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Photoinduced optical anisotropy and reorientation in copolymers containing 4-methoxyazobenzene side groups and methyl methacrylate units using linearly polarized 633 nm light

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Abstract

Liquid crystalline (LC) and non-LC copolymers that contain 4-methoxyazobenzene side groups and methyl methacrylate units were synthesized to compare the photoinduced reorientation behavior using the polarization absorption spectra of thin films. Irradiating with non-polarized 365 nm light saturated the *Z*-isomer in the copolymer films and subsequent exposure to a linearly polarized (LP) 633 nm light generated a photoinduced optical anisotropy (ΔA) for all *Z*-isomer films based on an axis-selective *Z*-to-*E* photoisomerization. When a copolymer did not exhibit a LC nature, ΔA gradually increased until 60–80 mol% of the *Z*-isomers isomerized to the *E*-isomers, but decreased upon further photoisomerization reaction. On the other hand, the magnitude of the photoinduced ΔA of a film continuously increased for LC copolymers until *E*-isomer formation was saturated. Thermal amplification of the photoinduced ΔA was observed for LC copolymers, but the thermal treatment resulted in the disappearance of the photoinduced ΔA for the non-LC copolymers. The axis-selective *Z*-to-*E* photoisomerization that preserves the direction of the transition moment of both isomers caused the photoinduced ΔA and increased the liquid crystalline nature of the film during the *Z*-to-*E* photoisomerization to induce the self-organization of the mesogenic groups.

Keywords: Azobenzene; Polymer liquid crystals; Photoinduced orientation

1. Introduction

Manipulating the molecular orientation in azobenzene-containing polymeric films is of great interest for reversible optical data storage, polarization holograms, and optical devices such as optical switches and birefringent films [1–8]. For these purposes, various types of azobenzene-containing materials have been synthesized to create molecular oriented structures using linearly polarized (LP) light exposure [9–17]. A conventional technique to control the molecular orientation of the azobenzene moiety is based on an axis-selective *E*-to-*Z* photoisomerization using LP light [1]. Due to the different thermodynamic stabilities of the *E* and *Z* isomers, the axis-selective *E*-to-*Z* photoisomerization using LP light and the simultaneous *Z*-to-*E* back-reaction of azobenzene groups cause reorientation perpendicular to the polarization (**E**) of the LP light. Thermal amplification of the photoinduced optical anisotropy was reported for azobenzene-containing polymers where the *Z*-isomers are relatively stable [18–23]. Additionally, out-of-plane reorientation of the film is also generated when the film is exposed to an excessive dose of light since the photoreactive groups parallel to the light propagation are not very reactive [23–26]. That is, the in-plane reorientation may be accompanied by a biaxial molecular reorientation along the plane perpendicular to **E**. Therefore, it is difficult to generate an in-plane reorientation of the azobenzene groups parallel to **E** based on the axis-selective *E*-to-*Z* photoisomerization.

Recently, new techniques based on the polarization-axis-selective *Z*-to-*E* photoisomerization have been reported for the photoinduced reorientation of azobenzene groups when a non-polarized ultraviolet (NPUV) light is exposed to an *E*-isomer film to form excessive *Z*-isomers prior to irradiating with LP light for the *Z*-to-*E* photoisomerization [20,27–32]. The *Z*-isomer of the azobenzene groups also exhibits the axis-selective photoabsorption of light. Since, the formation of the *Z*-isomer of the azobenzene groups changes the absorption properties to the longer wavelength region, the *Z*-isomer of the azobenzene moiety exclusively possesses photoreactivity and not the *E*-isomer if the irradiating wavelength is appropriately

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selected [20]. One feature of this technique is that the reorientation direction of the azobenzene groups is parallel to **E**. Hence the creation of a slantwise uniaxial molecular oriented structure is feasible.

