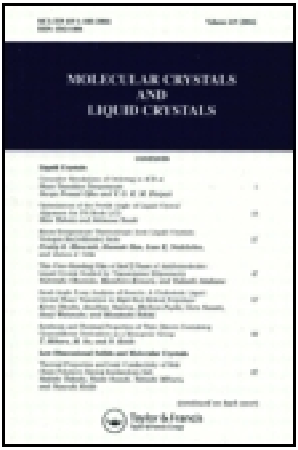

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Photoinduced Orientation and Holographic Recording in Polyester Films Comprising Azobenzene Side-Groups Using 633 nm Red Light

Naoya Otsuki [a] , Noriyuki Fujioka [a] , Nobuhiro Kawatsuki [a] & Hiroshi Ono [b]

[a] Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, Shosha Himeji, Japan

[b] Department of Electrical Engineering, Nagaoka University of Technology, Kamitomioka Nagaoka, Japan

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Naoya Otsuki
Noriyuki Fujioka
Nobuhiro Kawatsuki
Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, Shosha Himeji, Japan

Hiroshi Ono
Department of Electrical Engineering, Nagaoka University of Technology, Kamitomioka Nagaoka, Japan

New liquid crystalline polyesters comprising azobenzene side groups are synthesized to compare liquid crystalline nature of the materials and to investigate the photoinduced orientation behavior using linearly polarized (LP) 633 nm red light. Because of the axis-selective Z-to-E photoisomerization of the azobenzene moieties, the irradiating with a LP 633 nm light to a Z-isomer film induces a molecular reorientation parallel to the polarization of the light, which generates a positive optical anisotropy of the film. A polarization holography of a Z-isomer film using orthogonally polarized 633 nm light is presented.

Keywords: azobenzene; photoorientation; polarization holography; polymer liquid crystal

INTRODUCTION

Photoinduced orientation in azobenzene-containing polymeric films has been received much attention because of its application to various kinds of optical devices such as optical memory, holography and birefringent devices [1,2]. Most of these studies are based on an axis-selective *E*-to-*Z* photoisomerization of the azobenzene moieties

Address correspondence to Nobuhiro Kawatsuki, Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, 2167 Shosha Himeji, 671-2201 Japan. E-mail: kawatuki@eng.u-hyogo.ac.jp

using a linearly polarized (LP) light. Alternatively, a new photoinduced reorientation of azobenzene groups using a red-light based on an axis-selective *Z*-to-*E* photoisomerization reaction has been recently reported [3,4]. This technique leads a high order in-plane orientation of the azobenzene groups parallel to the polarization of LP light although it requires thermal treatment after the exposure [4].

Since polyesters are usually synthesized by a polycondensation method from equivalent amount of diols and diesters, polyesters in which the alternate azobenzene side groups are introduced are easily prepared when the diol and the diester monomers possess different kind of azobenzene side groups. In this paper, we synthesized new polyesters comprising 4-methoxy- and 4-cyano-azobenzene side groups and compared their spectroscopic and liquid crystalline properties to examine the interaction among the different kind of azobenzene moieties. Photoinduced reorientation of the *Z*-isomer films and a reversible polarization holography based on an axis-selective photoinduced reorientation are investigated using a LP 633 nm He-Ne laser.

