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Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 6. Biaxiality and Three-Dimensional Reorientation

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ABSTRACT: A liquid-crystalline polymer of 6-[4-(4-ethylphenyl)diazenylphenyloxy]hexyl methacrylate and copolymer of the azobenzene monomer with 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl were cast as thin films. When the polymer films with *cis*-azobenzenes were subjected to irradiation with linearly polarized light at 436 nm, biaxiality of the azobenzene moieties was induced during the in-plane alignment process; when they were exposed to unpolarized light at 436 nm, three-dimensional manipulation of the polymer liquid crystals was brought about. The three-dimensional alignment behavior was examined by UV, FTIR, and polarizing optical microscopy techniques and by measuring the change in transmittance through crossed polarizers. It was found that the azobenzene moieties were aligned along the propagation direction of the irradiation light through repetition of trans−cis−trans isomerization. The induced anisotropy was large (an approximate order parameter as 0.36), reversible, and stable (more than 5 months at room temperature). Nonphotoactive mesogens, cyanobiphenyl, underwent three-dimensional reorientation efficiently together with the azobenzene moieties due to the cooperative motion.

Introduction

Azobenzene groups can exist in two configurations: the cis form and the more stable trans form. When exposed to light of a certain wavelength, the stable trans form can be photoisomerized to the cis form. Cis−trans isomerization can occur thermally or/and photochemically. Recent years, azobenzene-containing polymeric systems have received increasing attention because of their unique and unexpected properties which allow various applications triggered by light.[1−4] One of the attractive phenomena is photoinduced alignment of the azobenzene moieties on irradiation of linearly polarized light.[1] Using linearly polarized light, only azobenzenes with the molecular long axis perpendicular to the direction of the electric field vector of the incident light become inactive, but the others will be activated for isomerization accompanied by a slight motion of their molecular long axis until they are perpendicular to the direction of the electric field vector. This results in a macroscopic alignment of azobenzene moieties with the molecular long axis perpendicular to the polarization direction of the incident light. Nonphotoactive moieties undergo reorientation together with azobenzene moieties both in liquid-crystalline polymers and in amorphous polymers.[5−11]

The effects of the structural factors and the experimental conditions on the photoinduced alignment behavior have been studied before.[7−9] One can easily control the alignment direction two-dimensionally by changing the polarization direction of the irradiation light. During the in-plane alignment process, photoinduced biaxiality of azobenzene moieties was observed in liquid-crystalline, amorphous, and Langmuir−Blodgett film systems.[10−13] This was interpreted as a result of the alignment of the azobenzene moieties along the propagation direction of the irradiation light.[12] When the azobenzene moieties are aligned with the molecular long axis along the propagation direction of the irradiation light, the photoisomerization does hardly take place, since the propagation direction of light is always perpendicular to its electric field vector.

For unpolarized light, only the propagation direction is, in principle, perpendicular to the electric field vector of the unpolarized light. Thus, when unpolarized light is used, the azobenzene moieties become aligned only in the propagation direction of the irradiation light. Haitjema and co-workers have reported that azobenzene groups changed from more or less random to more perpendicular orientation on irradiation of unpolarized white light.[14] The homeotropic alignment change in azobenzene-containing polymer liquid crystals was investigated by German scientists by the use of unpolarized light.[15,16] Recently, we have reported three-dimensional manipulation of an azo polymer liquid crystal with unpolarized light.[17] By changing incident direction of the irradiation light, three-dimensional manipulation of the azo polymer liquid crystal was brought about. In this paper, we report photoinduced biaxiality of azobenzene moieties by using linearly polarized light and three-dimensional manipulation of azobenzene moieties as well as nonphotoactive cyanobiphenyl mesogens on irradiation of unpolarized light.

Experimental Section

Figure 1 shows structures and abbreviations of the azo homopolymer and copolymer used in this study. The monomers, 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl and 6-[4-(4-ethylphenyl)diazenylphenyloxy]hexyl methacrylate, were prepared by using a procedure similar to the literature.[18] Polymerization was performed as reported previously.[7] Mo-