Kempe et al. reported that a competition both axis-selective *E*-to-*Z* and *Z*-to-*E* photoisomerization reactions of liquid crystalline copolymers with 4-cyanoazobenzene side groups occurred with exposure to LP green or red lights [28]. They found that the azobenzene groups reoriented parallel to **E** when the *Z*-isomer film was irradiated with LP 633 nm light, although the prolonged exposure resulted in a reorientation perpendicular to **E** since the *E*-isomer of 4-cyanoazobenzene group formed slightly absorbs 633 nm light [28]. Alternatively, we studied the thermally enhanced reorientation of liquid crystalline polymethacrylate films with 4-methoxyazobenzene (4MAz) side groups using LP 633 nm light [20,32,33]. Since the *trans*−4MAz group does not absorb at 633 nm, the photoreaction of the *E*-isomer film at 633 nm is eliminated. The influence of the alkylene spacer length between 4MAz and the methacrylate backbone on the reorientation behavior was also investigated [20]. A small degree of photoinduced optical anisotropy parallel to **E** was thermally amplified when the film was annealed at elevated temperatures. These new reorientation techniques are based on the polarization-selective photoreaction of the *Z*-isomers, which are prepared by exposing to NPUV light in advance. However, the detailed photoisomerization reaction of the *Z*-isomer film, the influence of the liquid crystalline nature of the material, and the origin of the axis-selectivity of the *Z*-to-*E* photoisomerization that creates an optical anisotropy of the *E*-isomer film parallel to **E** were not thoroughly investigated.

In this paper, influence of the composition of the azobenzene groups on the photoinduced reorientation behavior of *Z*-isomer films of methacrylate copolymers that contained 4MAz groups was investigated using LP 633 nm light. The LC and non-LC methacrylate copolymers that contained 4MAz side groups and methyl methacrylate (MMA) units were synthesized. The photoinduced optical anisotropy of the copolymer films was measured by polarization UV–vis spectroscopy and the mechanism of the axis-selective *Z*-to-*E* photoisomerization reaction was clarified. The photoinduced optical anisotropy was amplified for the LC copolymers when the exposed film was annealed in the liquid crystalline temperature range of the copolymer, but the optical anisotropy for the non-LC copolymer films was disappeared after annealing at the elevated temperatures. The liquid crystallinity of the copolymer film played an important role in the photoinduced reorientation behavior of the 4MAz groups and the thermal amplification of the optical anisotropy.

2. Experimental

2.1. Materials and polymer synthesis

All starting materials were from Tokyo Kasei Chemicals and were used without further purification. Methacrylate monomers with 4MAz side groups were obtained according to the literature [20]. To remove the inhibitor, MMA (Tokyo Kasei) was distilled prior to the copolymerization. Random copolymerization was performed utilizing a free radical solution polymerization in tetrahydrofuran (THF) with 2,2′-azobis(isobutyronitrile) (AIBN) (Fig. 1). The composition of the copolymer was controlled using different feed ratios of the azobenzene monomer and MMA. ^{1}H–NMR spectra (Bruckor DX-500 FT-NMR) and FT-IR (JASCO FTIR-410) confirmed all monomer and copolymer syntheses. Table 1 summarizes the composition, molecular weight, and thermal properties of synthesized copolymers.

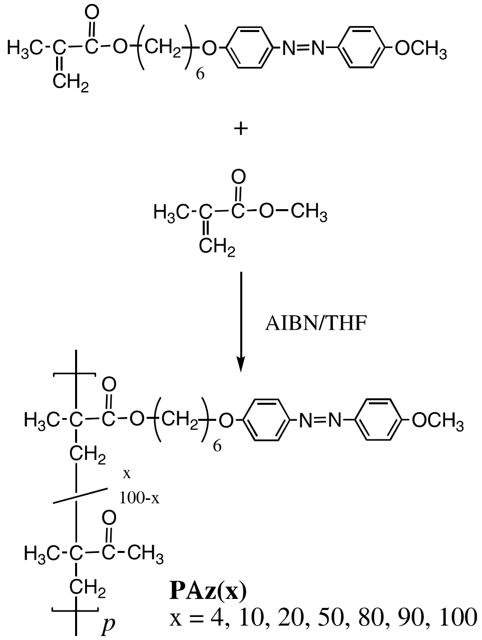

Fig. 1. Chemical structure of copolymers used in this study.

2.2. Photoreaction

Thin films of the synthesized copolymers were prepared by a spin-coating method from a methylene chloride solution onto quartz substrates. The stylus contact method using a Taly-Step (Rank Taylar Hobson) determined that the films were 0.2 μm

Table 1
Composition, molecular weight, and thermal property of copolymers

	x	Molecular weight [a]		Thermal properties [b] (°C)
		M_n (10^{-4} g/l)	M_w/M_n	
PAz(4)	4	1.5	2.0	G 111 I
PAz(10)	10	2.7	1.9	G 81 I
PAz(20)	20	2.9	1.7	G 59 I
PAz(50)	50	3.6	2.0	G 59 I
PAz(80)	80	2.1	1.9	G 57 N 117 I
PAz(90)	90	3.2	2.0	G 60 N 126 I
PAz(100)	100	2.3	1.7	G 74 Sx 94 N 134 I

[a] Determined by GPC with polystyrene standards.

