

Generation of Graded Index Profile of Poly(methyl methacrylate) by a Photochemical Reaction

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Abstract: Fabrication of a graded index profile was possible via photochemical reaction of cinnamoyl groups with 350 nm wavelength UV light to form crosslinked structures. Such structural change may induce the change in the refractive index. In order to generate graded index profile in the PMMA polymer optical fiber (POF) with cinnamoyl groups by photochemistry, a methyl methacrylate monomer containing a cinnamoyl functional group in the side chain were prepared. This monomer was then copolymerized with methylmethacrylate with various compositions not only to utilize advantages of poly(methyl methacrylate) but also to overcome the drawbacks of the cinnamate homopolymer. Changes of refractive indices were investigated with various contents of cinnamoyl group and varying irradiation time. Large change in the refractive index ($\Delta \approx 0.01$) and its proper profile shape ($g \approx 2.2$) can be obtained by changing irradiation time.

Keywords: graded index, photochemical reaction of cinnamoyl groups, polymer optical fiber, PMMA .

Introduction

With the rapid progress of information technology, the quantities of data to be transmitted (data, voices or images) are increasing extraordinarily in every field. As a result, intensive studies have been performed over the last decades. One of the most significant outcomes was the fabrication of glass optical fiber (GOF) for long distant data communication. However, GOF is restricted in terms of core size due to its inherent brittleness in spite of its superior properties such as low attenuation and large bandwidth. Thus, compared with large core fibers, it has disadvantages in requiring frequent connections such as local area networks (LANs) or home networks. Hence, polymer optical fiber (POF) with a large core is very attractive in short data communications requiring frequent connections. Polymers also have advantages such as ease of processibility and easy incorporation of functional molecular groups.

There have been many investigations into photoinduced refractive index changes of organic photochromic dyes¹⁻⁴ such as azobenzenes, fulgides, and diarylethenes. Two-

dimensional patterns of refractive indices fabricated by use of these photochemical reactions have been applied to memory, switching,⁵ and waveguide.⁶ Compared with traditional procedures, polymer devices utilizing photochromic reactions have many advantages, including high efficiency, low cost, and the absence of need for etching or photoresist use. Recently, a study on fabrication of a graded index⁷ by photochemical reaction was reported,² wherein a nitro derivative was selected as a photochemical active dopant and dispersed in poly(methyl methacrylate) (PMMA) films.

In this study, the cinnamoyl derivative as a photochemically active monomer was copolymerized with methyl methacrylate (MMA) to generate the graded index (GI) profile. This copolymerization enables to enhance long-term stability by preventing the migration of low molecular dopant and compensates for poor mechanical properties and high absorption of the cinnamoyl unit.

Experimental

Synthesis.

Methyl(E)-2-hydroxy-4-methoxycinnamate: A benzene solution (100 mL) of 2-hydroxy-4-methoxybenzaldehyde (15.2 g, 0.1 mol) and methyl (triphenylphosphoranylidene)-

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acetate (34.0 g, 0.102 mol) was stirred for 2 hrs at room temperature, followed by washing with water. Conventional workup gave pale yellow crystals of methyl (E)-2-hydroxy-4-methoxycinnamate. Purification for removing byproduct (triphenyl-phosphine oxide) was made by column chromatography on silica gel (Merk grade 7734) using a 3 : 1 mixture of hexane and ethyl acetate as an eluent. Chemical structure of reactants are shown in Figure 1.

Methyl(E)-2-(methacryloyloxy)-4-methoxycinnamate (MMC): Methacryloyl chloride (0.1 mol) dropwise at 65 °C is added to benzene solution (150 mL) of methyl (E)-2-hydroxy-4-methoxy-cinnamate (0.1 mol) and triethylamine (excess 0.1 mol). Triethylamine salt is removed by filtration and recrystallization is repeated in hexane until no reactants are detected in the NMR spectrum. Chemical structures are also shown in Figure 1.