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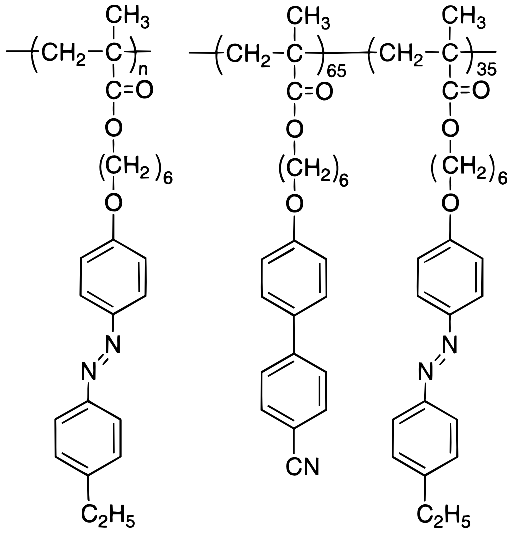

AB6 **CB-AB6-35**

Figure 1. Structures and abbreviations of the polymer liquid crystals used in this study.

Table 1. Thermodynamic Properties and Molecular Weights of the Polymer Liquid Crystals Used in This Study[a]

polymer	phase transn temp (°C)	ΔH (kJ/mol)	ΔS (J/mol·K)	M_n	M_w/M_n
AB6	G 95 S 118 I	4.6	11.8	19 000	2.1
CB-AB6-35	G 40 N 125 I	2.0	5.0	29 000	2.9

[a] G, glass; S, smectic; N, nematic; I, isotropic; ΔH, the corresponding phase transition enthalpy; ΔS, the corresponding phase transition entropy; M_n, number-average molecular weight; M_w, weight-average molecular weight.

lecular weight was measured by gel permeation chromatography (GPC; JASCO DG-980-50; column, Shodex GPC K802 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes. The content of the azo units in the copolymer was calculated from UV spectra (JASCO U-550) of the copolymer and the monomer in tetrahydrofuran solution. Thermotropic properties were obtained with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. Three scans were performed to check the reproducibility. The liquid-crystalline phase was determined by X-ray diffractometry (MAC Science MXP^3, model 5301; Cu Kα_1 radiation from a 1.6 kW anode X-ray generator at 105 °C for **AB6** and at 90 °C for **CB-AB6-35**). Table 1 lists some properties of the polymer liquid crystals.

Thin polydomain films were obtained as described before.[7] Borosilicate glass and CaF_2 glass were used as substrates depending on the type of measurements. Thickness of the polymer films was estimated to be ~500 nm or ~1 μm by absorption spectroscopy on the basis of the molar extinction coefficient of the azobenzene moiety. Figure 2 shows the optical setup used for measurement of three-dimensional reorientation. Photoirradiation was performed with a 500 W high-pressure mercury lamp at room temperature unless otherwise stated. Monochromatic light at 436 nm was selected by a combination of glass filters. The intensity was 30 mW/cm^2, when the irradiation light impinged normally on the film, except the intensity-dependent measurement. A sample on a rotation holder was placed between two crossed polarizers, the polarization directions of which were set at 45° with respect to projection of the irradiation light on the film surface. In a sample coordinate system, the irradiation beam and the probe beam were in the *xy* plane, and the substrate was in the *xz* plane. The incident angle θ and probe angle φ were the angles of the irradiation beam and probe beam with respect to the *x* axis, respectively. Both were varied from 0° to 180°. The transmittance of probe light (He–Ne laser, 633 nm) through the crossed polarizers was measured as a function of irradiation time or probe angle at different incident angles of the irradiation light. Before irradiation with unpolarized light at 436 nm, transient *cis*-azobenzenes were produced by exposing the polydomain films to unpolarized light at 366 nm for 1 min, as confirmed by absorption spectroscopy and polarizing microscopy. Induced alignment was also evaluated by using a polarizing microscope (Olympus, BX50), UV and IR spectroscopy (JASCO FTIR 610), and polarized UV spectroscopy. All spectra were recorded with the measurement beam normal to the substrate surface.

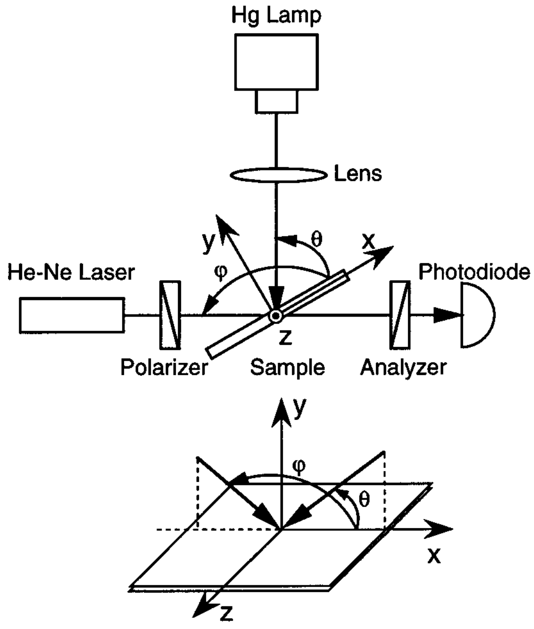

Figure 2. Optical setup for measurement of the three-dimensional alignment change: θ, incident angle; φ, probe angle.

