Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Taehyoung Zyung [a], Jang-Joo Kim [a], Wol-Yon Hwang [a] & Sang-Don Jung [a]

[a] Electronics and Telecommunications Research Institute, P.O. Box 8, Daeduk Science Town, Daejon, 305-606, Korea

Version of record first published: 04 Oct 2006.

To cite this article: Taehyoung Zyung , Jang-Joo Kim , Wol-Yon Hwang & Sang-Don Jung (1994): Effects of Photobleaching Wavelength on The Resulting Refractive Index Profiles in Nonlinear Optical Polymeric Thin Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 247:1, 49-58

To link to this article: http://dx.doi.org/10.1080/10587259408039190

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 49–58
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Printed in the United States of America

EFFECTS OF PHOTOBLEACHING WAVELENGTH ON THE RESULTING REFRACTIVE INDEX PROFILES IN NONLINEAR OPTICAL POLYMERIC THIN FILMS

TAEHYOUNG ZYUNG, JANG-JOO KIM, WOL-YON HWANG AND SANG-DON JUNG
Electronics and Telecommunications Research Institute, P.O.Box 8, Daeduk Science Town, Daejon, 305-606, Korea

Abstract Photobleaching process and the resulting refractive index profiles of the nonlinear optical polymeric thin films have been investigated for the formation of active and passive waveguide devices. The material, a PMMA based copolymer with stilbene derivative as side chain, is formed to thin films by spin coating. Two different wavelengths of 458nm and 514.5nm generated from Ar^+ ion laser are selected as the bleaching light, which are located near the absorption maximum and the absorption edge of the material, respectively. Bleaching rate of the thin films measured by transmission experiment is found to be linearly proportional to the power of the incident light, indicating that the photobleaching is one photon process. Evolution of the refractive index profiles with bleaching time is obtained using the inverse WKB method with the measured guiding mode indices. The refractive index profiles bleached with 458nm are steeper than those bleached with 514.5nm as expected. A simple kinetic model with the parameters deduced from the transmission experiment is used to delineate the refractive index profiles and the resulting profiles are compared with the experimental ones.

INTRODUCTION

Nonlinear optical polymers, which possess large nonlinearity and low dielectric constant combined with good processibility, have attracted a great deal of interest because of their potential application to the integrated optics[1]. Electro-optic switches and modulators with a few tens of GHz bandwidth have already been demonstrated[2,13].

Side-chain polymers containing optically nonlinear moieties as pendant group have been known to possess advantages over other forms of organic nonlinear materials such as cross-linking polymers, main chain polymer, etc[3]. The advantages include high nonlinearity, low optical loss and easy processibility.

Various techniques have been used for the fabrication of channel waveguide for active devices: poling, photobleaching, reactive ion etching or channel field, etc. Among these, photobleaching offers simple processibility and controllability[4]. Several authors[5,6,7] have published the fabrication of channel waveguides by this tehnique, but less attention has been paid to the refractive index profiles of the film formed by the method. Detailed information on the refractive index profile is important not only for the optimization of the bleaching process itself but also for the design of the waveguide using desired processes with selection of proper photobleaching wavelength, time, and so on.

In this paper, we investigate the photobleaching process in a PMMA based copolymer with stilbene derivative as side chain and the resulting refractive index profiles, and utilize the bleaching parameters such as absorption coefficient and quantum efficiency obtained from transmission experiment to delineate the refractive index profile. Also, we investigate the evolution of refractive index profile with bleaching time.

EXPERIMENTAL

The optically nonlinear polymer under study here is the stilbene derivative copolymer of which structure is shown in inset of Figure 1. The compound was obtained from Hoechst-Celanese Co. The solution of the copolymer was formed into thin films by spin-coating on quartz substrates. The thicknesses of films are 1μm for transmission experiment, about 4μm for the measurement of refractive index and 0.25μm for UV absorption spectrum. The spin-coated thin films were baked for a couple of hours to evaporate the residual solvent before using.