Copolymerization. A 250 mL round flask was charged with benzene solution of MMA, MMC (20 wt% monomers), and azobisisobutyronitrile (AIBN, 0.1~0.05 wt% initiator). The solution is degassed through inert nitrogen gas for 20 min. Precipitation of polymers was repeated in methanol until no monomer was detected by NMR spectra. Cinnamoyl polymers were finally dried in vacuo at room temperature. ¹H NMR (500 MHz) spectra were analyzed to confirm synthesized materials and estimate the copolymerization ratio. Chemical shift of NMR spectra was reported in parts per million (ppm) using tetramethylsilane as an internal reference.

Refractive Index Measurement. When UV light is irradiated to the cinnamate polymers, C=C bonds react with one another to become dimers; C=C bonds are also broken to form rectangular rings.⁸

The copolymer was dissolved in chlorobenzene in 10~15 wt% and then spin coated at 1,500 rpm on a quartz substrate. UV (dr. Hönle UVASpot 400T; intensity of UV lamp 10~15 mw/cm²) is irradiated on the film. The refrac-

tive index was measured with a Metricon 2010-Prism coupler. Samples are then pelletized with KBr in order to observe FT-IR spectra. To find the refractive index profile as a function of the depth in the film, the copolymer films were stacked together and then irradiated with a UV lamp during specified times.

Results and Discussion

Monomer Synthesis. The first synthesis involved making the cinnamoyl functional group in the monomer. The product was prepared from 2-hydroxy-4-methoxybenzaldehyde and methyl (triphenyl phosphoranylidene)acetate. In this step, methyl(E)-2-hydroxy-4-methoxycinnamate and triphenylene phosphor oxide are obtained together. The yield of this step was about 80%. Byproduct, triphenylene phosphor oxide, has to be removed since it affects the next polymerization step. Column chromatography was used for separation.

The next step is to introduce a vinyl functional group for radical copolymerization with MMA. The synthesis was carried out by reacting stoichiometric amounts of methyl(E)-2-hydroxy-4-methoxycinnamate, methacryloyl chloride and triethylamine in benzene. Triethylamine salt was removed by filtration and recrystallization was performed in methanol. The ¹H NMR spectrum of MMC is shown in Figure 2(a). Monomer with a reactive double bond and a photochemically active cinnamoyl side group was synthesized successfully.

Copolymers. Benzene solution of 20% monomer and 0.1% AIBN was charged in a round flask and was reacted in an oil bath at 65 °C. In this condition, MMA and MMC was copolymerized in feed ratios of 14:1, 7:1, 2:1. The composition in the copolymers was determined by ¹H NMR spectra. The composition of the copolymer was nearly the same as the initial feed ratio of MMA and MMC. The ¹H NMR spectrum of the 7:1 copolymer is shown in Figure 2(b).