Results and Discussion

Photoinduced Biaxiality of Azobenzene Moieties. The previous paper has shown that large anisotropy with relatively fast response was generated when the *cis*-azobenzene moieties were exposed to linearly polarized light at 436 nm which is located in the absorption band of the n–π^* transition.[9] Resulting *trans*-azobenzenes were aligned with the molecular long axis perpendicular to the polarization direction of the irradiation light. By using IR or UV spectroscopy, it was found that some of azobenzene moieties were forced to move out of the substrate during the photoinduced in-plane alignment process.[10–13] We also observed the photoinduced biaxiality of the azobenzene moieties after the polymer films were irradiated with linearly polarized light at 436 nm (10 mW/cm^2) with the polarization direction parallel to *x* axis. In the IR spectra shown in Figure 3, the absorption band at 1252 cm^{-1} and bands at 1601 and 1500 cm^{-1} are assigned to the stretching vibration of C–O–C_{Ar} (aromatic carbon) bond and the vibration of the skeleton of benzoic ring of the azobenzene groups, respectively. To see the difference clearly, curves a and b were shifted from the baseline. The difference spectrum showed that these absorptions were reduced after exposure. We thought the reduction was due to the photoinduced biaxiality of the azobenzene moieties. During the in-plane alignment process, a certain proportion of the azobenzene moieties could be aligned even along the propagation direction of the irradiation light. When azobenzene moieties aligned

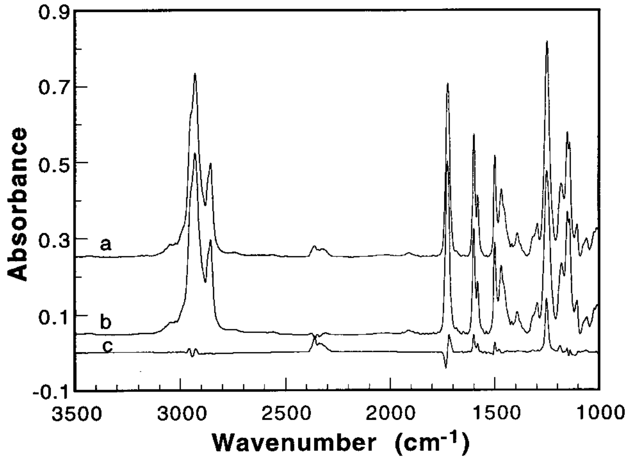

Figure 3. IR spectra of the polymer liquid crystal **AB6**: a, before irradiation; b, after irradiation with linearly polarized light at 436 nm for 10 min; c, difference spectrum of unexposed and exposed films.

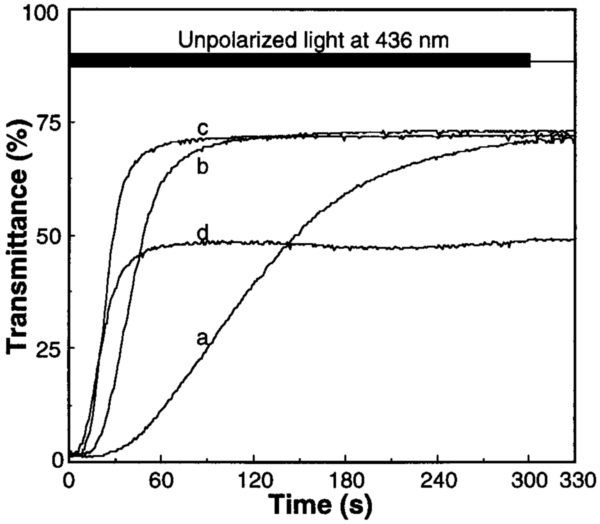

Figure 4. Change in transmittance of the probe light, which was always perpendicular to the irradiation light, through crossed polarizers as a function of irradiation time at various incident angles: a, 10°; b, 30°; c, 50°; d, 70°.