[b] Determined by DSC. G, amorphous glass; N, nematic; Sx, unspecified smectic; I, isotropic.

thick. Photoreactions were conducted by irradiating with a 250 W high-pressure mercury lamp attached with interference filters at 365 nm (FWHM = 10 nm, 30 mW cm^{-2}) and a 13 mW LP 633 nm He–Ne laser (Melles Griot) expanded to a 4 mm diameter (average intensity of 103 mW cm^{-2}). To irradiate with LPUV light, Glan-Taylor polarizing prisms were used. The optical anisotropy of the film was measured by a polarization optical microscope (POM) and polarization UV–vis spectra. To determine an accurate degree of the photoreaction, the absorption coefficiencies of *E*- and *Z*-isomers should be clarified. At present, we use Eq. (1) to estimate the *E*-to-*Z* photoisomerization reaction of the azobenzene groups [23b]:

$$Z-\text{isomer} = \left(\frac{A_0-A_r}{A_0}\right)\times 100(\%) \tag{1}$$

where A_0 and A_r are the absorbances at 360 nm before and after exposure for **PAz(4)**, **PAz(10)**, **PAz(20)** and **PAz(50)**, and at 345 nm for **PAz(80)**, **PAz(90)** and **PAz(100)**.

2.3. Characterization

Polarization UV–vis spectra were measured using a Hitachi U-3310 spectrometer equipped with Glan-Taylor polarizing prisms. A POM (Olympus BX-51) equipped with a Linkam TH600PM heating and cooling stage was used to observe the optical anisotropy and thermal properties. The photoinduced optical anisotropy (ΔA) and dichroism (DR) of the film are expressed in Eqs. (2) and (3):

$$\Delta A = A_{\parallel} - A_{\perp} \tag{2}$$

$$\text{DR} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \tag{3}$$

where $A_{\perp}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively. The DR value was calculated by polarized UV–vis spectroscopy at $\lambda_{\max}$ of the film.

3. Results and discussion

3.1. Thermal and spectroscopic properties of copolymers

The synthesized copolymers show one glass transition when the 4MAz composition is less than 50 mol%, but copolymers with a 4MAz composition of 80 mol% or more exhibit a liquid crystalline nature, as summarized in Table 1. The copolymerization of the MMA unit diminishes the smectic liquid crystalline character that is observed for homopolymer **PAz(100)** and clearing temperature (T_{ni}) decreases as the MMA composition increases. T_{ni} of the copolymer with a mesogenic monomer and a non-mesogenic monomer decreases as the non-mesogenic monomer composition increases for other type of LC copolymers [34]. All synthesized copolymers are dissolved in common organic solvents such as toluene, chloroform and THF, and thin films of the copolymers are easily prepared by a spin-coating technique. The resultant films are transparent and isotropic in nature.

Absorption spectra of the copolymers in a methylene chloride solution reveal the absorption maxima at 360 nm for all the copolymers and the absorption coefficiency is proportional to the 4MAz composition as plotted in Fig. 2(a). This means that the azobenzene groups in solution are without a mutual interaction. For the copolymer films, the absorption spectra of **PAz(4)**, **PAz(10)** and **PAz(20)** are similar to the solution. However, the absorption spectrum with a higher content of the 4MAz groups is different from the solution and $\lambda_{\max}$ depends on the 4MAz composition as shown in Fig. 2(b)

