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Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 1. Effect of Light Intensity on Alignment Behavior

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ABSTRACT: Polydomain films of liquid crystalline polymer (**MACB-AB6**) with low content (6 mol %) of azobenzene units were prepared and irradiated with linearly polarized light at 366 nm, thus inducing an alignment of the photochromic side groups as well as the nonphotoactive mesogens, the cyanobiphenyl groups. An induced order parameter, *S*, was obtained from polarized UV and IR spectroscopy, and it increased with increase in temperature at first and then decreased due to phase transition. The effect of light intensity on the alignment behavior has been investigated in detail. Alignment change can take place even for a low intensity (0.7 mW/cm^2) of irradiation light. Irradiation light at high intensity induced alignment as well as a phase transition at relatively low temperature. A higher saturation order parameter and faster achievement of the order parameter were obtained, since a higher concentration of *cis*-azobenzene was produced when the film was exposed to polarized light with a higher intensity. This is due to the angular-dependent absorbance of irradiation light by the azobenzene moieties.

Introduction

Recent years, azo polymers have attracted increasing attention because of their potential uses in various photonic applications.[1,2,4−13,24−26] It has been known for more than a decade that linearly polarized light can induce reorientation of azobenzene groups through photochemical *trans*−*cis*−*trans* isomerization cycles.[3] Azobenzene groups exhibit angular-dependent absorption of linearly polarized light.[4] Using polarized light, only azobenzene that has fallen perpendicular to the direction of the electric field vector of the incident linearly polarized light will become inactive, but the others will be activated for isomerization accompanied by a slight motion of their transition moment until they are perpendicular to the direction of the electric field vector. This results in an anisotropy induced by the orientation of the azobenzene groups. The resulting anisotropy can be “erased” by irradiation with circularly polarized light or random light and then introduced again with linearly polarized light.

Amorphous high T_g polymers containing azobenzene groups have been investigated by Natansohn and coworkers recently.[5,6] Those polymers exhibited a change in the refractive index on irradiation with a laser beam. Polymer liquid crystals with azobenzene moieties in the side chain were also proposed as materials for optical storage,[7] because the “writing” was fairly stable below the clearing temperature of the polymer liquid crystals; hence, the materials had long term stability. The induced alignment can be “erased” by heating the polymer liquid crystals above the clearing temperature or by irradiation with light as mentioned above. One of the most interesting observations for the polymer liquid crystals was that if only a low content of the azobenzene mesogens was present in the side chain, the nonphotoactive mesogens underwent reorientation together with the azobenzene groups, thus amplifying the effect over the limits given by the concentration of the azobenzene groups.[8−10] This is due to a cooperative motion existing between the photoactive and nonphotoactive mesogens.[10] It makes the liquid crystalline copolymers more useful in photonic applications.

There are many factors that affect the alignment behavior, including the structure of the polymer liquid crystals and the condition for optical experiment. Such effects as the size of azobenzene,[11] the substituent on azobenzene groups[12] and the thickness of film[13] on optical behaviors have been reported before. To our knowledge, few literature has detailed the effect of light intensity.[14] In this paper, photoinduced alignment of polymer liquid crystal, **MACB-AB6**, with a low content (6 mol %) of azobenzene moieties in the side chain, was studied. The effect of light intensity on alignment change was investigated in detail by using polarized UV and IR spectroscopy.

Experimental Section

The structure of the polymer liquid crystal **MACB-AB6** is shown in Figure 1. Monomers, 4′-[(6-(methacryloyloxy)hexyl)oxy]-4-cyanobiphenyl and 6-[(4-((4-ethylphenyl)diazenyl)phenyl)oxy]hexyl methacrylate, were prepared using a procedure similar to the literature.[15] Polymerization was performed in dry DMF with 1 mol % AIBN as an initiator. The feed ratio of the azobenzene monomer was 7 mol %. The monomers were allowed to copolymerize under vacuum at 60 °C for 2 days. The polymerization was stopped by dripping the reaction mixture into methanol. The copolymer was dissolved in THF and precipitated again in methanol and finally dried under vacuum until constant weight. Results of characterization of the polymer are summarized in Table 1. Thermotropic properties were obtained with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. At least three scans were performed to check the

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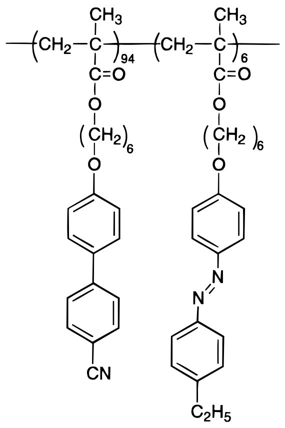

MACB-AB6

Figure 1. Structure and composition of the polymer liquid crystal, **MACB-AB6**, used in this study.