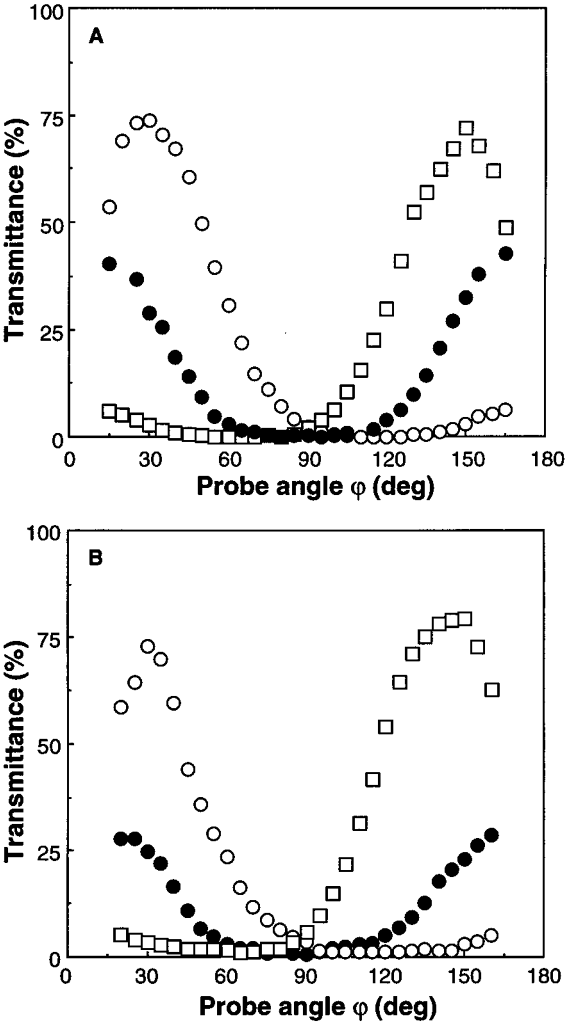

Figure 5. Change in transmittance of the probe light through crossed polarizers as a function of probe angle. Experiments were performed after the alignment change was achieved at the incident angle of 60° (□), 90° (●), and 120° (○), respectively. A, **AB6**; B, **CB-AB6-35**.

with their transition moments in the *yz* plane which was perpendicular to the electric field vector of the linearly polarized light, photoisomerization does not readily take place. Therefore, biaxiality principally exists when alignment change is induced using linearly polarized light. To obtain uniaxial alignment, as described in the following sections, we can expose the polymer film to unpolarized light.

Three-Dimensional Manipulation of Azobenzene Moieties. With the probe light perpendicular to the irradiation light (Figure 2), transmittance of the probe light was detected continuously as a function of irradiation time at various incident angles of the irradiation light. The intensity of probe light passed through the parallel and crossed polarizers with isotropic polymer film (transient *cis*-azobenzene) between them was defined as the 100% and 0% transmittance, respectively. At the beginning of the experiment, no or little light could transmit through the analyzer. As the 436 nm unpolarized light was introduced, the transmittance increased rapidly with time until a maximum level was reached (Figure 4). The increase of transmittance was due to the generation of birefringence. This fact means that alignment change was induced in the azo polymer liquid crystal **AB6** on irradiation of the unpolarized light at each incident angle. When the unpolarized light was switched off, no decay of the induced transmittance was observed. The decrease of the response was attributed to the reduction of light intensity, because the irradiated area increased when the incident angle became small. An intensity-dependent alignment change was investigated. It is interesting to note that the azo polymer liquid crystal is very sensitive to the irradiation light. Alignment change was induced in **AB6** at a very low intensity even at the intensity of 70 μW/cm^2.

After alignment was achieved at a certain incident angle, the change in transmittance through the aligned film was measured as a function of probe angle by rotating the sample with respect to the probe light (see Figure 5A). At the incident angle of 60° for the irradiation light, an asymmetric profile was obtained. The maximum transmittance appeared at the probe angle of 150°, at which the probe light was perpendicular to the irradiation light; the minimum transmittance appeared at the probe angle of around 60°, at which the probe light was parallel to the irradiation light. When the incident angle was changed to 120°, the transmit-