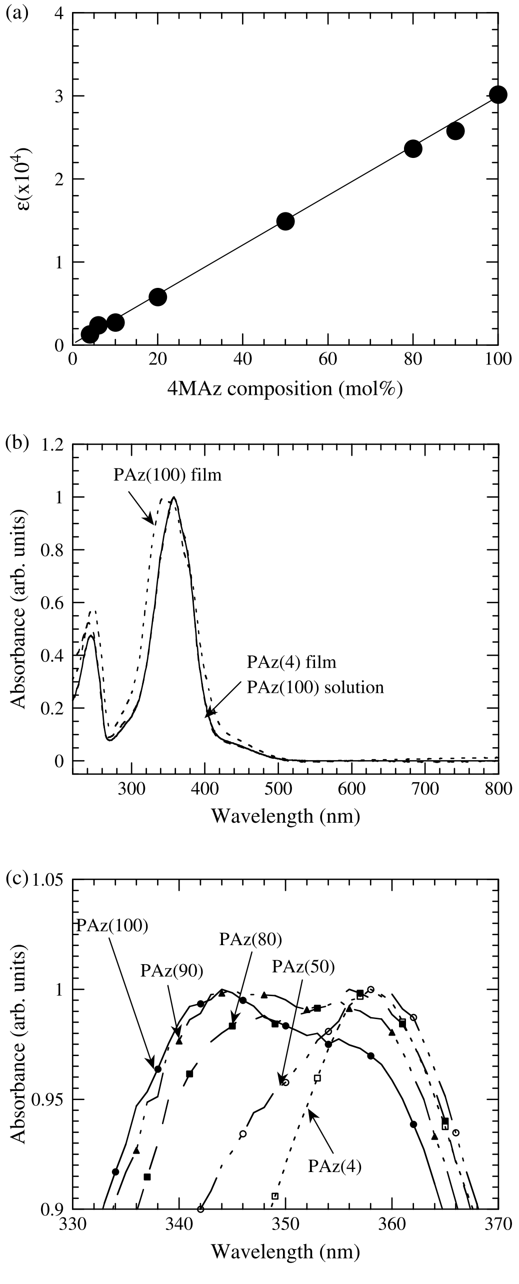

Fig. 2. (a) Absorption coefficiency of copolymer solution in methylene chloride as a function of the 4MAz group content. (b) Absorption spectra of **PAz(4)** and **PAz(100)** films, and **PAz(100)** in methylene chloride solution. (c) Close-up of absorption spectra of **PAz(4)**, **PAz(50)**, **PAz(80)**, **PAz(90)** and **PAz(100)** films.

and (c). A systematic shift in the absorption bands to a shorter wavelength and a slight broadening in the spectra are observed as the 4MAz composition increases for **PAz(50)–PAz(100)**. Two absorption maxima are detected at 360 and 345 nm, and the absorbance at 345 nm increases as the 4MAz composition increases. Brown et al. reported a detailed spectroscopic study of polymethacrylate copolymer films comprising disperse red 1 (DR1) and MMA [34]. They observed a blue shift in the absorption spectra as the azobenzene groups increased and concluded that the blue shift was due to the antiparallel association of the neighboring azobenzene groups. Date and coworkers also observed a blue shift in the absorption in thin films of poly(olefin sulfone)s comprising the mesogenic 4-cyanobiphenyl side groups and long alkyl side chains, when the concentration of the mesogenic groups increased [36]. Tong et al. reported the ratios of H- and J-aggregates in the diblock copolymer liquid crystalline films that comprised of polystyrene units and 4MAz groups [37]. The blue shift due to the molecular aggregation in a thin film comprised of mesogenic side groups was detected in other types of liquid crystalline polymeric films [38–40]. In our case, the blue shift is independent on the liquid crystallinity of the material. Therefore, the formation of the molecular association is generated when the solvent evaporates to form a thin film, which results in a new absorption band at 345 nm, when the concentration of the mesogenic groups is higher. The increase in the MMA composition reduces the interaction of the 4MAz groups due to the dilution effect.

3.2. *E-to-Z Photoisomerization by irradiating with 365 nm light and thermal relaxation*

Irradiating a thin film containing 4MAz groups with 365 nm light causes it to undergo an *E*-to-*Z* photoisomerization reaction. The lifetime of the resulting *Z*-isomers are relatively long at room temperature [20,23]. Fig. 3(a) plots the change in the absorption spectrum of a **PAz(50)** film upon irradiating with non-polarized (NP) 365 nm light. It reveals that the absorption band around 360 nm of the *E*-isomer decreases and the absorption around 450 nm increases due to the formation of *Z*-isomers. Other copolymer films show similar spectral changes. Fig. 3(b) plots the amount of photoisomerized *Z*-isomers for the copolymer films as a function of exposure dose. For all copolymer films, the amount of the *Z*-isomers is saturated between 70–95 mol% when the exposure doses are approximately 1 J cm^{-2}. The rate of photoisomerization is faster and more of the *Z*-isomer is formed for copolymers with a higher composition of MMA than those with a lower MMA composition. These results suggest that photoisomerization likely occurs for copolymers with a lower 4MAz composition due to the lower density of the chromophore units. On the other hand, as the 4MAz composition increases, the interaction among the chromophores decreases the photoisomerization and reduces the saturation of the *Z*-isomers.