Reference Line. The intensity and area of the C=C bond

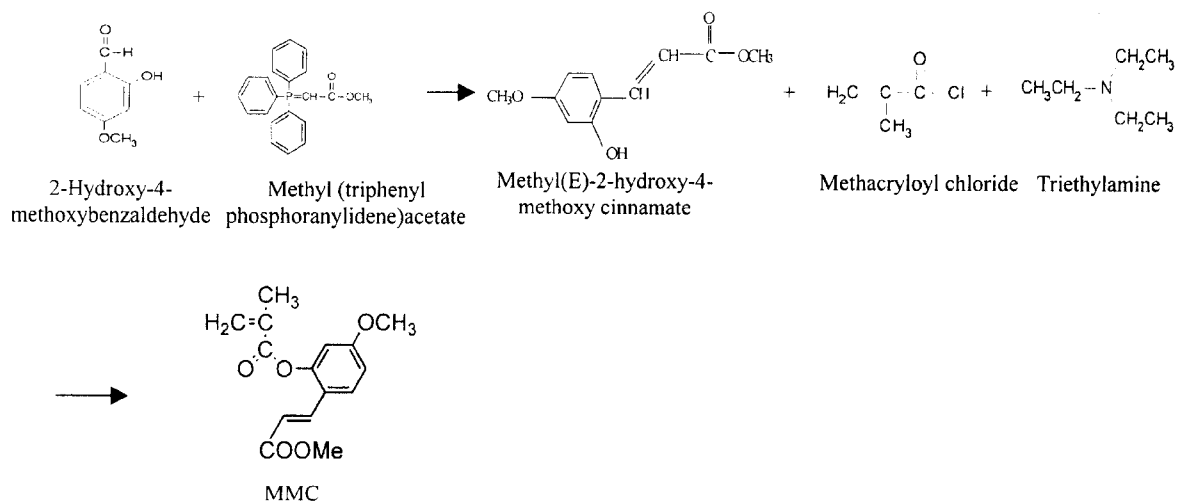


Figure 1. The synthesis of a photochemically active cinnamoyl monomer, methyl (E)-2-(methacryloyloxy)-4-methoxycinnamate (MMC).

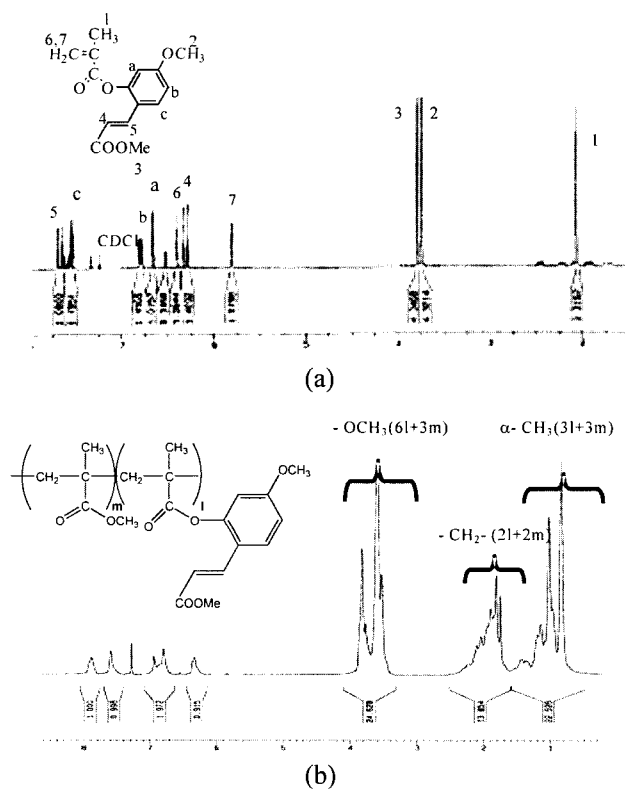


Figure 2. ¹H-NMR spectra of (a) MMC and (b) copolymer (PMMA : PMMC = 7 : 1).

peak decreases in IR spectra with irradiation time and the refractive index changes as the structure changes. Therefore the C=C bond intensity is correlated with the refractive index. In Figure 3, the absorption band around 1635 cm⁻¹ is C=C bond stretching vibration and that around 1700 cm⁻¹ shows C=O bond stretching vibration, which is used as a reference band by calculating the peak area and intensity of the C=C bond absorption band.

To find the relationship between the C=C bond intensity ratio and the refractive index, 10~15 wt% of chlorobenzene solution is spin-coated on a quartz substrate and then exposed to UV light for various time periods. The FT-IR spectra and refractive indices are measured for each film. C=C bond intensity ratios versus refractive indices of the 14:1, 7:1, and 2:1 copolymers can be plotted with linear equation. For example, the 2:1 copolymer is shown in Figure 4 which shows linear correlation.

Refractive Index Changes versus MMC Contents.