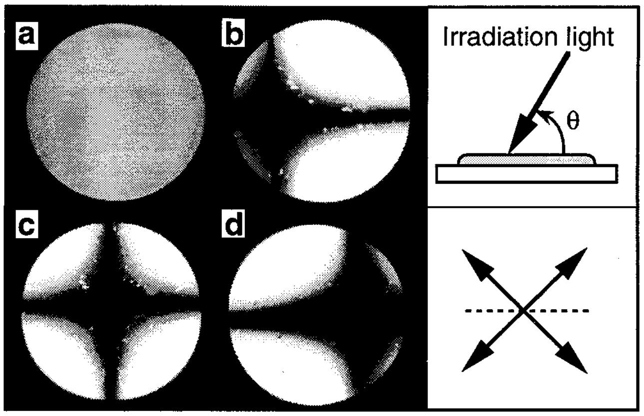

Figure 6. Conoscopic observation of three-dimensional manipulation of the polymer liquid crystal **AB6**. The polarization direction (double-arrowed line) of polarizers was 45° with respect to the projection (dotted line) of the irradiation light. a, Before irradiation (polydomain state); b–d, after irradiation (10 min) at the incident angle of 60°, 90°, and 120°, respectively.

tance exhibited a reverse tendency. However, the maximum and the minimum transmittance appeared still with the probe light perpendicular and parallel to the irradiation light, respectively. The asymmetric profiles in the transmittance for angles of incidence of 60° and 120° indicated that the azobenzene moieties were aligned along the propagation direction of the irradiation light. The characteristic of asymmetry originated from the asymmetric changes in birefringence and in optical path when the tilted azobenzene mesogens were rotated with respect to the probe light. At the incident angle of 90°, a symmetric profile in the transmittance was observed with the minimum transmittance at the probe angle of 90°. These results strongly imply that the azobenzene moieties were aligned in the propagation direction of the irradiation light. The unpolarized light at 436 nm not only induced cis–trans isomerization of the azobenzene moieties but also aligned the resulting *trans*-azobenzenes along its propagation direction. The measurement is very similar to the crystal rotation method for determination of tilt bias angle of a nematic liquid crystal.[19] The lower transmittance at the incident angle of 90° was ascribed to the smaller phase shift of the probe light which could be calculated according to eq 1 in ref 19. In Figure 4, the lower transmittance at the incident angle of 70° is due to the same reason.

The simplest method to study the orientation of a liquid-crystalline phase is polarizing microscopy in the conoscopic mode. Homeotropically aligned liquid crystals appear as dark crosses, where the cross-point represents the optic axis. The three-dimensional orientation was evidenced most convincingly by conoscopic observation in which thick films (~1 μm) were used to obtain clear images. Figure 6 shows that the conoscopic images which were taken at 5 months after the alignment change had been induced. The optic axis of the liquid crystals appeared after irradiation and shifted position according to the incident angle of the irradiation light. These results reveal not only that alignment change was induced by the unpolarized light but also that the alignment direction was governed by the propagation direction of the irradiation light. The induced alignment was very stable at room temperature and remained unchanged even after 5 months. The induced alignment was also stable on further irradiation of 436 nm unpolarized light at the same incident angle, in contrast to the results reported in the literature, in which the tilt angle was controlled by the amount of exposure energy.[20,21] When the polymer film in an initially polydomain state was exposed to the unpolarized light, no or little appreciable change in the alignment of the azobenzene moieties was detected. Hence, the induced alignment is stable on further irradiation of the unpolarized light. As reported previously,[9] one of the advantages of generating *cis*-azobenzenes at first would be high mobility of the *trans*-azobenzenes photochemically produced in situ from the cis form, which is evidently favorable for alignment change. In addition, the existence of *cis*-azobenzene obviously increases absorption of the irradiation light at 436 nm.

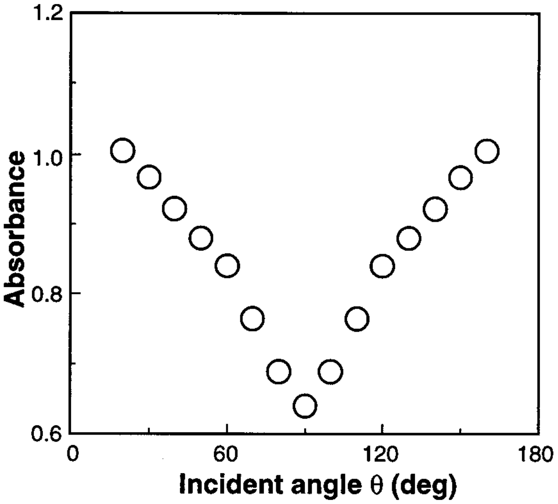

Figure 7. Change in absorbance at 350 nm of the polymer liquid crystal **AB6** as a function of the incident angle. Spectra were detected after irradiation at various incident angles for 10 min.