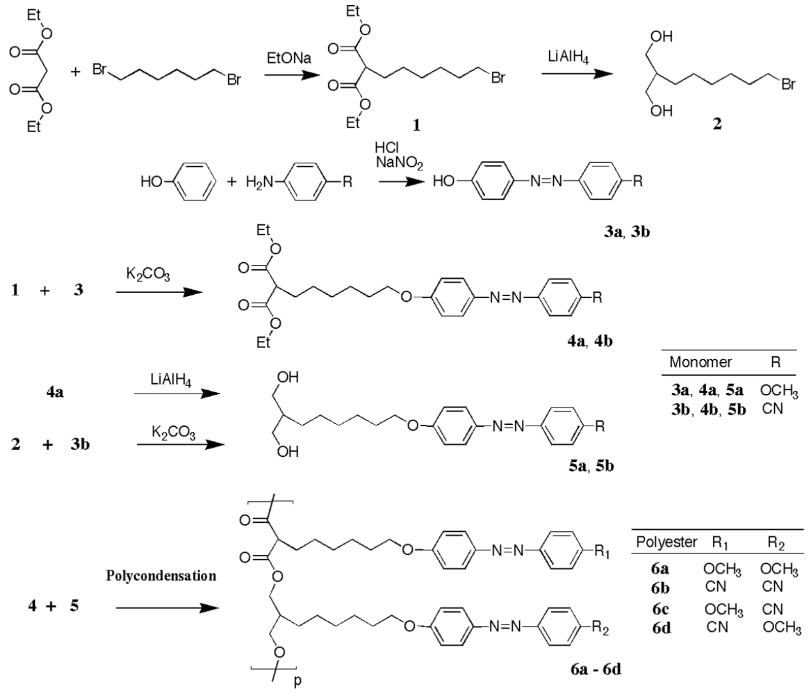
EXPERIMENTAL SECTION

Materials and Polymer Synthesis

All starting materials from Tokyo Kasei Chemicals were used without further purification. Synthetic procedure of diols, diesters and polyesters are outlined in the Scheme. All synthesized monomers were confirmed by ^{1}H-NMR and FT-IR spectroscopy. Polyesters were synthesized by the melt-polycondensation of corresponding equimolar diols and desters using $Zn(OAc)_2$ as a catalyst. Synthesized polyesters were purified by reprecipitation method from chloroform solution to methanol. Table 1 summarizes molecular weight and thermal properties of synthesized polyesters.

Photoreaction and Characterization

Thin film (200 nm thick) on a quartz substrate was prepared from a polymer in methylene chloride solution by a spin-coating technique. Photoirradiation was carried out using a high-pressure Hg lamp with an interference filter at 365 nm to generate *E*-to-*Z* photoreaction of a film, and a LP 633 nm He-Ne laser for the *Z*-to-*E* photoisomerization. Photoorientation behavior was evaluated by a polarized UV-vis spectroscopy.



SCHEME 1

TABLE 1 Molecular Weight and Thermal and Spectroscopic Properties of Synthesized Polyesters

Polymer	R_1	R_1	Molecular weight[a] $M_n \times 10^{-3}$	M_w/M_n	Thermal property, °C[b] (ΔH mJmg^{-1})	λ_{max} (nm) ($\varepsilon \times 10^{-4}$) Film[c]	Solution[d]
6a	OCH_3	OCH_3	5.6	1.3	G43 S_x88(5.5) N135(3.5)I	344	358 (2.7)
6b	CN	CN	4.0	2.6	G39 N161(3.1) I	344	363 (2.5)
6c	OCH_3	CN	3.6	2.7	G42 S_mA158(8.2) I	337	360 (2.8)
6d	CN	OCH_3	4.2	2.1	G45 S_mA176(5.7) I	337	360 (2.6)

[a] Determined by GPC. Polystrylene standards with THF as eluant.
[b] Determined by DSC. 2nd heating.
[c] In methylene chloride.
[d] On quartz substrate.

RESULTS AND DISCUSSION

Synthesis, and Spectroscopic and Thermal Properties of Polymers

All polymers **6a–6d** were synthesized by polycondensation from diesters and diols containing azobenzene side groups. When using a diester and a diol with different kind of azobenzene groups, polyesters with alternatively different kind of azo-side groups are synthesized (**6c** and **6d**). Number average of molecular weight of the polymers is in the range of 3,600–5,600, indicating approximately 10–18 units are polycondensed. All polymers are soluble in common organic solvents such as chloroform and an optically transparent thin film is prepared by a spin-coating technique.

Absorption maxima ($\lambda_{\max}$) in methylene chloride solution exhibits between 358–363 nm, while a blue shift of $\lambda_{\max}$ is appeared for all films. The blue shift is due to the H-aggregates of the azobenzene groups. The absorption spectrum of **6a** exhibits $\lambda_{\max}$ around 344 nm and an absorption tailing around 360 nm, which correspond to the H- and J-aggregates, respectively. This spectrum is similar to a polymethacrylate film containing 4-methoxyazobenzene side groups [4]. For other polymer films, J-aggregates at longer wavelength are not observed. Interestingly, the blue shift of **6c** and **6d** films is greater than other films. Strong H-aggregation of these polymer films occurs since the interaction between 4-methoxyazobenzene and 4-cyanoazobenzene side groups is large due to donor-acceptor effect.

All polymers exhibited liquid crystalline nature as summarized in Table 1. Both smectic and nematic phase are observed for **6a**, which is similar to the polymethacrylate with 4-methoxyazobenzene side groups [4]. The **6b** shows nematic LC phase and **6c** and **6d** exhibit smectic A phase, which is confirmed by fan-shaped texture. Kosaka *et al.* reported the induced smectic A phase was appeared for a copolymer with electron donating and accepting mesogenic side groups [5]. The interaction between 4-methoxyazobenzene and 4-cyanoazobenzene side groups induces a smectic A phase. Additionally, an equimolar mixture of **6a** and **6b** exhibits an induced smectic A phase between 41°C and 162°C. A study on the polymer blend will be reported in detail elsewhere.