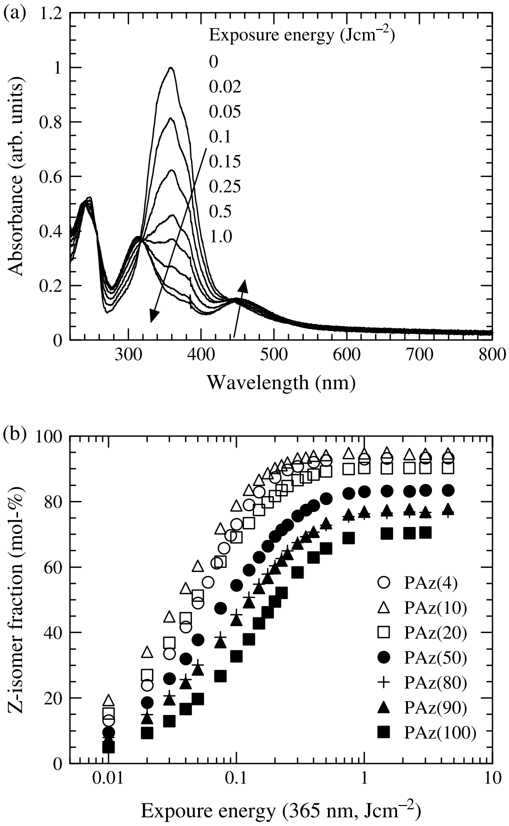

Fig. 3. (a) Changes in absorption spectrum of a **PAz(50)** film upon 365 nm light exposure. (b) Photoisomerized *Z*-isomer fraction as a function of 365 nm light exposure energy.

All the copolymer films thermally relax to the *E*-isomer when the *Z*-isomer film is stored at room temperature. Fig. 4(a) plots the decrease in the fraction of *Z*-isomers when the films are exposed to NP 365 nm light for 1.5 J cm^{-2} to saturate the *Z*-isomer formation and the resultant films are stored at room temperature. It takes more than one day to thermally return to the *E*-isomer film. Fig. 4(b) shows that the absorption band at 345 nm for a **PAz(50)** film decreases and the band at 360 nm increases after thermal relaxation to the *E*-isomer film. The **PAz(80)**, **PAz(90)** and **PAz(100)** films that initially possess an absorption band around 345 nm due to the molecular association described in Section 3.1 exhibit similar phenomena. This means that the *E*-to-*Z* photoisomerization reaction with 365 nm light accompanies the destruction of molecular association.

3.3. *Photoreaction of Z-isomers and photoinduced optical anisotropy using LP 633 nm light*

We previously reported that the *Z*-isomers of the 4MAz groups in a **PAz(100)** film can preferentially photoisomerize to the *E*-isomers by irradiating with 633 nm light, but a photoreaction does not occur for the *E*-isomers [20]. For all the copolymer films, the *Z*-to-*E* photoisomerization is generated with exposure to LP 633 nm light as plotted in Fig. 5. The decrease in the *Z*-isomers upon irradiating with LP 633 nm light occurs when the copolymer films are pre-exposed to NP 365 nm light for 1.5 J cm^{-2} prior to exposing to 633 nm light. In contrast to storing the *Z*-isomer films at room temperature (Fig. 4(a)), the *Z*-to-*E* photoisomerization using

