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Yiliang Wu; Jun-Ichi Mamiya; Osamu Tsutsumi; Akihiko Kanazawa; Takeshi Shiono; Tomiki Ikeda

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Photoinduced alignment of polymer liquid crystals containing azobenzene moieties in the side group

VII. On He-Ne laser beam irradiation

YILIANG WU, JUN-ICHI MAMIYA, OSAMU TSUTSUMI,
AKIHIKO KANAZAWA, TAKESHI SHIONO and TOMIKI IKEDA*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Photoinduced alignment in a polymer liquid crystal prepared from 6-[1-[4-(2-cyano-4-nitrophenylazo)phenyl]piperazino]hexyl acrylate and 4'-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl was investigated for the first time on irradiation with a polarized He-Ne laser beam at 633 nm. The azobenzene moieties as well as the inert cyanobiphenyl mesogenic units were aligned with the molecular long axis perpendicular to the polarization direction of the irradiation light. Alignment induced on short irradiation was reversible, while that induced under prolonged irradiation was irreversible due to the occurrence of crosslinking which might be caused by photoinduced decomposition of the azobenzene moieties during the photoirradiation process.

1. Introduction

In the last decade, polymers containing azobenzene chromophores have been extensively investigated as recording media [1–16]. Polymer liquid crystals (PLCs) show a unique combination of the properties of low molecular mass liquid crystals and the properties of polymers which allow for the preparation of thin films. Therefore, azobenzene-based PLCs have attracted special attention [8–16]. Photoinduced orientation and reorientation of PLCs containing azobenzene moieties have been explored on irradiation with linearly polarized light by many investigators [10–16]. Large, stable and reversible anisotropy was brought about in the PLCs. The accepted mechanism involves photochemically induced *trans*–*cis*-isomerization and subsequent thermal and/or photochemical *cis*–*trans*-back-isomerization. Only those azobenzene moieties with the molecular long axis perpendicular to the direction of the electric field vector of the linearly polarized light become inactive, while the others will be activated for isomerization. By repetition of the *trans*–*cis*–*trans*-isomerization cycles of the azobenzene moieties accompanied by rotation of their transition moments, the optic axes of the azobenzene groups become aligned perpendicular to the polarization direction of the incident actinic light. Non-photoactive mesogenic groups undergo reorientation together with

the azobenzene moieties due to cooperative motion or dipole interaction.

In most of the cases, the photoinduced alignment change in PLCs, amorphous azo polymers and LB film systems was generated on irradiation with polarized light from a mercury lamp (366 or 436 nm) [3, 14, 15], a Xenon lamp (448 nm) [10], an argon ion laser (488 or 514.5 nm) [5–7, 11–13, 16], a Nd:YAG laser (532 nm) [4], and other sources. From a practical viewpoint, it is anticipated that information will be written into the azo polymers with miniature diode lasers [16, 17]. One approach is to create such lasers cheaply and with short wavelength [18]. Another method is to develop materials responsive to inexpensive commercial lasers giving long wavelengths, such as a He-Ne laser with wavelength at 633 nm. Azobenzene derivatives show absorbance varying from the UV to the visible region [19], but the absorption maximum of azobenzene moieties can be easily shifted by chemically tailoring the structure. For example, with increase in the strength of donor and acceptor groups at the 4- and 4'-positions of the azobenzene moieties, the absorption maximum was shifted towards the red region [15]. This factor may allow us to design azobenzene-containing PLCs responsive to inexpensive lasers. In this paper, we have demonstrated, for the first time, the generation of alignment change in a novel PLC on irradiation with a polarized He-Ne laser beam.

*Author for correspondence, e-mail: tiked@res.titech.ac.jp

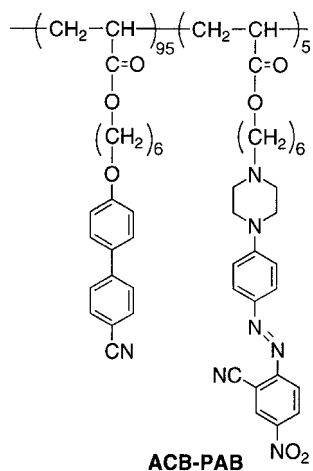


Figure 1. Structure and composition of the polymer liquid crystal **ACB-PAB** used in this study.