Two different wavelengths of 458nm and 514.5nm from Ar^+ ion laser (Spectra-Physics 2020-5) were used as bleaching light. 514.5nm is located at absorption edge and 458nm near the absorption maximum of the material under this study. Transmission of bleaching light through the film was obtained as a function of bleaching time for various incident power of the light. The incident light was expanded to the diameter of 1cm and passed through the aperture which was placed in front of the sample. The aperture with 1~1.5mm diameter passed only the central part of the laser beam, in which the intensity of the radiation can be considered to be constant. The transmitted light was detected by Si-photodiode and the intensity vs. time was recorded with X-t recorder. In order to get refractive index profiles, thick samples were irradiated by the laser beam expanded to 1cm diameter with laser power of 50mW at both bleaching wavelengths for desired time interval. The refractive index profiles were obtained using the inverse WKB method[8] with measured mode indices by prism coupling method[9]. Wavelength of 830nm from

laser diode(Lasermax INC., 6491) was used for refractive index measurement.

RESULTS AND DISCUSSION

The evolution of absorption spectra of irradiated samples with 514.5nm and 458nm light beam is shown in Figure 1. Broad absorption centered at around 420nm decreases and absorption peak around 340nm increases gradually with bleaching time, which indicates the photobleaching originates from the trans-cis photoisomerization. The infrared spectra of unbleached and almost bleached samples also support that the origin of photobleaching is the trans-cis photoisomerization. Upon bleaching, the peak at 960cm^{-1} corresponding to trans C-H vibration disappeared but that at 675cm^{-1} corresponding to cis C-H vibration appeared without any new additional peaks.

Absorption spectra of the thoroughly bleached sample under the irradiation of 514.5nm exhibit some indication of the residence of trans molecules. On the contrary, no peak corresponding to the absorption by the trans-molecules has been observed for the thoroughly bleached samples with 458nm suggesting that almost all the trans-molecules were transformed into cis-molecules.

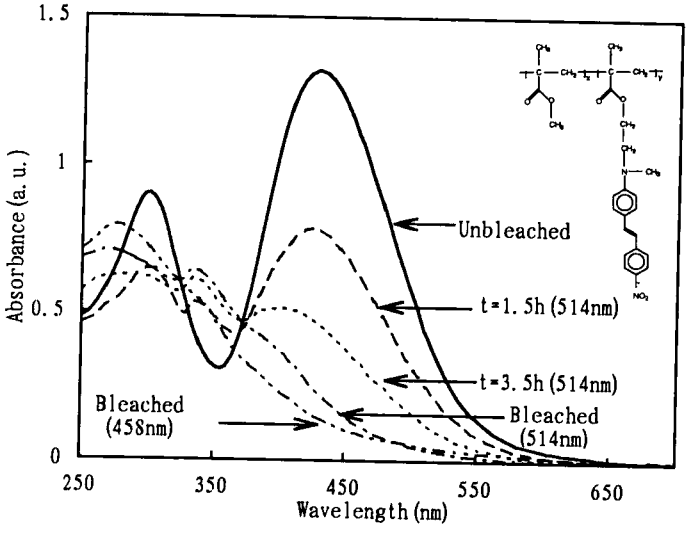
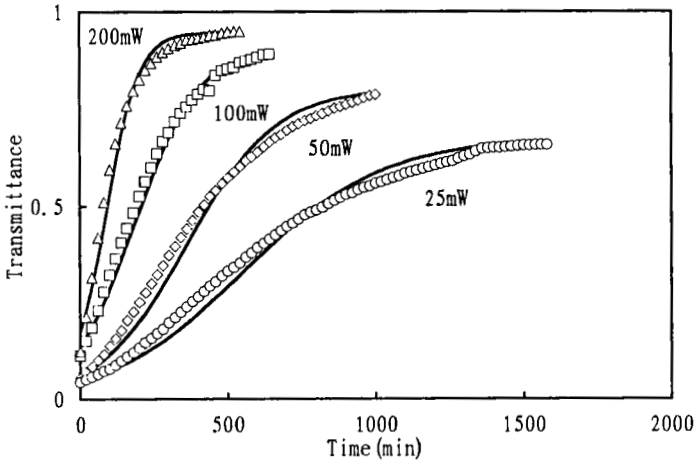
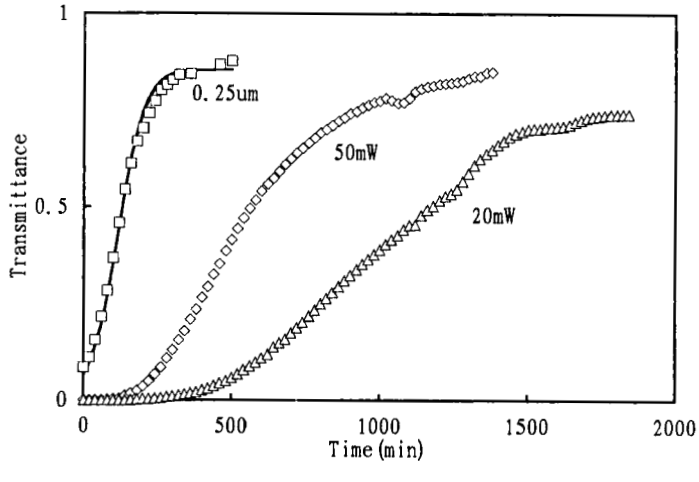


