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Synthesis and Characterization of Methacrylate-based UV-crosslinkable Copolymers for Polymeric Optical Waveguides

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Fluorinated acrylic copolymers containing UV crosslinkabe pendant groups were synthesized and characterized. After the copolymerization of octafluoropentyl methacrylate (OFPMA) and hydroxyethyl methacrylate (HEMA), crosslinkable pendant groups were introduced into the copolymer through the reactive groups of HEMA. The chemical structure, thermal stability, and optical properties of the UV-curable copolymers were investigated before and after UV-irradiation. The refractive indices of the crosslinked copolymers were in the range from 1.4500 to 1.4822, and channel waveguides were also fabricated by UV-embossing method.

Keywords: fluorinated acrylic copolymer; polymer optical waveguide; UV curing

INTRODUCTION

Recently, polymeric optical waveguides have been widely utilized in the optics industry as various optical communication components and parts for integrated optics [1,2]. In comparison with inorganic materials, polymeric materials have many advantages as optical waveguide materials; flexibility, easy controllability of refractive index, and simple and low-cost fabrication process, to name only a few. However, most polymers consisted of hydrocarbons show a large transmission loss in near-IR region due to the vibrational overtone absorption of C−H bonds. Therefore, deuterated or fluorinated polymers have been

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investigated as candidates of low optical loss. Deuterated or halogenated polyacylates [3,4], fluorinated polyimides [5–7], fluorinated poly(aryl ether)s [8,9], and perfluorocyclobutane (PFCB) aryl ether polymers [10,11] have been studied as waveguides.

Poly(methyl methacrylate) (PMMA) is an ideal material for optical applications because of its good optical properties and easy film-forming processability [3,4,12]. In this study, we synthesized fluorinated methacrylate-based copolymers containing UV-induced or thermally crosslinkable pendant groups. Their chemical structure, thermal stability, and refractive indices were investigated. Also, channel-type waveguides were fabricated by UV-embossing method, and the characteristics of the waveguides was analyzed.

EXPERIMENTAL

Materials

1H,1H,5H-octafluoropentyl methacrylate (OFPMA, Oakwood Products) was used as received. Hydroxyethyl methacrylate (HEMA, Aldrich) was purified with aluminum oxide. Triethylamine (Et_3N) and methacrylic anhydride (MAAN) were obtained from Aldrich and used without further purification. Tetrahydrofuran (THF), dichloromethane (DCM) and n-hexane were purchased from DC Chemical.

Synthesis of P(OFPMA/HEMA) (60 mol% OPFMA)

OFPMA (13 mmol, 5 g) and HEMA (8.6 mmol, 3.88 g) were dissolved in THF (10 mL) under nitrogen, and AIBN (0.1 g) was added to the mixture. The mixture was then stirred at 60°C for 15 h under nitrogen. Upon completion of the reaction, the product was precipitated with an excess of n-hexane. The dried product was re-dissolved in THF, re-precipitated with n-hexane, and dried in vacuum.

Functionalization of Copolymer using Methacrylic Anhydride (MAAN) (60 mol% OFPMA)

A copolymer (8.62 mmol, 2 g) was dissolved in the co-solvent of DCM/THF (75:25 by volume), and triethylamine (6.9 mmol, 0.96 mL) was added under nitrogen. The mixture was stirred for 10 min at room temperature. Then, MAAN was added dropwise, and the reaction mixture was stirred for 4 h under nitrogen. The product was precipitated with an excess of n-hexane. The dried product was re-dissolved in THF, re-precipitated with n-hexane, and dried in vacuum.

Preparation of Copolymer Solution

The functionalized copolymer was dissolved in THF (10–40 wt%), and diphenyl(2,4,6-trimethylbenzyl) phosphine oxide (TPO) (5 wt% of the copolymer) was dissolved in the copolymer solution as a photoinitiator. The solution was filtered through a 0.5 μm PTFE membrane filter.