Table 1. Thermodynamic Properties and Molecular Weights of MACB-AB6[a]

polymer	phase transition temp (°C)	ΔH_{NI} (kJ/mol)	ΔS_{NI} (J/mol·K)	M_n	M_w/M_n
MACB-AB6	G 44 N 115 I	1.8	4.6	25,000	2.0

[a] Key: G, glass; N, nematic; I, isotropic; ΔH_{NI}, change in enthalpy of N−I phase transition; ΔS_{NI}, change in entropy of N−I phase transition; M_n, number-average molecular weight; M_w, weight-average molecular weight.

reproducibility. Molecular weight was measured by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8 + G500H8) calibrated with standard polystyrenes. The eluent was chloroform. The content of the azobenzene units was calculated from UV spectra (Shimadzu UV-200S) of the copolymer and the monomer in THF solution.

Thin films (about 2 μm thickness) were obtained by dissolving the copolymers in THF solvent and casting onto clean glass substrates. Solvent was allowed to evaporate slowly at room temperature. After dried in an oven to remove residual solvent, the films were heated above the clearing temperature and then annealed at a temperature just below T_{NI} (nematic−isotropic phase transition temperature) to yield a polydomain nematic (N) phase. The thin polymer film placed in a thermostated block was exposed to light from a 500 W high-pressure mercury lamp passed through a polarizer. The wavelength was chosen at 366 nm by using three cut-off filters (Toshiba; UV-D36C, UV-35, and IRA-25S). After irradiation, the film was quenched to low temperature by using a cold aluminum block, and then the polarized UV and IR (JASCO FTIR-3) spectra were measured at room temperature. The concentration of *cis*-azobenzene in the polymer films was measured *in situ* in the spectrometer. The absorbance at 360 nm was measured with an unpolarized beam immediately after the irradiation light was switched off. No significant difference was observed in the absorbance measured by these two different methods. In addition, the photoinduced anisotropy was evaluated by polarizing microscopy at room temperature.

Results and Discussion

Photoinduced Alignment of MACB-AB6. The absorption maximum in the UV spectrum of polymer liquid crystal **MACB-AB6** is located at around 350 nm due to a $\pi-\pi^*$ transition of the azobenzene groups. There also exists a weak absorption band at around 450 nm due to an $n-\pi^*$ transition. When the polymer film was exposed to 366-nm unpolarized light, it was observed that the absorbance at 350 nm decreased while the other band at 450 nm increased slightly for *trans*-*cis* isomerization. After irradiation, the film was kept in the dark for several days, and it was observed that the polymer film showed the same spectrum as that before irradiation due to *cis-trans* thermal back isomerization. As shown in Figure 1, the contents of azobenzene units was 6 mol %. Four azobenzene units per polymer chain were estimated from the number-average molecular weight and the composition.

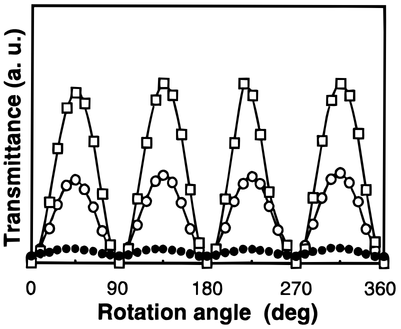

Figure 2. Angular-dependent transmittance of **MACB-AB6** film evaluated by polarizing microscopy after irradiation at 95 °C with linearly polarized light (2.8 mW/cm^2) at various irradiation times: (●) 3 min; (○) 5 min; (□) 30 min.

