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Photo-optical Control with Large Refractive Index Changes by Photodimerization of Poly(vinyl cinnamate) Film

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Photochemical reactions in polymer films can induce various changes in physical properties of polymer films such as solubility, transparency, thickness, and refractive index.[1] The photochemically induced refractive index change in polymer films is an important method for controlling optical properties of polymers[2] and attracts increasing interest from both a fundamental standpoint and its applicability for various optical devices, such as holographic image recording, optical switching, and waveguide lithography (making channel waveguides).[3] For their realization, large changes in refractive index in polymer films are desired. It is necessary especially for the waveguide lithography that both the large changes in refractive index and the transparency in the wide visible region are realized at the same time. The advantage of applying photochemical reactions in polymer films for waveguide lithography is the simplicity of the procedures compared to the traditional ones that use techniques such as reactive ion etching[4] and photolocking,[5] including selective photopolymerization[6−8] procedures requiring many steps. Recent publications[2,9−17] have discussed photoinduced refractive index changes of organic polymers containing photochromic dyes. However, a number of photochromic dyes have absorption bands in the visible wavelength region after photoirradiation, although the material should be transparent over the visible region. In order to explore various applications of photo-optical control systems for optical waveguides, polymer materials that show transparency and changes in refractive index larger than those already reported are to be investigated.

Poly(vinyl cinnamate) (PVCm) is a well-known photopolymer used as a negative-tone photoresist. Photodimerizaton of cinnamoyl groups in the PVCm film induces cross-links between polymer chains so that the polymer film becomes insoluble. PVCm has also been studied as a material for optical waveguides,[18] in which channel waveguides were processed by laser-beam writing. Laser-beam exposure gives rise to large solubility differences by cross-linking in exposed areas, resulting in a negative-tone photoresist after developing. However, the use of photoinduced changes in refractive index due to dimerization for making channel waveguides has not been reported. Recently, refractive index changes in a copolymer involving cinnamoyl groups were used for holographic recording.[19]

In the present communication, we used PVCm as a polymer material. The PVCm with weight average molecular weight of 8 × 10^4 was supplied from Sowa Kagaku Co. Ltd. and used after reprecipitation. The chemical structures of PVCm and its dimerized form are shown in eq 1.

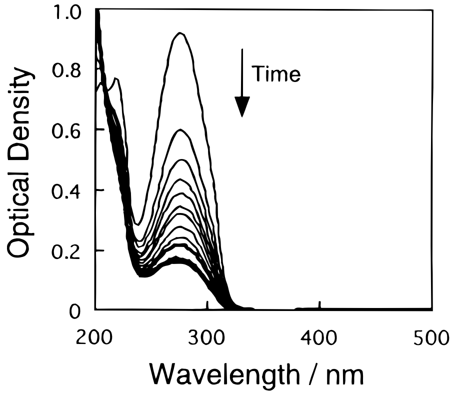
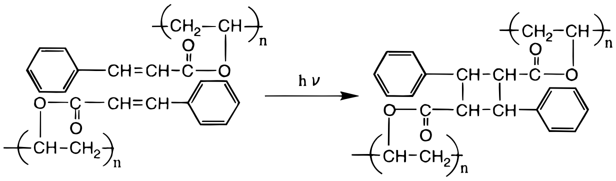


Figure 1. Absorption spectra of a 0.4 μm thick film of PVCm during UV irradiation with a high-pressure mercury lamp with a UV29 filter at irradiation times of 0, 5, 10, 20, 30, 40, 50, 60, 90, 95, and 100 min, from top to bottom, at 275 nm.



(1)

Cinnamoyl groups in PVCm film photodimerize under UV irradiation.[1,20] The photodimerization can occur both inter- and intramolecularly. During photodimerization, the loss of π-conjugation from a benzene ring to a carbonyl group leads to a large change in electronic delocalization, with a large change in the refractive index. Films for refractive index measurements with a thickness of about 2.5 μm were prepared by using a barcorter method from about 7 wt % solutions of PVCm in tetrahydrofuran on fused silica substrates. Films for absorption spectrum measurements were prepared by spin-coating from about 1 wt % solutions in chloroform or tetrahydrofuran on fused silica substrates (thickness: about 0.4 μm) and were dried under vacuum at 95 °C for one day.

The photoirradiation of PVCm films was carried out by using a 450 W high-pressure mercury lamp with a UV29 filter. The change in absorption spectra of the PVCm film during photoirradiation is shown in Figure 1. The photodimerization of cinnamoyl groups results in a large decrease in the absorption peaks at 275 and 220 nm. An isosbestic point is observed at 210 nm. The final conversion of the photodimerization of PVCm was estimated to be about 80% from the changes in the absorption spectra. The absence of absorption at wavelengths longer than 350 nm proved that PVCm is transparent over a wide wavelength region.

The refractive indices of PVCm film before and after photodimerization were measured by using an m-line method.[15,21] The light source for the measurement is a tunable He−Ne laser (LSTP-1010, Research Electro Optics). Figure 2 shows the refractive indices of PVCm film before and after irradiation in both TE and TM modes (n_{TE} and n_{TM}) at each wavelength (632.8, 612.0, 604.0, 594.0, and 543.0 nm). TE modes have the electric component parallel to the film plane, and TM modes have the magnetic component parallel to the film plane. After 300 min of UV irradiation with the 150 W Xe lamp