Fabrication of Channel Waveguide by UV-Embossing Method

To fabricate a channel waveguide, UV-embossing method was used. As the cladding layer UV-curable resin with the refractive index of 1.450 (WIR30-450, Chemoptics) was employed.

Characterization

FT-IR spectra were recorded on a Perkin-Elmer 2000 Explorer. Near-IR spectra were recorded on a SolidSpec-3700 DUV (Shimadzu). Thermal properties were measured using TA Instrument DSC 2920 and TA Instrument TGA Q50, respectively.

RESULTS AND DISCUSSION

Figure 1 illustrates the scheme to synthesize fluorinated methacrylate-based copolymers containing crosslinkable pendant groups. The copolymers with different compositions were prepared by radical copolymerization in THF using varying ratios of OFPMA and HEMA. Table 1 shows the molecular weight characteristics of three different copolymers. For UV-induced crosslinking of copolymers unsaturated carbon double bonds were introduced on the pendant groups of the copolymer chain. Recently, Koo *et al.* reported methacryloylation reaction using MAAN as an acrylating agent in DCM at room temperature

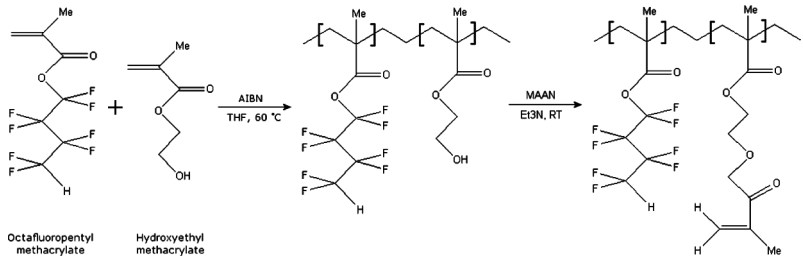

FIGURE 1 Schematic diagram showing copolymer synthesis of P(OFPMA/HEMA) and its functionalization.

TABLE 1 Molecular Weights of Copolymers

Nominal ratio (OFPMA:HEMA)	Mw	Mn	PDI
35:65	36,900	16,600	2.2
50:50	71,700	27,600	2.6
60:40	51,900	21,400	2.4

[12]. In this work, co-solvent of DCM/THF was used, because the fluorinated copolymers showed poor solubility in DCM and good solubility in THF. By using the co-solvent, we were able to obtain the functionalized copolymers containing crosslinkable pendant groups at mild conditions.

DSC curve in Figure 2(a) shows an exothermic peak in the second run of the functionalized copolymer after the initial heating cycle. It indicates that a chemical reaction occurred during the first heating run by thermal crosslinking of unsaturated carbon double bonds in pendant groups. Using TGA analysis, 5% of weight loss was observed at 290°C for the functionalized P(OFPMA70/HEMA30). UV-induced crosslinking of the functionalized copolymers was also investigated. As shown in Figure 2(b), the absorption peak at 1637 cm^{-1} due to the carbon double bond became weaker after UV-irradiation. The concentration of the carbon double bond in pendant groups decreased due to the UV-induced crosslinking.

The controllability of the refractive indices of an optical polymer is very important. Figure 3(a) shows the variation of the refractive index

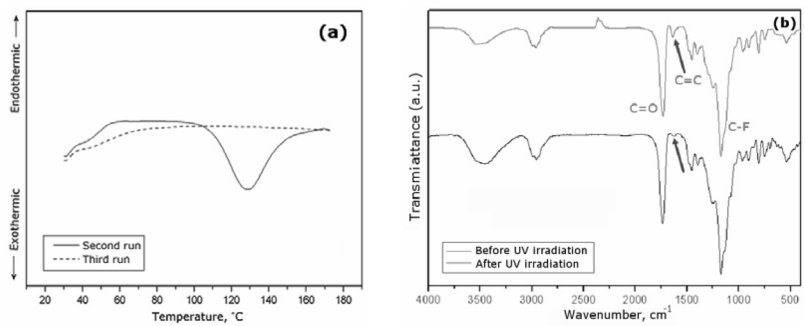

FIGURE 2 Thermal and UV-induced crosslinking evidences of functionalized copolymers: (a) DSC scans of functionalized P(OFPMA50/HEMA50), where the first run was from 30 to 100°C, and (b) FT-IR spectra of functionalized P(OFPMA35/HEMA65) before and after UV irradiation.