Refractive index changes of 14:1, 7:1 and 2:1 copolymers were measured with various UV irradiation time. The uppermost black circle and the lowermost inverse black triangle in Figure 5 indicate the refractive index of the copolymers not being exposed to UV light at all and exposed to UV light for 4 hrs. Refractive indices of copolymer became lower as UV-irradiation time elapses and saturated because C=C bonds are broken and exhausted with

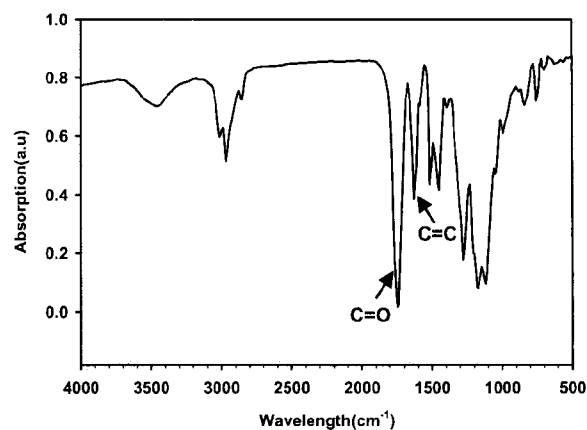


Figure 3. IR spectrum of PMMA-co-PMMC (2 : 1).

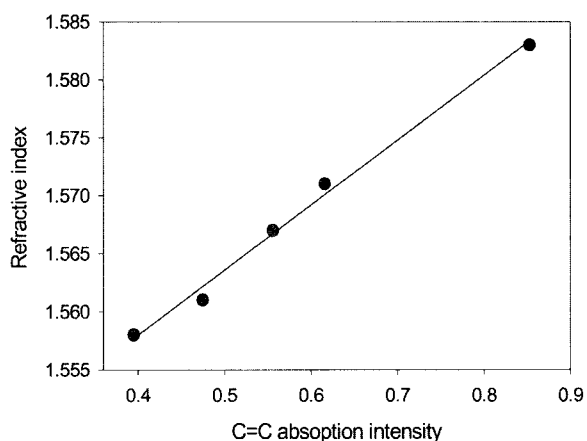


Figure 4. The relationship between C=C contents and refractive index in 2 : 1 copolymer.

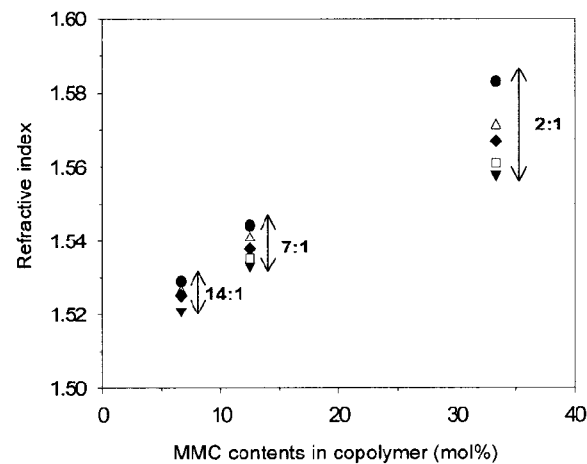


Figure 5. Refractive indices and refractive index changes with MMC contents in copolymer. Relative refractive index changes of 14:1, 7:1, and 2:1 copolymers are 0.006, 0.007, and 0.016, respectively.

UV-irradiation time. As seen in the figure, the refractive index increases linearly with the MMC mol content in the copolymer because refractive index, linearly relating to composition of copolymer, of PMMC is higher than that of PMMA. Refractive index changes according to UV irradiation also increase as MMC mol content increases. For utilizing the copolymer as GI-POF, the relative refractive index change should become more than 0.01. This result clearly shows that MMC content in copolymer is over 10 mol% to obtain a relative refractive index change over 0.01.