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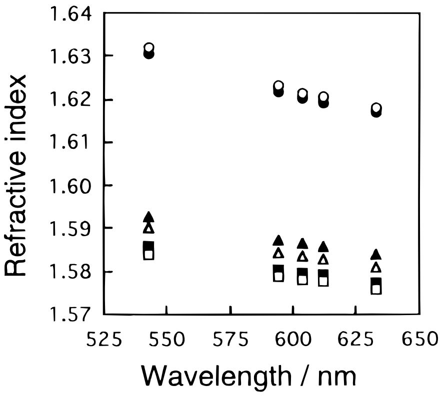

Figure 2. Wavelength dependence of refractive indices of PVCm film before (circle) and after 300 min (triangle) and 1200 min (square) Xe lamp irradiation with a UV29 filter. Open symbols are for *n* in TE mode; filled ones are for *n* in TM mode.

with a UV29 filter, we obtained changes in refractive index of 0.037 (from $n_{\mathrm{TE}} = 1.618$ to 1.581) at 632.8 nm from TE mode spectra and 0.033 (from $n_{\mathrm{TM}} = 1.617$ to 1.584) from TM mode spectra. These values are very large for refractive index changes induced by a photochemical reaction and are, as far as we know, the largest change in refractive index obtained by a photochemical reaction in a nonresonant wavelength region. These results show the applicability of photodimerization of PVCm for making channel waveguides.

The values of n_{TE} and n_{TM} are different especially after photoirradiation. The difference between n_{TE} and n_{TM} increased with the irradiation time, passed through a maximum, and then gradually decreased. This is explained as follows. The light intensity for the photoreaction is specified normal to the PVCm film, and so the vector of the electric field of the irradiating light is in the plane of the polymer film. The photoreaction occurs when the transition moment of cinnamoyl groups and the vector of the electric field of irradiating light are in the same direction. On irradiation, the cinnamoyl groups with transition moments in the plane of the film react preferentially and so the refractive index for the probing light whose electric component is in the plane of the film, n_{TE}, decreases more than n_{TM}, the refractive index for the probing light whose electric component is out of the plane of the film. At a certain time, the difference between n_{TE} and n_{TM} reaches a maximum and then gradually decreases. Similar phenomena are observed in the photoisomerization of azobenzene derivatives on polarized light irradiation.[15]

Molar refractions of PVCm and its dimerized unit were estimated by using their model compounds, ethyl cinnamate for PVCm and ethyl truxillate for the dimerized unit of PVCm. The relationship between refractive index, *n*, density, ρ (g/cm^3), molecular weight, *M*, and molar refraction, *R* (cm^3/mol) of the components is described by the Lorentz–Lorenz equation[22] (2). The

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} \tag{2}$$

value of *R* for ethyl cinnamate was calculated to be 54.24 cm^3/mol by using eq 2 with the values[23] of $n = 1.5598$ and $\rho = 1.0491$ g/cm^3. The value of *R* for ethyl truxillate was calculated to be 98.09 cm^3/mol by the summation of atomic refractions.[22] Thus, we obtained 52.18 cm^3/mol for a monomer unit of PVCm and 46.99 cm^3/mol for its dimerized form. The difference between the molar refractions of PVCm and its dimerized form is 10%. This value is very large compared to a value of 5% for the difference in molar refractions between norbornadienedicarboxylic acid and its photoisomer, quadricyclanedicarboxylic acid, which showed a refractive index change of 0.006 at a wavelength (633 nm) far from the resonant region.[24] Thus, the large difference of molar refractions between PVCm and its dimerized form would be the reason for the large change in refractive index of PVCm on photodimerization. The connection of two π-conjugated groups in a conjugated chain (e.g., a double bond) and the isolation of these π-conjugated groups by a photochemical reaction eliminating the double bond between these groups should generally lead to a polymer film with a photochemically-induced large refractive index change.

The final conversion for photodimerization of PVCm was estimated. The mole fraction of dimerized cinnamoyl groups is given by

$$X = \frac{\bar{R} - R_0}{R_1 - R_0} \tag{3}$$

where $\bar{R}$ is the mean molar refraction[24] after UV irradiation, R_0 is the molar refraction of the cinnamoyl group, R_1 is the half molar refraction of its dimerized unit, and *X* is the mole fraction of dimerized cinnamoyl groups after irradiation. R_0 and R_1 are obtained as mentioned above. $\bar{R}$ was calculated as follows.

First, we calculated ρ_0, the density of PVCm, by using eq 2 with the above-obtained value of R_0 and the experimental value of *n* for PVCm. Next, we measured the thickness of the PVCm film before and after irradiation by using an m-line method, and then the density of the polymer film after irradiation, $\bar{\rho}$, was calculated from the thickness changes and ρ_0. By introducing the values of $\bar{\rho}$ and *n* of the polymer film after irradiation (experimental value) into eq 2, we obtained $\bar{R}$.

By using the values of $\bar{R}$, R_0, and R_1, we obtained $X = 0.79$ from eq 3. This value shows good agreement with the one expected from absorption spectra and is very large for photodimerization in a solid film. Many years ago Reiser et al. reported that the value of final conversion was 0.5 in a solid PVCm film[25] and that most of the cyclic products were head-to-head dimers because of local correlation between cinnamoyl groups. The difference in the value of final conversion between these two cases might be attributed to the differences in the method of film preparation and/or film thickness, which probably affect the aggregation structure of cinnamoyl groups.

In conclusion, we measured the refractive indices of PVCm film before and after UV irradiation and obtained changes in refractive index by photodimerization of PVCm as large as 0.037 (TE mode) at 633 nm after 80% photodimerization. This is a very large change of the refractive index induced by a photochemical reaction. Also this polymer is transparent over the entire visible wavelength region. These suggest the applicability of photodimerization of PVCm for channel waveguides. The molar refractions of PVCm and its dimerized unit are estimated as a guide for the molecular design of systems with a large photochemically-induced refractive index change.

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