E-to-Z Photoisomerization Reaction Using 365 nm Light

It is well known that irradiating with 365 nm light generates E-to-Z photoisomerization reaction of the azobenzene groups. Figure 1 plots the E-isomer fraction as a function of the exposure energy of 365 nm

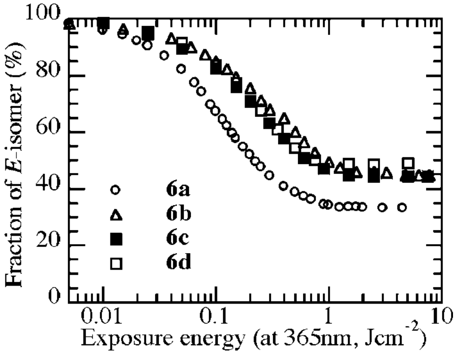


FIGURE 1 Fraction of E-isomer content when a spin-coated film is exposed to 365 nm light.

light. For all polymer films, the Z-isomer formation is saturated when the exposure energy is 1 Jcm^{-2} and more. The amount of Z-isomer formation is saturated at approximately 55–67%. It takes more than one day to recover the initial absorbance. Since the molecular motion during the E-to-Z photoisomerization is restricted in a solid film, the formation of Z-isomers is less than 67%. The higher content of Z-isomer formation was observed when the concentration of the azo-monomer unit was lowered [6]. All the Z-isomer films completely return to E-isomer films after storing for two days at room temperature. The first-order rate constants for both isomerization reactions are determined by fitting the experimental data to Eq. (1),

$$\ln(A_\infty - A_t)/(A_\infty - A_0) = -kt \qquad (1),$$

where A_t, A_0, and A_∞ are the absorbance at λ_{max} at time t, time zero, and infinite time, respectively. Table 2 summarizes the rate constants and change in λ_{max} of the polymer films and in solution. Despite the electron donor-acceptor type of 4-cyanoazobenzene groups, the thermal Z-to-E isomerization rate constant of **6b** film is almost similar to **6a**, **6c**, and **6d**. The thermal Z-to-E rate of **6b** in solution exhibits larger values than other polymers because the molecular mobility is not restricted. Additionally, λ_{max} of **6a–6d** films after the thermal Z-to-E isomerization slightly shifted to longer wavelength, suggesting a partial decomposition of the aggregation. However, the amount of the shift is much smaller than the polymethacrylate film with same azobenzene side groups [4]. Since Tg of **6a–6d** is around 40°C, molecular motion during the thermal Z-to-E isomerization will generate the re-aggregation of the azobenzene groups.

TABLE 2 First Order Rate Constants *Z*-to-*E* Thermal Relaxation at Room Temperature and $\lambda_{\max}$ of Polyesters

	Film			Solution[c]		
	$\lambda_{\max}$, nm			$\lambda_{\max}$, nm		
Polymer	Initial	Stored[b]	$k_{Z/E}$ (stored)[a] $10^5(\mathrm{s}^{-1})$	Initial	Stored	$k_{Z/E}$ (stored)[a] $10^5(\mathrm{s}^{-1})$
6a	344	344	4.0	358	357	2.1
6b	344	350	5.2	363	364	4.4
6c	337	339	5.1	360	358	2.7
6d	337	342	5.9	360	359	3.1

[a] Stored at room temperature.
[b] Stored for 2 days.
[c] In methylene chloride.

Photoreaction and Photoinduced Optical Anisotropy of *Z*-Isomer Films with LP 633 nm Light

It is known that *Z*-to-*E* photoisomerization using 633 nm light for polymethacrylate films with 4-methoxyazobenze or 4-cyanoazobenzene side groups is feasible although the absorption coefficients of *Z*-isomer of them at 633 nm are negligibly small [3,4]. Figure 2 plots the fraction of *E*-isomer when the *Z*-isomer films are exposed to 633 nm light as a function of exposure energy. For all polyester films, an irradiating of 200 J/cm^2 doses recovers the *E*-isomer films. In this case, the rate of *Z*-to-*E* photoisomerization for **6b** film is faster than other films as

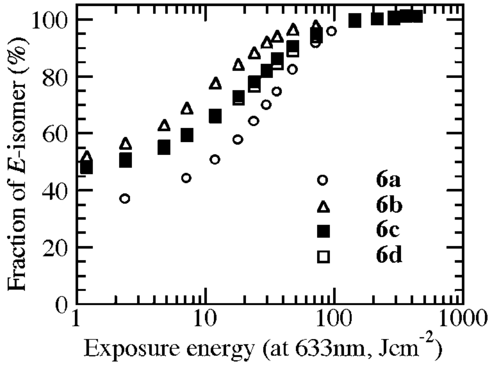


FIGURE 2 Fraction of *E*-isomer content when a *Z*-isomer film is exposed to 633 nm light.