Refractive Index Change versus Irradiation Time. To find the refractive index profile according to depth, thin films (20~30 μm) were stacked and irradiated; 2 : 1 copolymer for 15, 30 and 60 min, 7 : 1 copolymer for 1 and 3 hrs, and 14 : 1 for 4 hrs. After exposure, each film was separated and the film thickness and IR spectra were measured, as shown in Figure 6. From these results, it was found that penetration depth of UV is more than 150 μm.

Relative Refractive Index (Δ) and Profile Shape (g). In order to apply these materials as a GI POF, the most important characteristics are the relative index difference (Δ) and profile shape (g). The index difference has an effect on the numerical aperture and transmission speed of information. The numerical aperture is of major importance when launching light into the optical fiber and joining optical fibers together. It is determined by the refractive indices of the core and the cladding. Numerical aperture (NA) is,⁹

$$NA = \sin \theta_{max} \sqrt{n_1^2 - n_2^2} = n_1 \sqrt{2\Delta} \quad (1)$$

Here, relative index difference Δ is given by,

$$\Delta = \frac{n_1^2 - n_2^2}{2n_1^2} \cong \frac{n_1 - n_2}{n_1} \quad (2)$$

Here n_1 is the refractive index at the core center, and n_2 is the refractive index at the boundary of core. Δ has an effect on NA directly, so a larger Δ is better in a point of view of NA but transmission speed decreases as NA increases. Consequently, optimal Δ for GI-POF exists and the value is about 0.01. Generally the profile shape of the GI POF is represented as⁸:

$$n(r)^2 = n_1^2 \left(1 - 2\Delta \left(\frac{r}{R} \right)^g \right) \quad (3)$$

The dimensionless parameter g defines the shape of the index profile, r is the radial distance from the center, and R is the radius of the fiber. It is known that the g is related to transmission speed which becomes maximal when g is about 2. To obtain Δ and g value from the measured data, the equation (3) may be transformed as follows.

$$\log \left(1 - \left(\frac{n(r)}{n(R)} \right)^2 \right) = \log 2\Delta + g \log \left(\frac{r}{R} \right) \quad (4)$$

