Large photoinduced refractive index changes of a polymer containing photochromic norbornadiene groups

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We prepared a polymer containing pendant norbornadiene (NBD) moieties, P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA), and measured absorbance and refractive index spectra before and after photoisomerization of norbornadiene moieties. Large photoinduced refractive index changes of ~0.01 were obtained at 632.8 nm, the region far from the absorption band. A quantum yield of 0.50 was obtained for the photoisomerization of NBD moieties in this polymer. These values are sufficient to make efficient channel waveguides by photoisomerization. © *1997 American Institute of Physics.* [S0003-6951(97)01522-2]

Recently a lot of research has been carried out for optical waveguides, not only with inorganic materials but also with polymer materials.[1–3] Polymer materials have many advantages such as high processability and easy incorporation of functional groups of molecules inside. There is research which has studied photoinduced refractive index changes[4–8] of organic photochromic dyes, for example, azobenzenes, fulgides, and diarylethenes. The control of optical properties by photochemical reactions is called the photo-optical effect.[9]

Compared with traditional procedures, the procedures of directly forming channel polymer waveguides utilizing photochromic reactions, have many advantages because there is no need to use photoresist, etching, and because of high efficiency, and low cost. In such a case, a large refractive index change and high transparency as well as thermal and chemical stability are required for the dye molecules.

In the present letter, we used norbornadiene (NBD) as a photochromic dye. The NBD is also famous as a photochromic dye, and in past years the photoisomerization of NBD to quadricyclane (QC) has attracted much attention for solar energy storage.[10,11] NBD shows a large change in electronic distribution during the photoisomerization, in spite of a small change in molecular volume with the ability to set up a high concentration in film, a large transparency in the wide wavelength region especially in the visible region, and a high quantum yield of the photoisomerization. We bound NBD moieties to the polymer chains due to an easier film preparation with a high NBD concentration and high uniformity. Refractive index change of NBD during photoisomerization was reported to be about 0.006 in our previous letter[12] for some polymer films containing NBD groups.

In the present experiments, a NBD-containing polymer, P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA) was prepared through the free-radical copolymerization of methyl methacrylate (MMA) with glycidyl methacrylate (GMA), followed by the quantitative addition reaction of pendant glycidyl group in the polymer with 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNCA). Its chemical structure is shown in Fig. 1. This polymer with $M_n = 8.46 \times 10^4$ and $M_w/M_n = 2.10$ contains NBD moieties in side chains. The method of preparation of the polymer has been previously reported.[13]

Films for refractive index measurements were cast from about 10 wt % solutions of the polymer in chloroform by using a barcorter onto a fused silica substrate (thickness: about 3 μm). Films for quantum yield measurements were spin coated from about 3 wt % solutions in chloroform or tetrahydrofuran onto a silica substrate (thickness: about 0.8 μm). The films were dried under vacuum at room temperature for more than 1 day.

The absorption changes of this polymer film were measured during the photoirradiation using a high-pressure mercury lamp or a 150 W Xe lamp with UV29(+UVD36A) or UV31 filters. As is shown in Fig. 2, the absorbance decreased around 295 and 230 nm and increased around 242
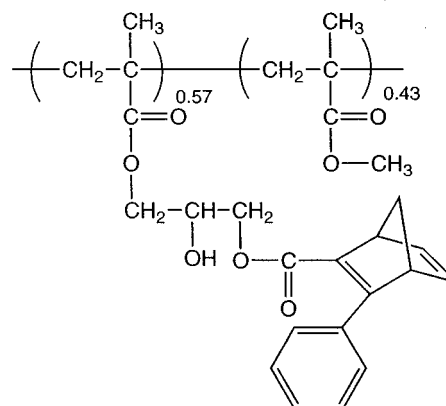

FIG. 1. Chemical structure of P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA).
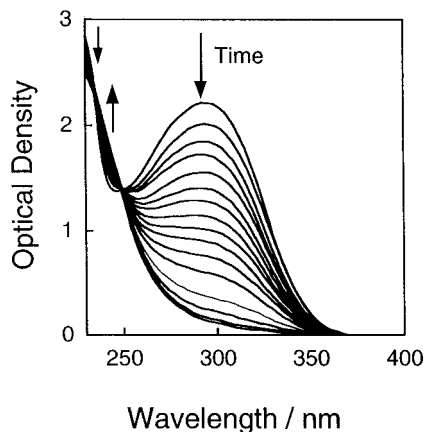
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FIG. 2. Absorption spectra of 1.3-μm-thick film of P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA) before and after irradiation in high-pressure mercury lamp with UV29; irradiation time is 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 105, 120, 150, 180, 210, and 240 s from top to bottom at 295 nm.

nm in the course of the photoisomerization with isosbectic points which can been seen at 250 and 235 nm. By judging from the no absorption for a wavelength longer than 370 nm, this polymer proved to be transparent in the wide wavelength region.