We also investigated the alignment behavior at the molecular level using UV and IR absorption spectroscopy. UV spectra of the polymer film after exposure to the unpolarized light at different incident angles were recorded. Figure 7 shows the change in absorbance at 350 nm as a function of the incident angle. A highly symmetric profile was observed. The absorbance decreased with increase of the incident angle at first and then increased. The minimum value appeared at the incident angle of 90°. This gave additional evidence for alignment of the azobenzene moieties in the propagation direction of the irradiation light.

Figure 8 shows the IR spectra of **AB6** before and after irradiation with unpolarized light at 436 nm, as well as the difference spectrum. Both the irradiation light and the measurement IR beam were normal to the substrate. After irradiation, the absorbance stemming from the vibration of benzoic ring of the azobenzene moieties and from the vibration of $C-O-C_{Ar}$ band decreased remarkably. The decrease of the absorbance verifies the preferred parallel arrangement of the azobenzene moieties relative to the propagation direction of the irradiation light. Moreover, the absorptions at 2945 and 2856 cm^{-1}, which are related to the symmetric and asymmetric vibrations of CH_2 groups, increased slightly after exposure. These results demonstrate that not only the azobenzene moieties but also some part of the spacer was aligned out of the substrate surface, since the transition moment of the CH_2 groups in the spacer is perpendicular to that of the azobenzene groups.

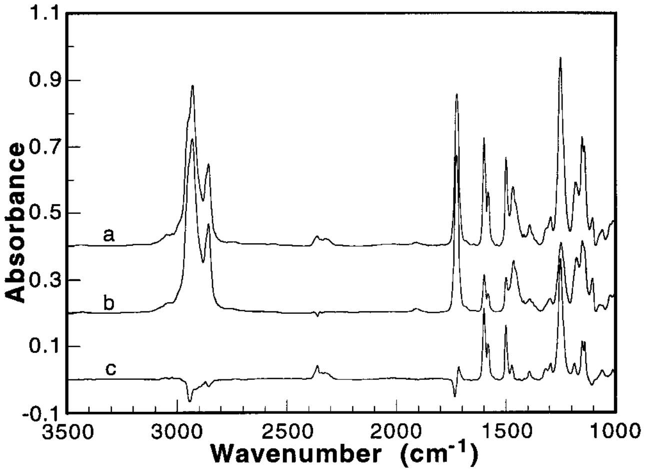

Figure 8. IR spectra of the polymer liquid crystal **AB6**. a, Before irradiation; b, after irradiation with unpolarized light at 436 nm for 10 min; c, difference spectrum of the unexposed and exposed films. The irradiation light was normal to the substrate.

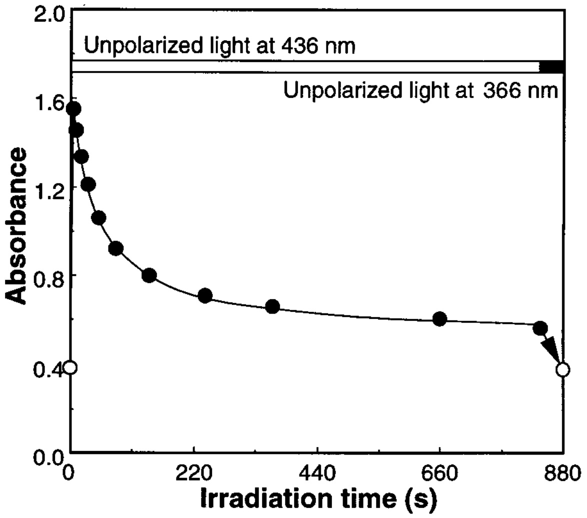

Figure 9. Change in absorbance at 350 nm of the homopolymer as a function of irradiation time. The absorption spectrum shows a typical one of *cis*-azobenzene (●) and a typical one of *trans*-azobenzene (○).