FIGURE 1 Absorption spectra of copolymer thin film at various bleaching times. Molecular structure of copolymer is shown in the inset.

The results of transmission experiments at two different wavelengths are shown in Figure 2. Transmittance increases with time for both wavelengths, indicating the photobleaching proceeds with time. The photobleaching process is faster for higher power of the incident radiation at same wavelength. Time required to achieve a certain



(a)



(b)

FIGURE 2. Transmission with various incident light power at (a)514.5nm (b)458 nm. Solid lines are fitting curves obtained from our kinetic model.

transmittance is inversely proportional to the power of the incident light, suggesting that the photobleaching is one-photon process for both wavelengths. The final transmittance achievable with the photobleaching increases as the incident power increases and the wavelength of the light decreases. This is consistent with the results of UV absorption spectra. The remaining trans-molecules in the film bleached with 514.5 nm radiation should result in lower final transmittance than irradiated with 458 nm light.

Refractive index profiles resulting from photobleaching are shown in Figure 3 for the wavelengths of 458nm and 514.5nm. The graded refractive indices are obtained for both wavelengths. The refractive index profiles formed by 458nm incident light are much steeper than those formed by 514.5nm light. Since the absorption at 458nm is much larger than that at 514.5nm, intensity of 458nm light will drop more rapidly than that of 514.5nm light as the lights propagate through the film. Therefore, the refractive index profiles formed by the bleaching light with higher absorption are expected to be steeper than those with lower absorption. The bleaching depth obtained from 514.5nm is deeper than obtained from 458nm, where the bleaching depth is defined as the depth giving half of the total refractive index change. This fact implies that the quantun efficiency of the reaction at the wavelenth of 514.5 nm radiation is larger than or comparable to that at 458nm even though the energy of the radiation is lower.

The photobleaching of isotropic dye molecules in a solid matrix was analyzed by Kaminow et. al[10]. According to their analysis, the transmission of bleaching radiation through the film is written as a linear function of time t,

$$\ln \frac{[T^{-1}(t) - 1]}{[T^{-1}(0) - 1]} = -\beta t \tag{1}$$

which is the same result as Simmon's[11]. Here, the time constant β is related to the quantum efficiency for bleaching Φ as following :

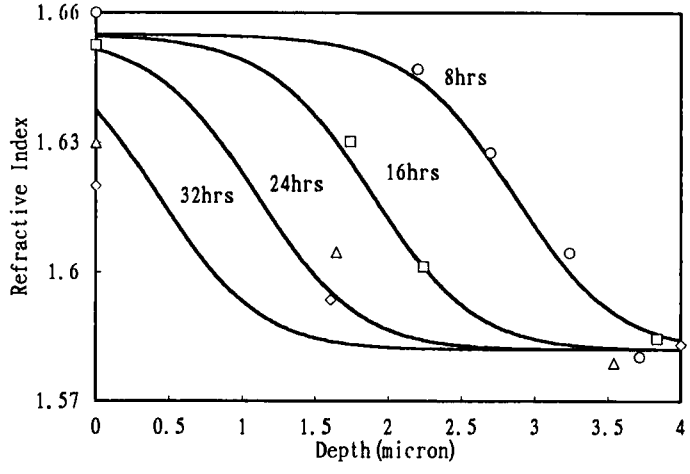
$$\beta = \sigma n_{IN} \Phi \tag{2}$$

where σ is absorption cross section, n_{IN} incident photon flux.