TABLE 3 First Order Rate Constants *Z*-to-*E* Photoisomerization Using 633 nm Light and λ_{max} of Polyesters

Polymer	$k_{E/Z}$ (633)[a] $10^3(s^{-1})$	λ_{max}, nm Exposed
6a	1.1	345
6b	2.2	352
6c	1.3	339
6d	1.2	340

[a] Irradiated with 633 nm light.

summarized in Table 3. Additionally, λ_{max} of the recovered *E*-isomer films are almost the same as those stored at room temperature, indicating the re-aggregation. Stumpe *et al.* reported that a prolonged irradiation with 633 nm light to a *Z*-isomer polymethacrylate film comprising 4-cyanoazobenzene side group induced a *E*-to-*Z* photoreaction due to a small absorption of *E*-isomers [3]. However, photoreaction of *E*-isomers of **6a–6d** films does not occur under 633 nm light irradiation. Since re-aggregation of the azo-groups occurs after the *Z*-to-*E* isomerization, the photoreaction at 633 nm will be inactive due to the blue shift of λ_{max}.

For the photoreaction of *Z*-isomer films with LP 633 nm light, positive photoinduced optical anisotropy, ΔA ($= A_{\parallel} - A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ mean absorption parallel and perpendicular to the polarization, **E**, of LPUV light, respectively), is generated due to the axis-selective *Z*-to-*E* photoisomerization. Figure 3 shows the absorption spectra of

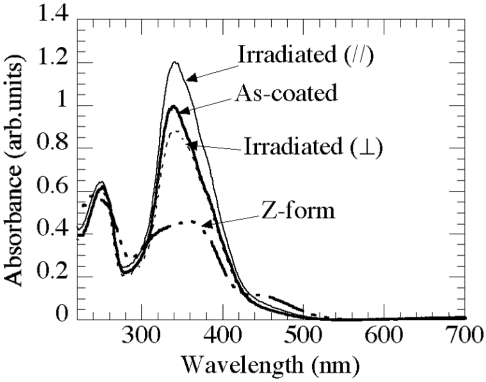


FIGURE 3 Absorption spectra of **6c** film before exposure, after exposure to NP 365 nm light for 1.5 Jcm^{-2} and subsequent irradiating with LP 633 nm light for 120 Jcm^{-2}.

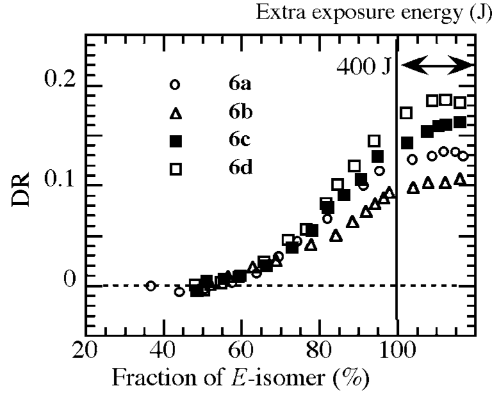


FIGURE 4 Photoinduced dichroism (DR) as a function of exposure energy of LP 633 nm light.

6c film before exposure, after exposure to a non-polarized (NP) 365 nm light (*Z*-form) and subsequent irradiating with LP 633 nm light. After exposure to LP 633 nm light, positive ΔA is generated, and $A_{\parallel}$ after irradiation becomes larger than the initial film. This means that the reorientation parallel to the polarization of LP light occurs upon the axis-selective *Z*-to-*E* photoisomerization. Figure 4 plots the photoinduced dichroism, $DR = \Delta A/(A_{\parallel} - A_{\perp})$, for **6a–6d** films as a function of the *E*-isomers fraction when the *Z*-isomer films are exposed to LP 633 nm light. For all cases, positive DR is generated. When the *E*-isomers fraction is less than 60%, generated DR values are very small ($DR < 0.02$). These values are similar to the case of *Z*-to-*E* photoisomerization of polymethacrylate with 4-methoxyazobenzene side groups [4]. In contrast, for **6a–6d** films, the generated DR values show a great increase when the *E*-isomer fraction becomes 60% and more ($DR > 0.1$). When the *E*-isomer fraction increases, LC character of the film will be recovered. Since the Tg of the polymer film is close to the room temperature, small photoinduced positive DR is amplified due to the LC nature. Additionally, DR values still increases when the all the azo-groups return to *E*-isomers, as plotted in Figure 4, suggesting that the self-organization proceeds.