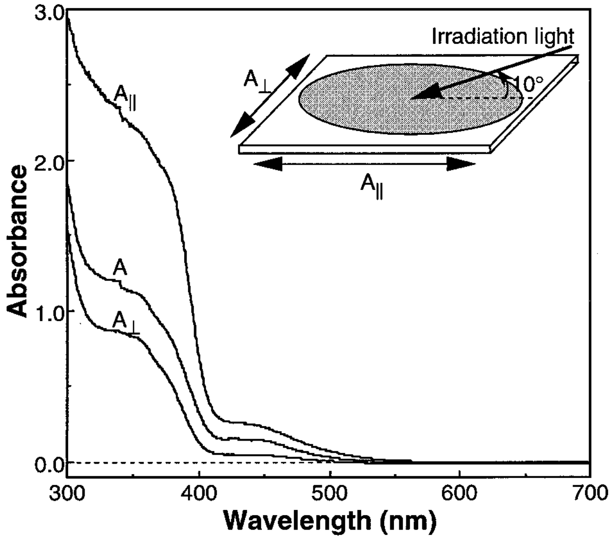

Figure 10. UV spectra of polymer liquid crystal **AB6** after irradiation with unpolarized light at 436 nm for 15 min at the incident angle of 10°. The spectra were detected with unpolarized measurement beam (A) and polarized measurement beam, the polarization direction of which was parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the projection of the irradiation light.

The change in absorbance of the azobenzene groups during the three-dimensional alignment process was followed using UV spectroscopy. When a polymer film with rich *cis*-azobenzenes was irradiated normally with unpolarized light at 436 nm, the absorbance at 350 nm increased rapidly at first due to cis–trans photoisomerization until a new photostationary equilibrium of trans and cis states was built up.[22] The maximum value observed was a little lower than that of the virgin film (film as cast), which implied the existence of small quantities of *cis*-azobenzene during the alignment process. The absorbance at 350 nm decreased on consequent irradiation of the unpolarized light. However, each absorption spectrum shows a typical one of the *trans*-azobenzene, and no isosbestic point was observed in the overall spectra. These results demonstrate that the decrease in absorbance is not due to trans–cis isomerization but to reorientation of the azobenzene groups perpendicular to the substrate. Erasure of the induced alignment was realized easily on irradiation of 366 nm unpolarized light at an incident angle different from that of the 436 nm writing light due to the occurrence of photochemical phase transition,[3,23,24] and the alignment was induced again on irradiation of the unpolarized light at 436 nm. Comparing the change in absorbance with the alignment curves (Figure 4), we can conclude that the three-dimensional alignment is achieved through multitude of trans–cis–trans isomerization but not cis–trans isomerization directly. The mechanism for the three-dimensional reorientation was considered the same as that for in-plane alignment change.[25,26]

The transition moment of a common azobenzene moiety lies along its molecular long axis. Therefore, the induced in-plane alignment of azobenzene moieties is usually evaluated by measuring the UV dichroism at the absorption band of the $\pi-\pi^*$ transition.[7] For assessment of the three-dimensional alignment, the same method can be applied if the tilt angle of the azobenzene mesogens is rather small. Figure 10 shows the polarized UV spectra of **AB6** after irradiation at the incident angle of 10° for 15 min. When the polarization direction of the measurement beam was parallel to the projection of the irradiation light, the maximum absorbance was observed; when these two directions were perpendicular to each other, the minimum absorbance was observed. The azobenzene moieties were aligned parallel to the propagation direction of the irradiation light. Since the incident angle was only 10°, we can assume that the in-plane anisotropy approximately equals to the real anisotropy. The dichroic ratio ($R = A_{\|}/A_{\perp}$) was calculated as 2.68, and the order parameter ($S = (R - 1)/(R + 2)$) was estimated to be 0.36, which was as large as that of homogeneous alignment achieved by using linearly polarized light.[9]

Cooperative Motion. Similar experiments were carried out on a liquid-crystalline copolymer **CB-AB6-35**. After a copolymer film with rich *cis*-azobenzenes was exposed to unpolarized light at 436 nm at 90 °C for 2 min, the change in transmittance through crossed polarizers with the aligned film between them was measured as a function of probe angle at room temperature. Figure 5B shows the results, which were the same as those of the homopolymer (Figure 5A). Three-

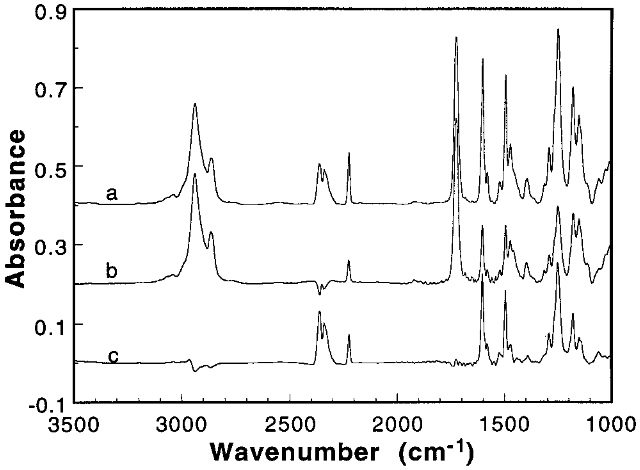

Figure 11. IR spectra of the polymer liquid crystal **CB-AB6-35**. a, Before irradiation; b, after irradiation with 436 nm unpolarized light for 2 min at 90 °C; c, difference spectrum of the unexposed and exposed films. The irradiation light was normal to the substrate.