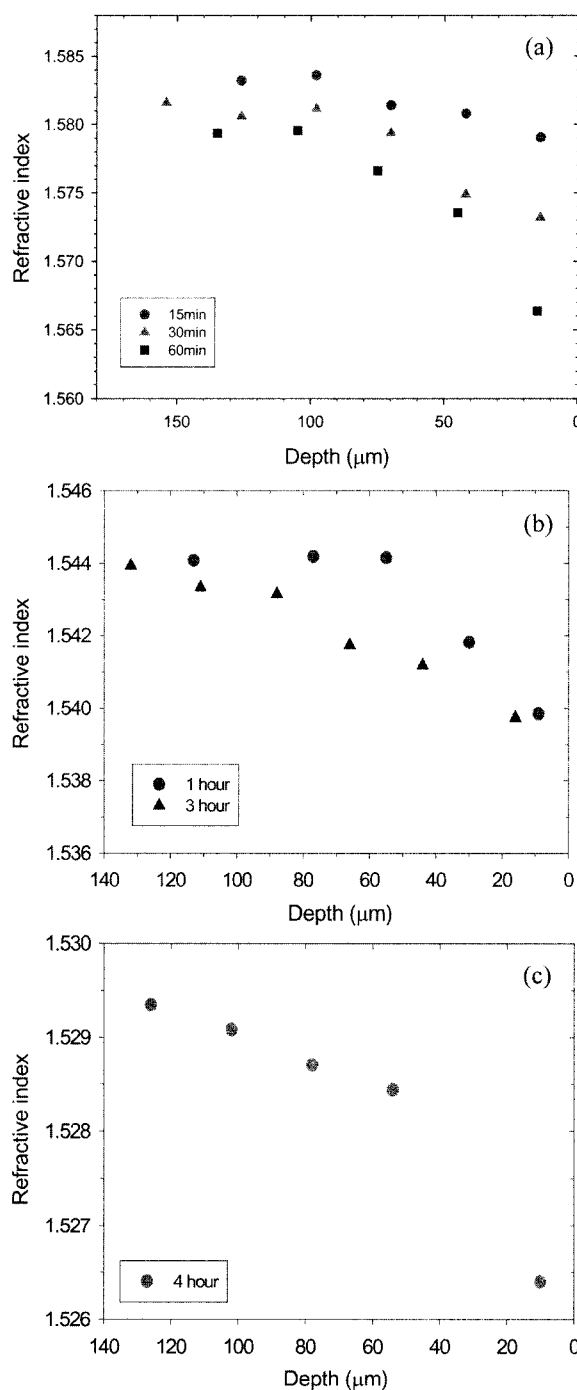


Figure 6. The refractive index changes and profiles in various copolymer with irradiation time. (a) 2 : 1, (b) 7 : 1, and (c) 14 : 1 copolymer.

Therefore, $\log(r/R)$ could be plotted with $\log(1 - (n(r)/n(R))^2)$ from the measured value.^{10,11} The slope is g and the extrapolated g value is $\log 2\Delta$. The values of the 2 : 1 copolymer are shown in Figure 7. g is 1.11 for 15 min, 1.65 for 30 min and 2.22 for 60 min irradiation time. Namely, the shape of the graded index profile changes with irradiation time; therefore

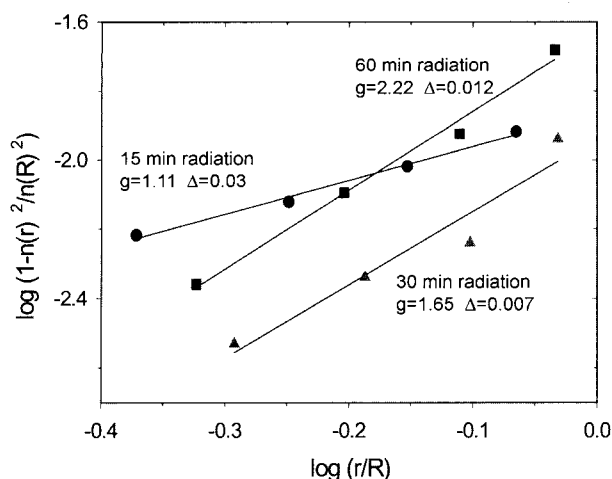


Figure 7. The evaluation of g value and Δ in 2 : 1 copolymer.

we can control the index profile by changing the exposure time.

Not only g but also Δ is an important factor for the GI-POF. Δ was 0.003 for 15 min, 0.007 for 30 min, and 0.012 for 60 min. Here 60 min irradiation is suitable for both g and Δ . For the 7 : 1 copolymer, the results shows the same tendency as the 2 : 1 copolymer. g increases with irradiation time but Δ is not sufficient with this material. The 14 : 1 copolymer also give g value in the proper range. However, again, Δ is not enough. The calculated g and Δ values are summarized in Table I.

Table I. The g and Δ Values of the Various Copolymers with Irradiation Time

Sample Code (MMA : MMC/Exposure time)	Δ	g
2 : 1/15 min	0.003	1.11
2 : 1/30 min	0.007	1.65
2 : 1/60 min	0.11	2.22
7 : 1/60 min	0.003	1.12
7 : 1/180 min	0.003	1.55
14 : 1/240 min	0.002	2.08

Conclusions

The degree of RI change and RI profile shape could be controlled by varying the composition of copolymer and the UV irradiation time. The MMA and MMC copolymer of ratio 2 : 1 showed a proper graded index profile shape (g value ≈ 2) and relative refractive index difference ($\Delta \geq 0.01$) with 60 min irradiation time. Because the photodimerization of the cinnamoyl group is proportional to the amount of UV irradiation, the irradiation time can be reduced as increasing UV lamp intensity. Therefore, it may be concluded that a GI-POF with controlled RI shape and difference of refractive index can be easily obtained by photochemical method.

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