The intensity of monitoring light transmitted through a pair of crossed polarizers, with a polymer liquid crystal film between them, changes due to the birefringence of the liquid crystal. In order to avoid any angular-dependent absorption of azobenzene moieties, light with a wavelength longer than 540 nm, which is far from the absorption band of azobenzene, was used as a monitoring light. Before irradiation, the polydomain film was not transparent and showed no angular-dependent transmittance when it was evaluated with the polarizing microscope equipped with crossed polarizers. After irradiation with 366-nm (2.8 mW/cm^2) linearly polarized light at 95 °C, a clear homogeneous alignment was obtained. The induced anisotropy was evaluated by measuring the transmittance through crossed polarizers with the polymer film between them as a function of the rotation angle. Figure 2 shows the results. The rotation angle is the direction of polarizer with respect to the direction of electric vector of irradiation light. When the direction of polarization of the irradiation light was perpendicular or parallel to the direction of polarizer of the microscope, no or little transmitted light was observed. On the other hand, when the angle between them was 45°, the transmittance was highest. Regular peaks and valleys with 90° separation indicate that all mesogens of the polymer liquid crystal are aligned into one in-plane direction to form a monodomain of the liquid crystalline phase.[16] The relative value of transmittance increased with irradiation time.

Angular-dependent absorbance of azobenzene moieties at 360 nm was measured by using polarized UV spectroscopy. The absorbance at 360 nm as a function of the rotation angle of polarized measurement beam is shown in Figure 3a. Before irradiation, the absorbance did not change with the direction of polarization of the measurement beam. After irradiation, an optical anisotropy was evidently brought about: when the direction of polarization of the measurement beam was perpendicular to that of the irradiation light, the absorbance reached the maximum and the value increased with an increase in irradiation time; when the polarization directions of irradiation light and measurement light were parallel, the absorbance was at the minimum

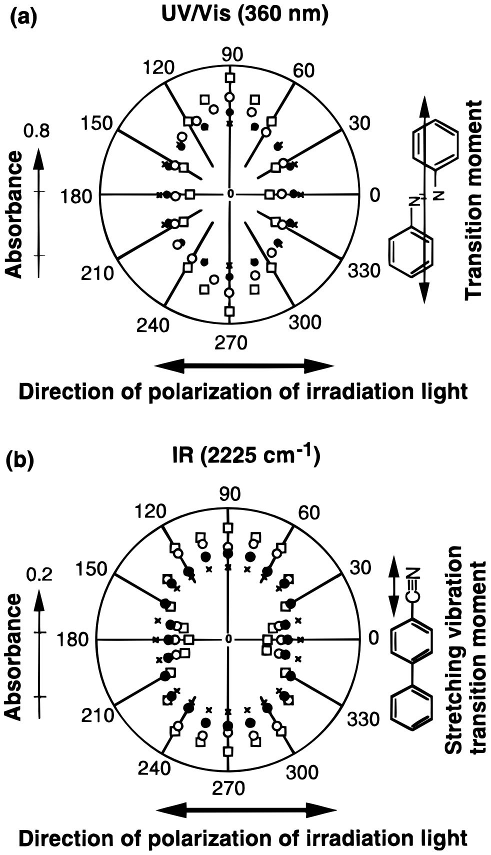

Figure 3. Angular-dependent absorbance of azobenzene (a) and cyanobiphenyl (b) moieties at 360 nm and 2225 cm^{-1}, respectively. The measurement was performed after the film was irradiated with 366-nm linearly polarized light (2.8 mW/cm^2) at 95 °C for various times: (×) 0 min; (●) 3 min; (○) 5 min; (□) 30 min.

and the value decreased with prolonged irradiation time. The figure indicates that the preferential orientation of the azobenzene groups is perpendicular to the electric vector of irradiation light. The induced anisotropy increased with increase of irradiation time until the maximum value.

Figure 3b shows the relationship between rotation angle and absorbance of CN group of cyanobiphenyl moiety obtained from polarized IR spectroscopy at 2225 cm^{-1}. An optical anisotropy was also induced and the cyanobiphenyl mesogens were aligned perpendicular to the electric vector of the irradiation light. This means that nonphotoactive mesogen, cyanobiphenyl, can undergo reorientation together with the azobenzene groups. Alignment of mesogens in **MACB-AB6** could be induced by irradiation with linearly polarized UV light at 366 nm, although the content of azobenzene was only 6 mol %. The cooperative reorientation of nonactive mesogens is a general phenomenon.[17−21] The induced anisotropy was stable at the induced temperature, and no relaxation was observed for more than 1 year at room temperature.