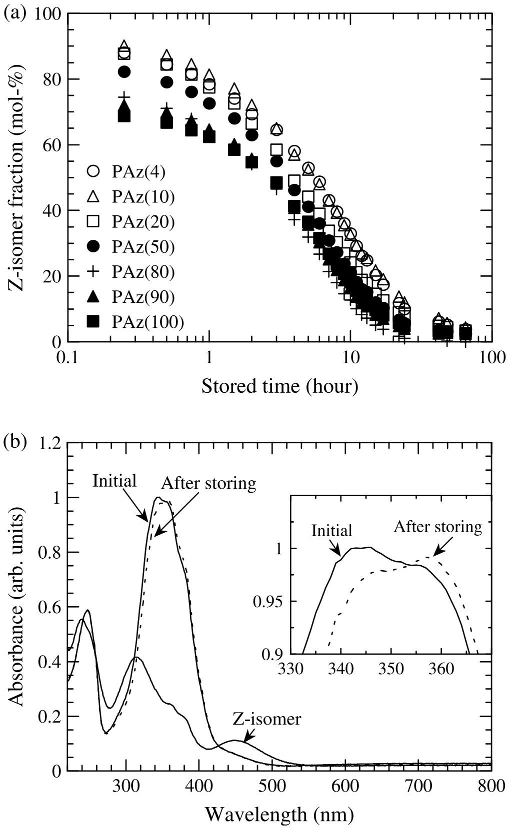

Fig. 4. (a) Thermally relaxed *Z*-isomer fraction when films, which were exposed to 1.5 J cm^{-2} of 365 nm light, were stored at 25 °C as a function of storing time. (b) Changes in absorption spectrum of a **PAz(50)** film before irradiating, after exposing to 1.5 J cm^{-2} of 365 nm light, and subsequently storing at 25 °C for two days. The inset shows a close-up spectrum.

633 nm light is completed within 1 h for all copolymers. Furthermore, similar to storing at room temperature, the amount of aggregation of 4MAz groups decreases for the *E*-isomer film.

It was reported that a positive optical anisotropy, $\Delta A > 0$, was generated for a **PAz(100)** film when LP 633 nm light was used to cause the *Z*-to-*E* photoisomerization [20]. For all the copolymer films in this study, irradiating with LP 633 nm light to *Z*-isomer films also induces a positive ΔA, which should be related to the polarization-axis-selective reaction of the *Z*-isomers isomerization to *E*-isomers. The *Z*-isomer axis-selectively absorbs LP light parallel to the N=N bond and the photoisomerization will undergo with preserving the direction of the N=N bond, while further theoretical analyses are required. Fig. 6(a) and (b) plot the photoinduced ΔA values at $\lambda_{\max}$ for non-LC copolymers of **PAz(4)**, **PAz(10)**, **PAz(20)** and **PAz(50)**, and LC ones of **PAz(80)**, **PAz(90)** and **PAz(100)** when exposing to LP 633 nm light as a function of the fraction of *E*-isomers, respectively. The ΔA values are normalized so that the absorbance at $\lambda_{\max}$ for the as-coated film is 1.0.

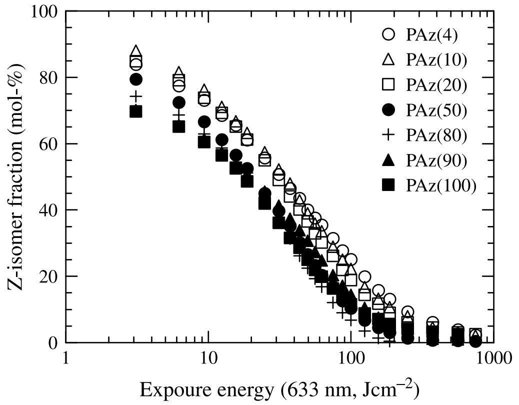

Fig. 5. Fraction of *Z*-isomer when films, which were pre-exposed to 1.5 J cm^{-2} of 365 nm light, were exposed to He–Ne 633 nm light as a function of irradiation energy.

