown in FIGURE 1. Copolymerizations of **1** with 6FDA and BTBz were conducted in NMP followed by a subsequent chemical imidization. The resulting poly(amide-co-imide)s were soluble in aprotic polar solvents with $[\eta] = 0.7 \sim 2.3$ dL/g. Light-yellow transparent film was obtained from NMP solution. Polymer structures were confirmed by IR and NMR spectroscopy and their thermal properties were investigated by DSC and TGA. The polymers were stable up to 350 $^{\circ}\text{C}$ showing Tg in the range of 280 \sim 330 $^{\circ}\text{C}$. Two-step thermal decomposition was observed due to the thermally less stable *p*-phenylenediacryloyl unit and stable imide unit.

Photosensitivity

UV absorption spectroscopy of the films upon UV irradiation exhibited gradual decrease of absorption peak at 330 nm which corresponds to the $\pi \rightarrow \pi^*$ transition of double bond in *p*-phenylenediacryloyl moiety, indicating [2+2] cycloaddition.[11] The polymers were more sensitive to 365 nm irradiation than to 254 nm. It was noteworthy that the polymer was sensitive to UV light without a sensitizer or additive. Effect of irradiation temperature was also investigated, which showed distinct increase of sensitivity at elevated temperature (up to 160 $^{\circ}\text{C}$). These increase is attributed to the flexibilization of main chain at high temperature.

Refractive Index Measurement

The refractive index of the irradiated polymer film was measured by prism coupling method. As shown in FIGURE 2, the refractive index of TE mode (n^{TE} , in-plane polarized) was decreased with respect to the irradiation time, while that of TM mode (n^{TM} , out-of-plane polarized) was slightly increased. During photocrosslinking, the loss of π -

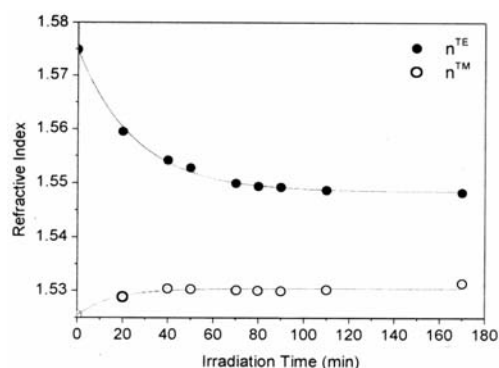


FIGURE 2. The change of refractive indices at 1.55 μm as a function of UV irradiation time at 150 $^{\circ}\text{C}$: solid and open circles represent n^{TE} and n^{TM} values for the polymer (2 μm) with $x=0.5$, respectively.

conjugation in the *p*-phenylenediacryloyl moiety leads to a large decrease in the electronic polarizability, resulting in decrease of refractive index. This is the case especially in the in-plane direction of the film due to the anisotropic nature of the polyimide chains. They are mainly aligned in the in-plane direction, and the direction of UV irradiation was perpendicular to the film plane, resulting in a large decrease in n^{TE} . [12] However, the intermolecular distances between the polymer chains become shorter as the intermolecular [2+2] cycloaddition proceeds, resulting in a decrease in the free volume, and consequently, an increase in n^{TE} as well as n^{TM} to a small extent. As a result, a large decrease in n^{TE} and a slight increase in n^{TM} were observed during the UV irradiation. The optical birefringence (Δn) was decreased (from 0.0306 to 0.0169, for 2 μm thick film) with the increased irradiation time. It is notable that the Δn was found to be decreased. It was reported that, in the case of electron-beam photo-modulation for fluorinated polyimides, [5] the Δn of polyimide was increased with respect to the irradiation time due to the fluorine abstraction induced by electron-beam bombardment. The refractive index of a non-irradiated film at 150 $^{\circ}\text{C}$ for 600 h remained almost constant demonstrating the thermal stability of the polymer film.

Fabrication of Straight Waveguide

By using the precise control of refractive index by UV irradiation, straight waveguide was fabricated by irradiating the film with a mask pattern of 5 μm x 5 mm line, which resulted in the RI of unexposed core slightly higher (c.a. 0.005) than that of the exposed cladding area. 10 μm of Cyclotene 3022[®] was used as a lower and upper cladding material, respectively. Compared to more than 17 steps required to fabricate waveguide device using a conventional lithographic process, less than 7 steps were employed to fabricate a single-mode optical

waveguide. Single mode near-field pattern was observed for TE-polarized beam by using 1.55 μm near-IR light as in FIGURE 3. For TM-mode, it was failed because of the RI mismatch between the core and lower and upper cladding materials. The n^{TM} of Cyclotene[®] ($n^{\text{TM}} = 1.545$) was slightly higher than that of core layer ($n^{\text{TM}} = 1.529$). The propagation loss was estimated from the cut-back method to be less than 0.45 dB/cm and 1.84 dB/cm at wavelengths of 1.3 μm and 1.55 μm , respectively. The high optical loss at 1.55 μm was supposed to be due to the overtone absorption band of the N-H bond in the polymer at around 1.53 μm , which was confirmed by near-IR spectrum of the polymer film. Currently, we are in the process of modifying the molecular structure of the polymer, in order to reduce the absorption at 1.55 μm .

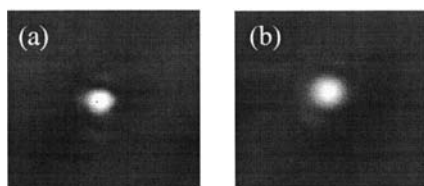


FIGURE 3. Near-field patterns of the waveguide with a dimension of $4.6 \times 5 \mu\text{m}^2$ at (a) 1.3 μm and (b) 1.55 μm , respectively.

This work was performed with the support from the Ministry of Commerce, Industry & Energy.

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