2. Experimental

Figure 1 shows the structure and composition of the PLC **ACB-PAB** used in this study. The monomers, 4'-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl and 6-{1-[4-(2-cyano-4-nitrophenylazo)phenyl]piperazino}-hexyl acrylate, were synthesized according to the literature with some modifications [20]. Polymerization was performed as reported previously with AIBN (3 mol %) as an initiator [14]. The feed ratio of the azobenzene monomer was 8 mol %. Thermotropic properties were measured with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of $10^{\circ}\text{C min}^{-1}$. Three scans were performed to check the reproducibility. The liquid crystalline phase was identified by polarizing optical microscopy (Olympus, BX50 equipped with a hot-stage—Models FP-90 and FP-82). Molecular masses were obtained by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6*2 + G4000H8 + G500 H8; eluent, chloroform) calibrated with standard polystyrenes. The content of azobenzene units was calculated from the electronic spectra (JASCO, V-550) of the copolymer and the azobenzene monomer in tetrahydrofuran (THF) solution. Table 1 shows the thermodynamic properties and molecular mass values.

Table 1. Thermodynamic properties and molecular masses of the polymer **ACB-PAB**^a.

Phase transition temperature/ $^{\circ}\text{C}$	ΔH_{NI} / kJ mol^{-1}	ΔS_{NI} / $\text{J mol}^{-1} \text{K}^{-1}$	M_n	M_w/M_n
g 34 N 105 I	0.75	2.0	4300	1.6

^a g, glass; N, nematic; I, isotropic; ΔH_{NI} , change in enthalpy at the N–I phase transition; ΔS_{NI} , change in entropy at the N–I phase transition; M_n , number-average molecular mass; M_w , mass-average molecular mass.

Unoriented thin films of the PLC were prepared as described before by casting a dilute THF solution onto clean borosilicate glass or CaF_2 crystal substrates [14]. The thickness of the polymer films was estimated to be less than $2 \mu\text{m}$ by absorption spectroscopy on the basis of the molar extinction coefficient of the azobenzene moiety. Annealing of the PLC films at a temperature just below the clearing temperature yielded a polydomain phase as confirmed by polarizing optical microscopy. The thin polymer film placed in a thermostatted block was exposed to 633 nm polarized light from a He-Ne laser at 95°C . The light intensity was 200 mW cm^{-2} . Polarized light (577 nm, 100 mW cm^{-2}) selected from a 500 W high pressure Hg lamp (filters: O-56, IRA-25S) was used to investigate the photoinduced decomposition phenomenon. After irradiation, the polarized UV/Vis and IR (JASCO FTIR-3) spectra were recorded at room temperature. In the case where the transition moment is parallel to the molecular long axis, the order parameter S can be estimated by the following equation,

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

where the dichroic ratio R is determined by polarized UV spectroscopy and given by the relationship $R = A_{\parallel}/A_{\perp}$. A_{\parallel} and A_{\perp} are the absorbances measured with the polarized beam parallel and perpendicular to the optical axis of the molecule, respectively.

3. Results and discussion

The copolymer exhibited a nematic phase between 34 and 105°C . A typical schlieren texture was observed by polarizing optical microscopy. The small enthalpy change (table 1) also supported the nematic phase behaviour. Figure 2 shows an absorption spectrum

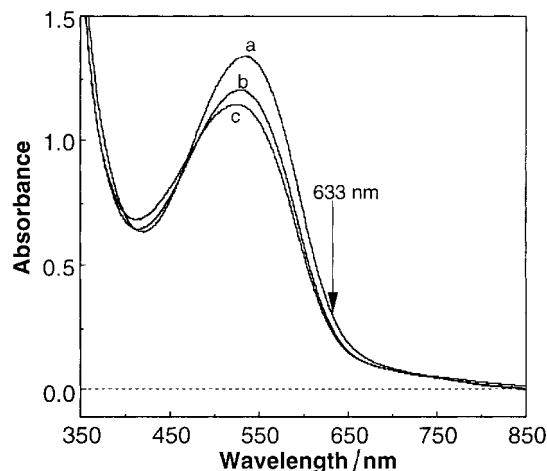


Figure 2. Absorption spectra of a polymer film measured before irradiation (curve a), and after exposure to 577 nm polarized light (100 mW cm^{-2}) at 95°C for 2 h (curve b), and 3 h (curve c).