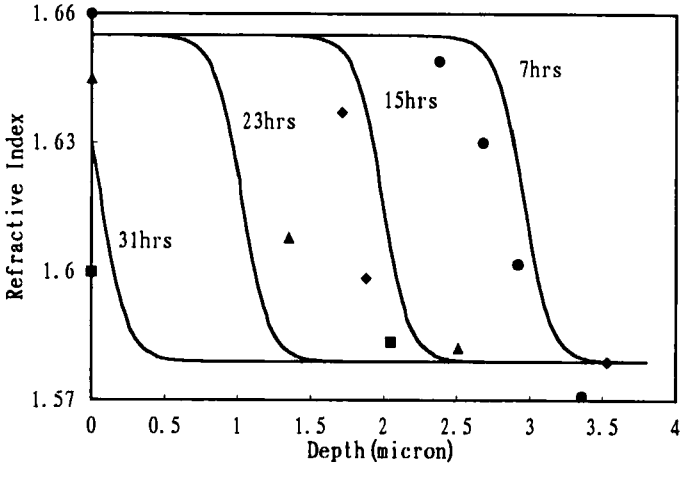
In general, the parameters deduced from the photochemical bleaching model can be used to delineate the refractive index profile. If we consider a simple photobleaching like above, the refractive index change at bleach depth x and at expose time t is given as ;

$$\frac{\Delta n(x,t)}{\Delta n^{T}} = 1 - [1 - \exp(Ax) + \exp(-Ax + \beta t)]^{-1} \tag{3}$$

where Δn^T is the difference of the refractive index between the unbleached and the totally bleached films. The parameter A is the absorption coefficient which is related to the



(a)



(b)

FIGURE 3. Refractive index profiles with various bleaching time at (a)514.5nm (b)458nm. Solid lines are theoretical curves obtained from our kinetic model. Discrete data points are experimental values for 8hrs(○), 16hrs (□), 24hrs(△), 32hrs(◇) in (a) and 7hrs(●), 15hrs(◆), 23hrs(▲), 31hrs(■), respectively.

absorption cross section and β is time constant related to quantum efficiency of photobleaching. The above equations were derived for one photon process under the assumptions that all of the reactant transforms to the product and there is no absorption due to the product.

A logarithmic plot of transmission versus time using Eq. (1) should give a straight line with a slope of β. Our plot of ln((1-T)/T) vs. time does not show a straight line as seen in Figure 4, indicating that the assumptions used for derivation of Eq. (1) are no longer valid in our case because of following reasons. Firstly, all of the reactant do not transform to the product. The trans-molecules still remain even after the reaction is completed, as seen in the UV-VIS absorption spectra of the bleached film at 514.5nm. This incomplete transformation may be due to the steric hinderance of the polymer matrix against the conformational change of the chromophores. Secondly, the absorption of cis-molecules is not zero even though it is smaller than that of trans-molecules as shown in UV spectra. The absorption of the bleached film by 458nm shows no absorption due to trans-molecules. However, the absorption due to cis-molecules is not negligible. Therefore, we must have a kinetic model including the effects of absorption by residual trans-molecules and photo-produced cis-molecules. The details of this modification starting from our governing rate equations will appeare in a separate paper in the near future. Here, we briefly mention the procedure and the results.