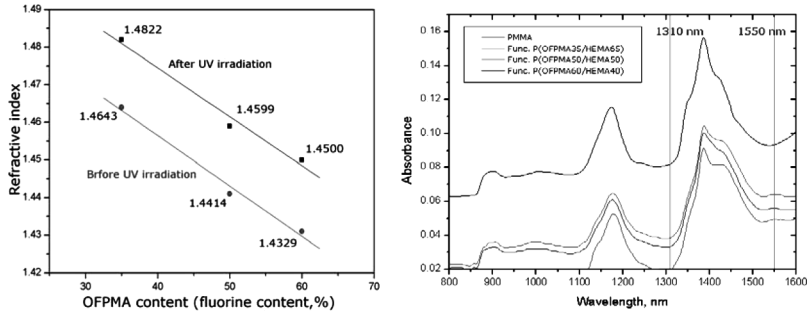

FIGURE 3 Optical properties of functionalized copolymers: (a) refractive index at 633 nm as a function of the fluorinated monomer content and (b) near-IR spectra of the functionalized copolymers.

with the fluorine content of the copolymer. The refractive indices of the copolymer decreased as the fluorine content increased. The refractive indices of the functionalized copolymer were in the range from 1.4500 to 1.4822, and their birefringence was less than 0.0002. Figure 3(b) shows the absorption loss of the fluorinated copolymers in the near-IR region. In comparison with PMMA, the absorption loss of fluorinated copolymers decreased as the fluorine content increased. The transmission loss of the copolymer was calculated to be in the range between 0.17 and 0.48 dB/cm at 1,310 nm. To fabricate a channel waveguide, UV-embossing method was used. UV-embossing method is a simple process comparing with a conventional lithography method. Figure 4(a) shows the schematic of the UV-embossing process.

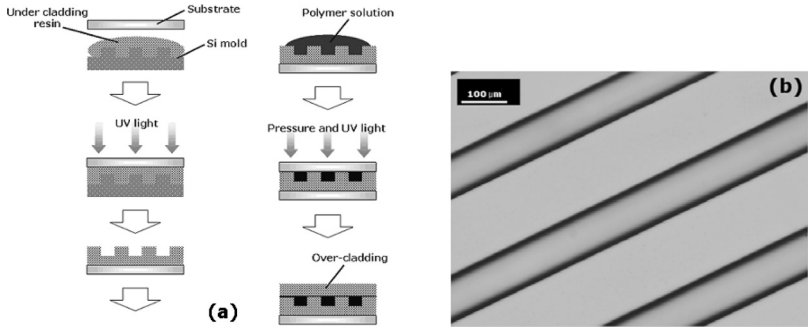

FIGURE 4 (a) Schematic diagram of the UV-embossing process and (b) optical microscopy image of channel waveguide.

As shown in Figure 4(b), a channel waveguide with the channel width of 100 μm using the copolymer synthesized in this study was successfully constructed.

CONCLUSIONS

We synthesized fluorinated methacrylate-based copolymers containing crosslinkable pendant groups. Thermal and UV-induced crosslinking of the functionalized copolymers were examined by DSC and FT-IR, respectively. The copolymers were easily cast as films and the crosslinked films were thermally stable up to 290°C. The refractive indices of copolymers were in the range from 1.4500 to 1.4822, and birefringence was less than 0.0002. A channel waveguide was successfully fabricated by UV-embossing, and the optical loss at 1,310 nm of the copolymers was calculated to be between 0.17 and 0.48 dB/cm.

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