Table 2. Orientational Functions of Different Chemical Groups of the Liquid-Crystalline Azo Homopolymer and Copolymer

wavenumber (cm^{-1})	AB6			CB-AB6-35		
	A_0	ΔA	$\Delta A/A_0$	A_0	ΔA	$\Delta A/A_0$
2225				0.1120	0.0682	0.61
1601	0.3257	0.2153	0.66	0.3728	0.2242	0.60
1500	0.2679	0.1655	0.62	0.3206	0.1832	0.57
1252	0.5683	0.3640	0.64	0.4403	0.2504	0.57

dimensional alignment change was brought about in the liquid-crystalline copolymer. The result was further confirmed by conoscopic observation. It must be noted here that temperature for the reorientation experiment was different between the homopolymer and the copolymer. Since the concentration of the photoactive chromophore was high in the homopolymer, the sensitivity to the light in the homopolymer was much higher than that in the copolymer. In the homopolymer, therefore, the change in orientation could be induced in the highly ordered glassy smectic phase, although the mesogen was not so mobile. In copolymer, reorientation could be achieved with cooperative motion in the liquid-crystalline phase.

Cooperative motion of nonphotoactive mesogens together with azobenzene moieties is a general phenomenon in the process of photoinduced in-plane alignment change.$^{5-11}$ It was found that this kind of cooperative motion existed in the three-dimensional alignment process as well. Cooperative motion was investigated using IR spectroscopy, as shown in Figure 11. The absorption band at 2225 cm^{-1} is attributed to the stretching vibration of cyano groups of the nonphotoactive cyanobiphenyl moieties. One can see that not only the absorptions of benzoic ring but also the absorption of cyano groups decreased dramatically after irradiation. To allow the quantitative comparison of the alignment efficiency of the cooperative motion, a three-dimensional orientational function referring to the normal of the substrate was defined as

$$R = \Delta A/A_0$$

where A_0 represents the absorbance before irradiation and ΔA the different absorbance. Table 2 summarizes the orientational functions of the absorbance bands at 2225, 1601 and 1500, and 1252 cm^{-1}, which correspond to the vibrations of cyano groups, benzoic ring, and the C−O−C$_{\mathrm{Ar}}$ bond, respectively. Compared with the homopolymer, the copolymer exhibited a little lower but comparable alignment efficiency. Although the orientational function of cyano groups was as large as those of benzene groups in the copolymer, direct comparison of them is difficult since the directions of transition moments of these chemical groups are not the same. However, if we take into account that the orientational functions of benzoic ring in the homopolymer and the copolymer were comparable, we might conclude that the cooperative motion took place effectively in the three-dimensional reorientation process. We note that the absorbance of carbonyl groups of **AB6** shifted toward high frequency after irradiation (Figures 3 and 8), although the optical density showed no reduction; no change was observed in that of the copolymer. The reason is unclear at present.

Conclusion

Photoinduced biaxiality of azobenzene moieties was observed during the in-plane alignment process on irradiation of the azo polymer liquid crystal with linearly polarized light. Three-dimensional alignment change was generated in the polymer liquid crystals when the polymer films with rich *cis*-azobenzenes were exposed to unpolarized light at 436 nm. Resulting *trans*-azobenzene mesogens were aligned along the propagation direction of the irradiation light through repetition of trans−cis−trans isomerization cycles. By changing the incident direction of the irradiation light, we make it possible to control the alignment of azobenzene mesogens three-dimensionally. The induced anisotropy was large, reversible, and stable at room temperature. Cooperative motion of nonphotoactive mesogens together with azobenzene moieties toward the propagation direction of the irradiation light was observed. The alignment efficiency of inert mesogens was as high as that of the azobenzene moieties. The three-dimensional reorientation of polymer liquid crystals may open a new way for high-density data storage since information can be stored as a change of the orientation direction of mesogens.

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