The quantum yield of photoisomerization of NBD to QC moieties for this polymer film at room temperature was determined from the first-order plot of the time-conversion curves.[14] The light source was a high-pressure mercury lamp with UV31 filter. Actinometry for the incident light was carried out with a photometer (Advantest TQ8210). The quantum yield was obtained from Eq. (1),

$$\ln\left(\frac{T}{1-T}\right) - \ln\left(\frac{T_0}{1-T_0}\right) = 2.3 \times 10^3 I_0 \varepsilon \Phi t, \qquad (1)$$

where T is transmittance of NBD moieties at irradiation time, t, T_0 is the transmittance before irradiation, Φ is the quantum yield for the isomerization, I_0 [einstein cm^{-2} s^{-1}] is the incident light intensity, and $\varepsilon = 4.8 \times 10^3$ (L mol^{-1} cm^{-1}) is the molar extinction coefficient of NBD moieties at 295 nm in 1,4-dioxane solution. A straight line was observed for the first half stage of the photoisomerization in this polymer film, from which the quantum yield for the photoisomerization of NBD moieties was found to be 0.50 at room temperature in the films. This value is very high, as compared with that for other photochromic dyes.

The refractive indices of the NBD-containing polymer film before and after photoisomerization were measured by using a m-line method.[15] The light source for the measurement is a tunable He–Ne laser (LSTP-1010, Research Electro Optics). The details of the apparatus are previously given.[7,16] Results are shown in Fig. 3. We measured coupling angles in the TE and TM directions at each wavelength (632.8, 612.0, 604.0, 594.0, and 543.0 nm), and obtained the thickness and refractive index in the direction perpendicular (n_{TE}) and parallel (n_{TM}) to the film thickness by fitting them for more than four modes at each wavelength. From Fig. 3, it is proved that this film has little birefringence, and refractive index of the isotropic film is calculated from Eq. (2),
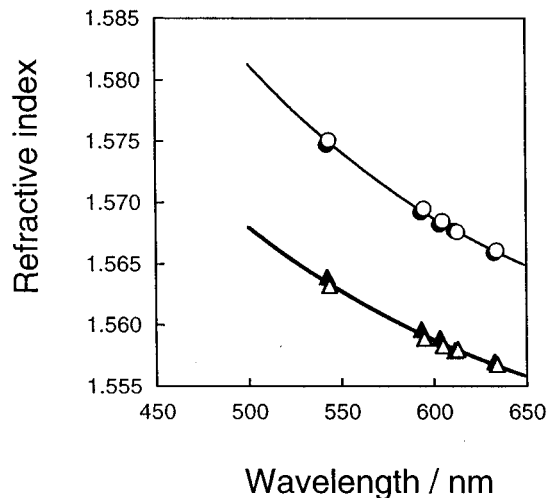

FIG. 3. Wavelength dependent of refractive indices before (circle) and after (triangle) 3 min irradiation in P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA) film. Open symbols are for n_{TE} filled ones are for n_{TM}, lines are fitting curves according to Eq. (3).

$$n = \frac{2n_{TE} + n_{TM}}{3}, \qquad (2)$$

where n is the refractive index of the isotropic film. The lines in Fig. 3 are fitting of the experimental values with Eq. (3)

$$n(\lambda)^2 = A + \frac{B}{\lambda^2}, \qquad (3)$$

where $n(\lambda)$ is the refractive index at wavelength, λ, and A and B are the constants. Equation (3) is a simplified form of the refractive index dispersion for a normal dispersion region. The measured values are well fitted to the line. By comparing the measured refractive indices before and after irradiation, it is clear that this polymer film shows large refractive index change of 0.092 ($n = 1.5660$ to 1.5568) at 632.8 nm and 0.0115 ($n = 1.5750$ to 1.5634) at 543.0 nm. These values are very large for refractive index changes induced by photoisomerization, and more over it should be noted that these values are obtained in a nonresonant wavelength region. These values show that it is possible to make waveguides utilizing photoisomerization of this NBD-containing polymer.

In conclusion, we measured refractive index changes induced by photoisomerization of NBD moieties in P(MMA$_{0.43}$-co-GMA$_{0.57}$-PNCA) film, and its quantum yield. The quantum yield for its isomerization is 0.50, which is very high. Refractive index change is also very large, about 0.01 in the region far from the absorption band. These values show that this NBD-containing polymer is a material suitable to change refractive index efficiently by photoirradiation, and has a potential applicability for optical devices, e.g., channel waveguides and photo-optical switching devices.

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