Order Parameter. The concept of the order parameter, S, is used for describing the degree of orientational order in polymer liquid crystals, where θ is the angle between the long axis of the molecule and the directrix of the system corresponding to their primary orientation.

$$S = \langle 3\cos^2\theta - 1\rangle/2 \qquad (1)$$

With an ideal parallel orientation, $S = 1$, and for a disordered state, $S = 0$. If the transition moment is oriented parallel to the molecular long axis, the order parameter has the following relationship with dichroic ratio, R.[22]

$$S = (R - 1)/(R + 2) \qquad (2)$$

For transparent film, the dichroic ratio can be determined by polarized UV or IR spectroscopy and given by the following equation:

$$R = A_{\parallel}/A_{\perp} \qquad (3)$$

$A_{\parallel}$ and $A_{\perp}$ are the absorbance measured with the polarized beam parallel and perpendicular to the optic axis of the molecule, respectively. In this study, although the well-aligned **MACB-AB6** film was transparent, strong light scattering was observed in the film with a low order parameter. Considering the light scattering, we can change equation (2) as

$$R = (A_{\parallel} - A_s)/(A_{\perp} - A_s) \qquad (4)$$

where A_s is the value of light scattering. The light scattering was estimated in the following way. With unpolarized beam, we measured absorbance at 360 nm of individual films in which mesogens were aligned. They showed light scattering, and we obtained A' as an apparent absorbance for each film. Next we heated the films to an isotropic state to obtain transparent films. Then we quenched the films rapidly by placing them on the cold aluminum block at −25 °C. After quenching, the films were still transparent, and we could measure true absorbance (A'') at 360 nm of the film. We used the relation $A_s = A' - A''$ for each film throughout the present study.

The induced alignment can be evaluated by measuring the order parameter of the resulting polymer film. Figure 4a shows the order parameters of the azobenzene moieties calculated from the polarized UV absorbance at 360 nm and (b) shows those of the cyanobiphenyl mesogens obtained from the polarized IR absorption at 2225 cm^{-1}. At a suitable temperature, an order parameter as large as 0.45 was achieved, which indicates a typical well-aligned nematic liquid-crystalline phase.[23] At a certain intensity, the order parameter increased with increasing temperature at the beginning, but when it reached a maximum, it decreased with increasing temperature. The azobenzene moieties have two effects during the alignment process. One is reorientation of the cyanobiphenyl mesogens and themselves through *trans*−*cis*−*trans* isomerization cycles. The other is to induce disorder through *trans*−*cis* isomerization, namely, inducing nematic to isotropic phase transition.[24−26] With the increase of temperature, the mobility of the mesogens for angular motion as well as *cis*−*trans* isomerization rate of azobenzene groups increases, which results in faster reorientation with increased values of the order parameter. At the same time, however, with the increase in temperature, the phase transition can take place more easily. These two contradictory factors may bring about the bell-shaped profiles between order parameter and temperature.

Effect of Light Intensity on Alignment Behavior. After exposure to polarized light at different intensity at 95 °C for 30 min, similar to Figure 2, angular-dependent transmittance of the **MACB-AB6** thin film

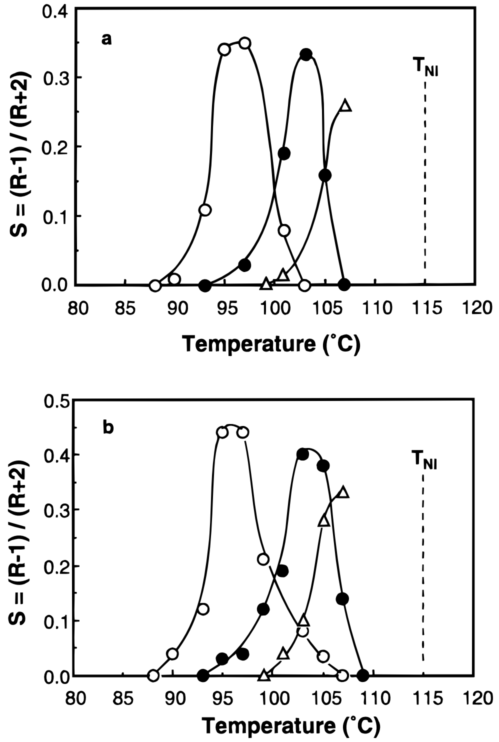

Figure 4. Order parameters of azobenzene (a) and cyanobiphenyl (b) moieties at various temperatures and light intensities. Films were exposed to 366-nm polarized light for 30 min. Key: (○) 2.8 mW/cm^2; (●) 0.7 mW/cm^2; (△) 0.3 mW/cm^2.