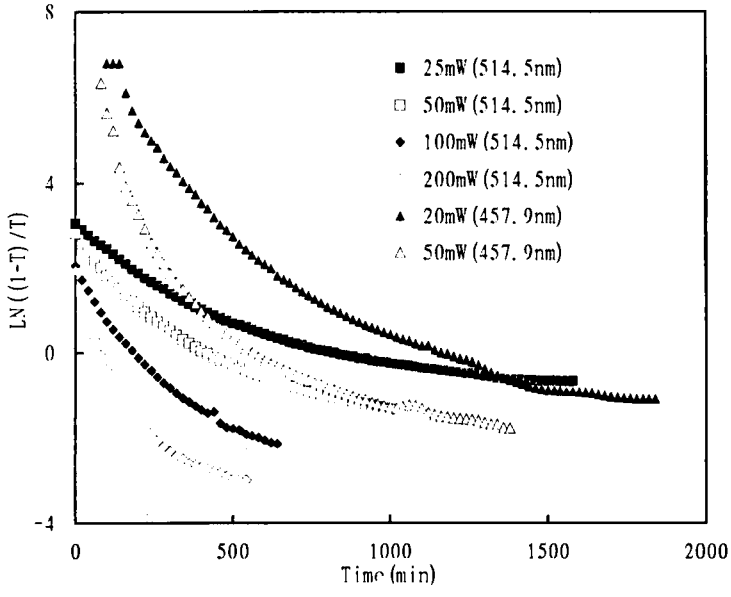


FIGURE 4. A logarithmic plot of transmission with bleaching time.

For a photoreaction

$M_t + h\nu$ ----------> M_c

with incomplete transformation of M_t to M_c, and some absorption from final product, our governing equations are similar to Newell's[12] but contain the concentrations of cis-molecules and residual trans-molecules instead of α_f the absorption constant. The rate equations were solved numerically because no analytical solutions were found. There are four parameters to be determined: quantum efficiency, final concentration of trans-molecules and absorption coefficients of trans- and cis-molecules. The parameters can be determined from the initial and the final transmittances, absorbances of the unbleached and the fully bleached samples. The quantum efficiency is determined from the comparison of the numerical calculation with the experimental data of the transmittance vs. time.

The best fitting curves to transmission data are shown in Figure 2(a) for the films irradiated with 514.5 nm light along with experimental data. As seen in the figure, the experimental transmission data can be well fitted with our simple kinetic model for 514.5nm irradiated sample. For 458 nm irradiation, the parameters were determined from the transmission data of a thinner film of 0.25μm to obtain reasonable initial transmittance. The fitting could be done well also as seen in Figure 2(b). These parameter values were used to calculate the refractive index profiles.

Since the trans-molecules still remain even after completion of photobleaching, the Eq. (3) can not be used directly as mentioned previously. Starting from our governing equations, we obtain the refractive index profiles as a function of the concentration of final products and residual trans-molecules. The parameters at 50mW laser power were obtained from the transmission data to be 2.73μm^{-1} of absorption coefficient A and 4.5 of time constant β for 514.5 irradiated film and 10.75μm^{-1} and 3.8 for 458nm irradiated film, respectively. The calcuated refractive index profiles with the parameters determined from the transmittance of the films are shown in Figure 3 and are compared with the experimental ones. The calculated and experimental profiles match quite well, especially at 514.5 nm. The reason why the larger differences appear at 458 nm is not clear at this moment. With refined parameters the calculated profiles are expected to give better description of the experimental data.

The parameters deduced from transmission experiments have shown to be used to delineate the refractive index profiles. The refractive index profiles determined by the way can be utilized for the modeling of waveguides and to predict the property of mode propagation, which we are studying now.

CONCLUSION

Photobleaching process and the resulting refractive index profiles of the nonlinear optical polymeric thin films have been investigated for the formation of active and passive waveguide devices. Transmission experiments were performed to get the information on photobleaching process. Bleaching rate is found to be linearly proportional to the power of the incident light, showing the photobleaching is one photon process. Refractive index profiles bleached with the radiation with higher absorbance are steeper than those bleached with the radiation with lower absobance.

A simple photochemical kinetic model including the effects of the absorption due to the remaining trans-molecules and cis photoproduct was shown to be applicable to the photobleaching process. Refractive index profiles were caculated using the parameters obtained from transmission experiments and were found to describe the experimental ones quite well. This is very valuable for design and in fabrication process of nonlinear optical polymer waveguide using photobleaching.

ACKNOWLEDGEMENTS

The authors thank gratefully to Dr. M. Y. Jin in Korea Research Institute of Chemistry and Technology for UV absorption measurements and Dr. J. T. Lee for helpful discussion. This work was supported from Korea Telecommunications.

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