(curve a) of the PLC in a solid film. The absorption maximum was observed at 534 nm. The molar extinction coefficient at the absorption maximum of the azobenzene groups in chloroform solution was determined as $3.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which was comparable to values for common azobenzene groups. By introduction of a second acceptor group into an *ortho*-position to the N=N bond, the absorption maximum was shifted towards the red region. There exists absorbance at 633 nm, although it is only one-fifth of the value of the absorption maximum. This allowed us to use a He-Ne laser at 633 nm as an actinic light source to generate alignment in the polymer film.

3.1. Photoinduced alignment behaviour

The photoinduced alignment behaviour was examined under steady-state irradiation using the He-Ne laser at 633 nm at a fixed temperature. After a thin film was irradiated at 95°C for 1 h, the polarized UV/Vis and IR spectra of the film were recorded at room temperature to evaluate the alignment efficiency. Figure 3 shows the polarized absorbance of the azobenzene moieties at 520.5 nm (the absorption maximum after irradiation) as a function of the polarization angle of the measurement beam. The polarization direction of the irradiation light was set at 90°. When the polarization direction of the measurement beam was perpendicular to that of the irradiation light (at 0° or 180°), the maximum absorbance was observed, whereas the minimum absorbance appeared when these two directions were parallel (at 90°). These results showed that anisotropy was brought about in the initially polydomain film and that the azobenzene moieties were aligned with the molecular long axis perpendicular to the polarization direction of the

irradiation light. As described in previous work [14], the value of the induced anisotropy can be evaluated from the order parameter of the liquid crystalline phase. The order parameter of the azobenzene moieties was calculated to be $0.18 (\pm 0.01)$, which is smaller than values obtained in previous work [14, 15]. This may be ascribed to the low absorption of the azobenzene moieties at 633 nm.

The anisotropy of the cyanobiphenyl groups can be determined by polarized IR spectroscopy. Figure 4 shows polarized IR spectra as well as a difference IR spectrum of a polymer film. The absorption band at 2225 cm^{-1} was assigned to the stretching vibration of cyano groups. Although the azobenzene moieties in the PLC contained cyano groups, the absorption observed stemmed mainly from the cyanobiphenyl mesogenic groups due to the low contents of the azobenzene units. Similarly, the absorbance was largest when the polarization direction of the measurement beam was perpendicular to that of the He-Ne laser beam, and the minimum absorption appeared when these two polarization directions were parallel. The order parameter of the cyanobiphenyl groups was estimated to be 0.13, which is smaller than that of the azobenzene moieties. We consider that the reason for this is a photoinduced bleaching of the azobenzene moieties which contributed to some extent to the anisotropy of the azobenzene moieties. This will be discussed in the following section in detail. Both figures indicate that the alignment change was induced in the PLC on irradiation with the He-Ne laser at 633 nm. To our knowledge, this is the first example of alignment of azobenzene-containing PLCs by a He-Ne laser.

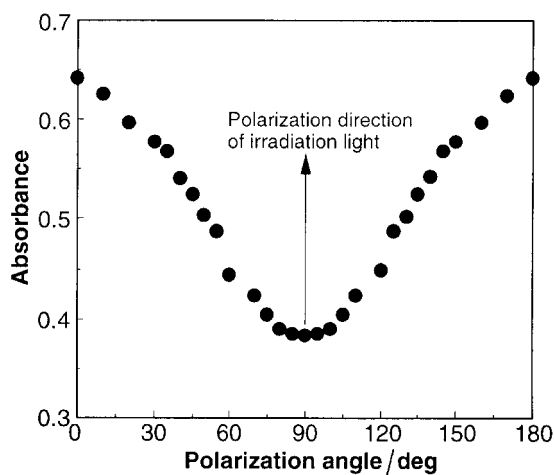


Figure 3. Change in absorbance of the azobenzene moieties at 520.5 nm as a function of polarization angle of the measurement beam. The arrow indicates the polarization direction of the irradiation light.

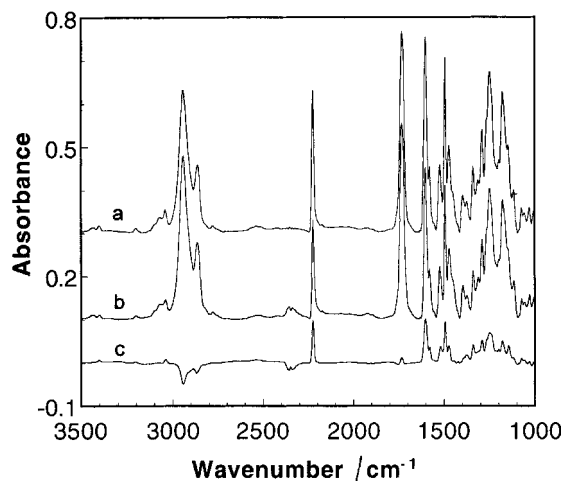


Figure 4. Polarized IR spectra and a difference spectrum (curve c) of the polymer film after irradiation. The spectra were recorded with the polarization direction of the IR beam perpendicular (curve a) and parallel (curve b) to that of the irradiation light.