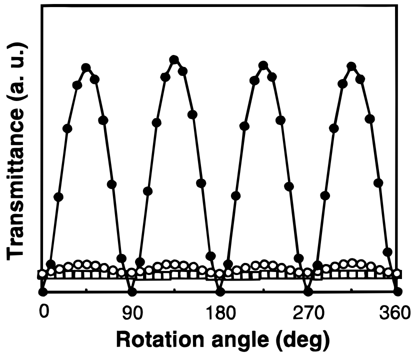

Figure 5. Angular-dependent transmittance of **MACB-AB6** film evaluated by polarizing microscopy after irradiation at 95 °C for 30 min with different light intensity. Key: (●) 2.8 mW/cm^2; (○) 0.7 mW/cm^2; (□) 0.3 mW/cm^2.

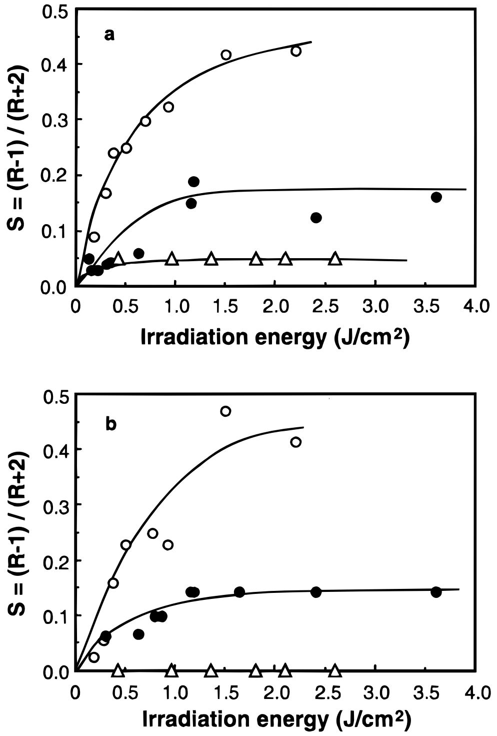

Figure 6. Order parameters of azobenzene (a) and cyanobiphenyl (b) moieties as a function of the irradiation energy at 95 °C. Key: (○) 2.8 mW/cm^2; (●) 0.7 mW/cm^2; (△) 0.3 mW/cm^2.

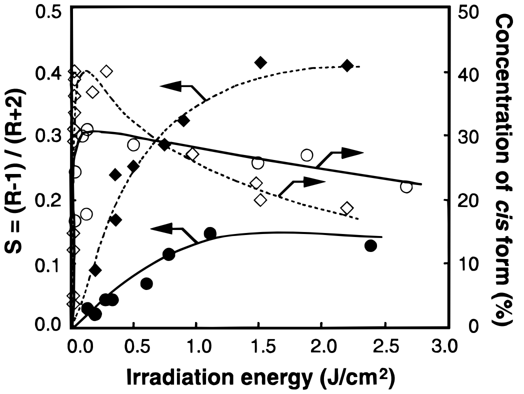

Figure 7. Change in order parameters and concentrations of *cis*-azobenzene as a function of irradiation energy. Samples were irradiated at 95 °C with linearly polarized light (366 nm) at 2.8 mW/cm^2 (- - -) and at 0.7 mW/cm^2 (—). [cis] % = 100(A_0 − A_E)/A_0, where A_0 and A_E are the absorbances at 360 nm at irradiation energy zero and at irradiation energy E.

was evaluated by polarizing microscopy as shown in Figure 5. When the intensity was 0.3 mW/cm^2, the transmittance did not change with the rotation angle; the polarized light at 0.3 mW/cm^2 could not induce homogeneous alignment in the polymer film. On the other hand, the polarized light at 0.7 and 2.8 mW/cm^2 could induce the alignment change in the film. It is clear that the transmittance increased with increase of intensity of irradiation light. Figure 4 also shows the effect of light intensity on the order parameter. Both the temperature range for alignment change and the favorable temperature at which the highest order parameter was achieved were affected by the intensity of the irradiation light. Alignment of the azobenzene moieties could be induced in the temperature range between 87 and 103 °C with light at 2.8 mW/cm^2; between 93 and 107 °C with light at 0.7 mW/cm^2 and from 99 °C with light at 0.3 mW/cm^2. The favorable temperatures for the photoinduced change in alignment are located at 96, 103, and 107 °C, which corresponded to the light intensity at 2.8, 0.7, and 0.3 mW/cm^2, respectively. Linearly polarized light at high intensity can induce both an alignment change and a phase transition at relatively low temperature.

