PHOTOPOLYMERS HAVING BENZYLIDENE-PHTHALIMIDINE SIDE CHAINS [#]

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1. Introduction

Photoresponsive polymer films have been attracting wide interest from a standpoint of applications to optical information storage and display devices. Among them, a system exhibiting linearly polarized light (LPL) induced in-plane anisotropy is fascinating; erasable optical information storage is performed conveniently with a single light source solely by changing a polarization plane angle of actinic LPL.[1-6] In this system, the anisotropy is brought about by a polarized axis-selective photoreaction of chromophores. On the other hand, we have previously reported that UV irradiation of thin films of poly(methacrylates) having pendent benzylidenephthalimidine(BPI) causes both *E/Z* isomerization and [2+2] cycloaddition of BPI moieties.[7] In this communication, we report dichroic properties of the above polymers upon irradiation with LPL and a result of in-plane alignment control of nematic liquid crystals (LCs).

2. Experimental Methods

A copolymer of *N*-(2-methacryloyloxyethyl)benzenylidenephthalimidine and methyl methacrylate (Cp-BPI) was prepared according to a method described in a previous paper. [7] A 1.2 wt% benzene solution of CpBPI was spread on quartz plates by a spin-coating technique, and the resulting 110-nm-thick films were dried at 60°C for 1 hr *in vacuo*. Then, the films were

irradiated with 313 or 365 nm LPL from a 500 W high pressure Hg lamp through a set of glass filters, and the polarized absorption spectra was measured.

An LC cell was fabricated by sandwiching a nematic LC, NPC-02, of $T_{NI} = 35^{\circ}\text{C}$ between a glass plate coated with 40-nm-thick film of CpBPI and a lecithin-treated glass plate. A cell gap between two plates was adjusted to 5 μm with spherical glass spacers. The LC cell was irradiated with 313 or 365 nm LPL as previously mentioned. Then, the LC cell was set between a probing polarized He-Ne laser and a crossed polarizer, and the transmittance was measured as a function of the angle of a cell axis and an electric vector of probing light. The extent of LC alignment was evaluated by a contrast value, $T_{\text{max}}/T_{\text{min}}$, where T_{max} and T_{min} stands for a maximum and a minimum of the transmittance of probing light, respectively.

3. Results and discussion

Dichroism evaluation Polarized absorption spectra are shown in Fig. 1. A dichroic property was evaluated by dichroic ratio (DR), which is define as follows:

$$DR = \frac{A_{\perp} + A_{\parallel}}{A_{\perp} - A_{\parallel}}$$

where $A_{\perp}$ and $A_{\parallel}$ denotes for the absorbances at 328 nm, of which the direction of an electric vector of polarized probing light is perpendicular and parallel to that of the actinic LPL, respectively. As shown in Fig. 2, the DR value increased upon increasing the irradiation energy of LPL, and was saturated at an irradiation energy of about 300 mJ/cm^2 irrespective of irradiation wavelength.

Fig. 1. Polarized absorption spectra of CpBPI film after irradiation with polarized UV light.

Fig. 2. DR value of CpBPI film irradiated by (Δ) 313 and ($\circ$) 365nm light as a function of exposure energy.

LC alignment regulation

As shown in Fig. 3, the transmittance changed periodically in every 90 degree upon rotating the LC cell. This means that the in-plane LC alignment regulation was brought about by the irradiation with LPL and was attributable to polarized-axis-selective photoreaction of BPI moieties. A director of LC was proved to be perpendicular to the electric vector of the actinic LPL by the experiment using dichroic dye doped LCs. The extent of LC alignment regulation was dependent on irradiation wavelength; an LC cell irradiated with 365-nm light showed a better contrast value (Table. 1). This wavelength dependence of LC alignment regulation does not coincide with the result observed in the dichroic ratio study. In order to clarify the reason for the above fact, a photochemical behavior of BPI was investigated using the model compound **1**, since the direct analysis of CpBPI was difficult due to a little change of UV spectrum upon *E/Z* isomerization. In solution, only the *E/Z* isomerization occurred upon irradiation.

Fig. 3. Angular dependence of transmittance of a monitoring He-Ne laser through the LC cell exposed to linearly polarized 365nm light at room temperature; □: 0 mJ/cm², ○: 490mJ/cm².

Table 1. Photocontrol of LC alignment ^{a)}

Irradiation wavelength (nm)	Contrast
313	1.2
365	12.5

^{a)} Irradiation energy was 490mJ /cm²

Table 2. *E* and *Z* isomer ratio of **1** at a photostationary state in EtOH

Irradiation wavelength (nm)	<i>E</i> (%)	<i>Z</i> (%)
313	50	50
326	44	56
365	25	75

As shown in Table 2, the isomer ratio at a photostationary state was wavelength-dependent, and the fraction of *Z*-isomer was larger when the wavelength was longer. Although it is well-known that the photoisomerization in polymer solid is significantly suppressed due to the restricted mobility of chromophores[8], it might be reasonable to assume that the relationship between the degree of isomerization is still valid in polymeric matrices. Therefore, we presumed that the *Z*-

isomer is responsible for the induction of LC alignment. We have already reported on similar wavelength-dependent behavior of LC alignment photoregulation with stilbene derivatives and concluded that the *E*-isomer of stilbene has an ability for the induction of LC alignment.[9] This is in coincidence with the result observed here because the *Z*-isomer of BPI has *E*-stilbene skeleton. It is interesting to mention that the irradiation with light of shorter wavelength gave better LC alignment regulation for stilbene derivatives, whereas the longer wavelength was preferred for CpBPI.

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