3.2. Reversibility

It is well-known that photoinduced alignment change in azo polymers is reversible. The induced anisotropy can be erased thermally or photochemically. In the present study, the induced alignment described above (on irradiation with the He-Ne laser beam for 1 h) could be erased by heating the polymer film above the clearing temperature. To our surprise, it was found that the alignment achieved by prolonged irradiation, such as 3 h, could not be erased thermally. To investigate the irreversibility more fully, linearly polarized light at 577 nm selected from a Hg lamp was used to generate the alignment change. Table 2 shows the photoinduced alignment on irradiation with the 577 nm polarized light at 95°C for different irradiation times, and the thermal erasure of the induced alignment. The larger order parameter of the azobenzene moieties was attributed to their higher absorption at 577 nm and probably to a deep photobleaching effect. The alignment achieved on irradiation with the polarized light within 2 h could be erased thermally; however, the alignment induced on irradiation for 3 h could not be erased totally. After the anisotropic film was kept at 140°C (higher than T_{NI}) for 1.5 h, and then cooled to the liquid crystalline phase, there still existed a certain anisotropy in the resultant film. After exposure to polarized light at 577 nm at 95°C for 5 h, the polymer film was treated with THF solvent for 1 min. It was observed that the irradiated area was insoluble. Crosslinking had taken place during photoirradiation! After removal of the solvent and a thermal treatment of the liquid crystalline phase for 1 min, anisotropy was kept in the remaining film as confirmed by polarizing optical microscopy. This result gave a satisfactory explanation for the irreversibility of the alignment change achieved under prolonged irradiation. The photoinduced alignment change was accompanied by crosslinking photoinduced locally. The occurrence of crosslinking dramatically improved the thermal stability of the induced anisotropy.

Table 2. Photoinduced and thermal erasure of the alignment in the PLC.

Irradiation time/h	Order parameter	Erasure
1	0.20	yes
2	0.25	yes
3	0.41	0.25 ^a , 0.34 ^b , 0.09 ^c

^a After treatment at 140°C for 3 min, the polymer film was quickly quenched to a low temperature.

^b The thermally treated film a was heated at 140°C for 30 min and cooled to 90°C at a rate of 10°C min⁻¹.

^c The thermally treated film b was heated at 140°C for another 60 min and then cooled to 90°C at a rate of 10°C min⁻¹.

Changes in the UV spectra were observed after irradiation. As shown in figure 2, the absorption maximum decreased and shifted towards the blue region, and the absorption at around 420 nm increased. Similar changes in absorption spectra have been reported for the similar azobenzene moieties [7, 21]. The change in absorption spectra was attributed to photoinduced decomposition of the azobenzene moieties. No appreciable difference was observed between the IR spectra measured before and after irradiation. This might be ascribed to the low contents of azobenzene units. During the photoinduced alignment process, azobenzene moieties were in some way photodecomposed, resulting in some crosslinking which fixed the alignment change. The occurrence of crosslinking might be due to intermolecular coupling of the decomposed chemical species. The detailed mechanism is unclear at present.

4. Conclusion

In summary, a PLC with a new type of azobenzene has been designed and synthesized. The maximum absorption of the azobenzene moieties was shifted towards the red region by bringing in the second acceptor group, which allows the use of a He-Ne laser as the actinic light source. An alignment change was generated on irradiation with the He-Ne laser at moderate intensity. The azobenzene moieties as well as the inert cyanobiphenyl mesogenic groups were aligned with their molecular long axes perpendicular to the polarization direction of the polarized laser beam. It was found that the azobenzene moieties were decomposed on prolonged irradiation by the laser beam at high temperatures. The alignment induced on short irradiation was reversible, while that induced on prolonged irradiation was irreversible, seemingly due to the occurrence of crosslinking that might be caused by photoinduced decomposition of the azobenzene moieties.

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