Figure 6 shows the change in the order parameter as a function of irradiation energy at a fixed temperature. It was found that the order parameter increased faster when the intensity of irradiation light was higher. In order to understand the effect of light intensity on the order parameter in detail, behavior of the azobenzene moieties during the alignment process was investigated. It was shown in Figure 7 that the concentration of *cis*-azobenzene changed with irradiation energy. Irradiation light at higher intensity produced a higher concentration of *cis*-azobenzene at first, and then the concen-

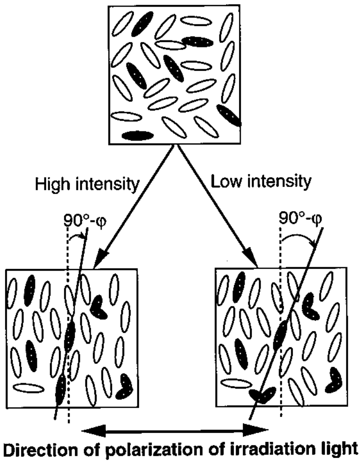

Figure 8. Illustration of photoinduced alignment of **MACB-AB6** with different intensity of irradiation light: open ellipse, cyanobiphenyl moiety; solid ellipse, azobenzene moiety.

tration decreased faster, which means a faster *trans*−*cis*−*trans* isomerization process. Comparing the curves of the order parameter and the concentration, we can conclude that irradiation light at higher intensity gave rise to a higher *trans*−*cis*−*trans* isomerization rate, therefore faster achievement of the saturation order parameter.

As shown in Figure 6, at the same irradiation energy, higher saturated order parameter could be obtained when irradiation light at higher intensity was used. Both Figure 4 and Figure 6 indicate that the efficiency of alignment increases with increase of intensity of irradiation light. It may be due to the following two reasons. First, as shown in Figure 7, if irradiation light at a lower intensity is used, when the order parameter reaches a saturation value, a higher concentration of *cis*-azobenzene exists in the film. Since *cis*-azobenzene shows no liquid-crystalline properties, the saturation value of the order parameter would be decreased by the higher concentration of the *cis*-azobenzene. Second, the effective irradiation intensity can be described as $I_{\text{effct}} = I_0 \cos^2 \varphi$, where φ is the angle of the direction of polarization of the irradiation light with respect to the direction of transition moment of the azobenzene moiety and I_0 is the intensity of irradiation light.[14] As demonstrated before, linearly polarized light at 0.3 mW/cm^2 could not generate an alignment change in the polymer film. It seems that there exists an intensity threshold I_{th} for the alignment behavior, below which the reorientation was assumed to cease. The reason may be ascribed to the concentration of *cis*-azobenzene produced by polarized light. In fact, only 10 mol % of *cis*-azobenzene was generated by the polarized light at 0.3 mW/cm^2, and it did not decrease after reaching the maximum value. In order to make I_{effct} exceed I_{th}, we can increase I_0 or decrease φ. If high I_0 is used, the angle φ can trend to 90°. On the other hand, if low I_0 is used, before φ approaches 90°, the reorientation will cease. As shown in Figure 8, $90° - \varphi$ is the angle between the direction of the molecular long axis and the optic axis of the uniformly oriented mesogens; the value of $90° - \varphi$ equals the value of θ mentioned before. The smaller the angle is, the higher the order parameter the polymer film will have. So if I_0 is higher, a larger φ will be achieved and therefore a smaller θ and higher order parameter.

Conclusion

Homogeneous alignment can be induced in a polymer liquid crystal, **MACB-AB6**, by using linearly polarized light at 366 nm. Nonphotoactive mesogens, such as cyanobiphenyl, can undergo an orientation together with azobenzene moieties although the content of azobenzene units is only 6 mol %. The results show clearly that the preferential orientation of the azobenzene and cyanobiphenyl mesogens is perpendicular to the electric vector of polarized actinic light. Order parameters of azobenzene and cyanobiphenyl were measured by using polarized UV and IR spectroscopy, respectively, based on the angular-dependent absorbance. With the increase in temperature, order parameters increased at first for higher *cis-trans* isomerization rate and then decreased for phase transition. A study on the effect of light intensity on alignment behavior indicated that a higher writing rate can be obtained by using irradiation light at higher intensity, because a higher writing intensity gave rise to a higher *trans*−*cis*−*trans* isomerization rate and hence faster achievement of the order parameter. At the same irradiation energy, a higher saturated order parameter can be obtained by using irradiation light at a higher intensity. These are due to angular-dependent absorbance of the azobenzene moieties and concentration of *cis* form of azobenzene produced by light.

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