Polarization Holography

Polarization holography was carried out using a *Z*-isomer film of **6d**. The film is irradiated with orthogonally polarized LP 633 nm light. Figure 5a illustrates the experimental setup. In this condition, grating

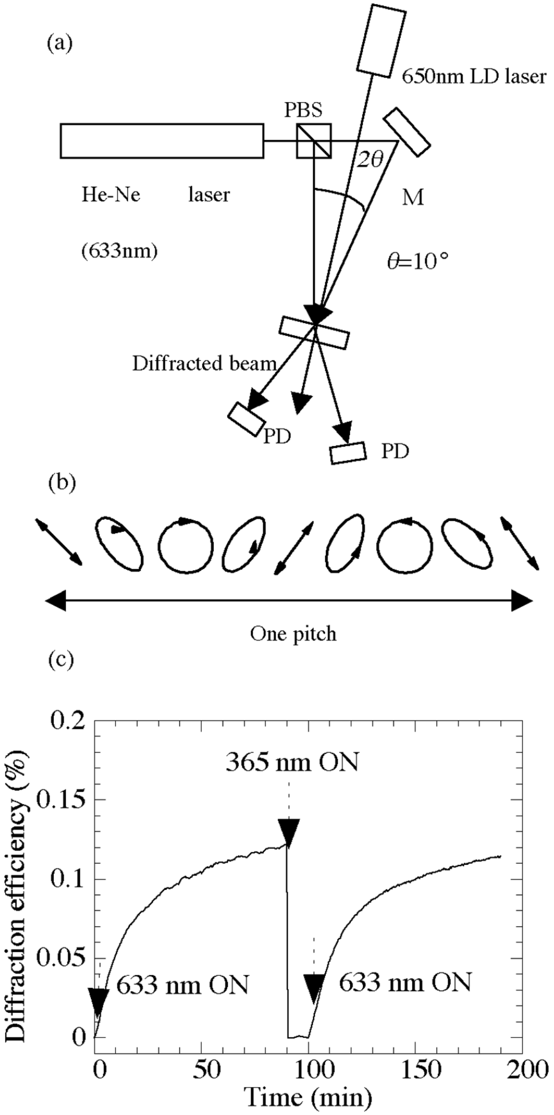


FIGURE 5 (a) Experimental setup for the polarization holography. (b) Schematic illustration of the polarization modulation of the interference light. (c) Diffraction efficiency upon a formation of the grating using LP 633 nm and erasing using NP 365 nm light.

periodicity is 1.8 μm and the polarization of the interference light beam is modulated as shown in Figure 5b. The intensity of 1st order diffraction beam was monitored using a 650 nm laser, at which the **6d** film does not photoreact. Figure 5c plots the intensity of the diffraction beam upon the hologram formation, irradiating with NP 365 nm light, and re-exposure with 633 nm interference light beams. It shows that the diffraction efficiency increases as the exposure dose of 633 nm light increases, and can be erased by irradiating with 365 nm light and again inscribed. Additionally, the formed polarization grating is stable at room temperature and the polarization of the 1st order diffraction beam is converted by 90°, showing a formation of a pure polarization grating [7].

CONCLUSION

Spectroscopic and thermal characteristics of new liquid crystalline polyesters comprising 4-methoxyazobenzene and 4-cyanoazobenzene side groups were investigated. Because of the donor-acceptor effect, polyester films with alternate azobenzene side groups revealed strong blue shift in the absorption spectra, and they exhibited smectic A LC nature. Irradiating with 365 nm light generated the *E*-to-*Z* photoisomerization, and a subsequent exposure to LP 633 nm light induced a positive anisotropy caused by the axis-selective *Z*-to-*E* photoisomerization for all polyester films. Polarization holography using orthogonally polarized LP 633 nm light to a *Z*-isomer film was carried out to make a pure polarization grating. The formed grating is erased by exposed to NP 365 nm light, and again inscribed by a re-exposing to the 633 nm interference light.

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