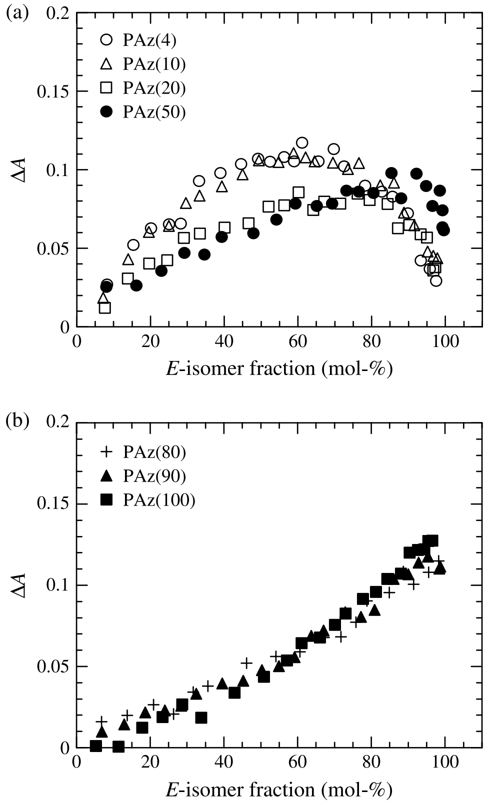

Fig. 6. Photoinduced optical anisotropy, ΔA, of *Z*-isomer of (a) non-LC copolymers, **PAz(4)**, **PAz(10)**, **PAz(20)**, and **PAz(50)** films, and (b) LC-copolymers, **PAz(80)**, **PAz(90)**, and **PAz(100)** films when exposing to LP 633 nm light as a function of the *E*-isomer fraction.

For the non-LC copolymer films, the generated ΔA values increases until the ratio of the *Z*-to-*E* photoisomerization reaches approximately 60–80 mol% and decreases upon further photoisomerization. The decrease in ΔA value is due to the photoisomerization of all the *Z*-isomers. The maximum ΔA values are 0.09–0.12 and are greater as the composition of MMA groups increases. When the composition of the 4MAz groups increases, the interaction among the adjacent 4MAz groups may disturb axis-selection, resulting in smaller ΔA values. In non-LC copolymer films comprised of DR1 and MMA, it was reported that the photoinduced birefringence deviated when the concentration of azobenzene groups was lowered and the molecular interaction reduced the mobility of the azo-side chain [35].

In contrast, for the LC copolymer films, the ΔA values increase as the degree of the *Z*-to-*E* photoisomerization proceeds. The maximum ΔA values are 0.11–0.13, which are obtained when all the 4MAz groups return to the *E*-isomers as plotted in Fig. 6(b). The photoisomerization to *E*-isomers recovers the LC nature of the film as the amount of *E*-isomers increases, while the *Z*-isomers do not exhibit LC nature. In this context, the amount of *E*-isomers is larger in a direction parallel to **E** due to the axis-selective *Z*-to-*E* photoisomerization similar to the case of non-LC copolymers. When the film recovers the LC nature, self-organization parallel to **E** is generated during the *Z*-to-*E* photoisomerization that improves the photoinduced ΔA values for LC copolymers.

3.4. Thermal amplification of the photoinduced optical anisotropy

Fig. 7(a) and (b) shows the polarized UV–vis spectral changes used to monitor the photoreaction and the reorientation behavior of the **PAz(90)** and **PAz(50)** films. Initially, the films are irradiated with NP 365 nm light in 1.5 J cm^{-2} doses to produce the photoreactivity at 633 nm. This process forms 73 and 86 mol% of the *Z*-isomer for **PAz(90)** and **PAz(50)**, respectively. When the film is exposed to LP 633 nm light for 372 J cm^{-2} for **PAz(90)** and for 24 J cm^{-2} for **PAz(50)**, the axis-selective *Z*-to-*E* photoreaction occurs and a small positive optical anisotropy ($\Delta A > 0$) appears. Annealing the exposed films for 10 min at 90 °C for **PAz(90)** thermally enhances the generated ΔA and the DR value is amplified from +0.056 to +0.82. Other LC copolymers show a similar thermal amplification for the photoinduced optical anisotropy as summarized in Table 2. Thermal amplification of other azobenzene-containing LC polymeric films with small photoinduced optical anisotropy was observed. [18,20,23] However, when the exposed **PAz(50)** film is annealed at 90 °C, photoinduced ΔA is not thermally enhanced as shown in Fig. 7(b). The annealing procedure causes the randomization of the orientation of the 4MAz groups, which results in the disappearance of the photoinduced optical anisotropy. The photoinduced optical anisotropy disappears when the exposed films are annealed around Tg of the copolymer or higher. It is clear that the thermal amplification cannot take place in the amorphous polymer. It should be noted that the absorption around 345 nm increases again after annealing as shown in the inset of Fig. 7(b), suggesting a thermally recovered molecular association. Similar results are obtained for other non-LC copolymer films. Difference of direction distribution of amount of *E*-isomers and LC nature of the material play important roles in the thermal amplification of the photoinduced optical anisotropy [18,23].

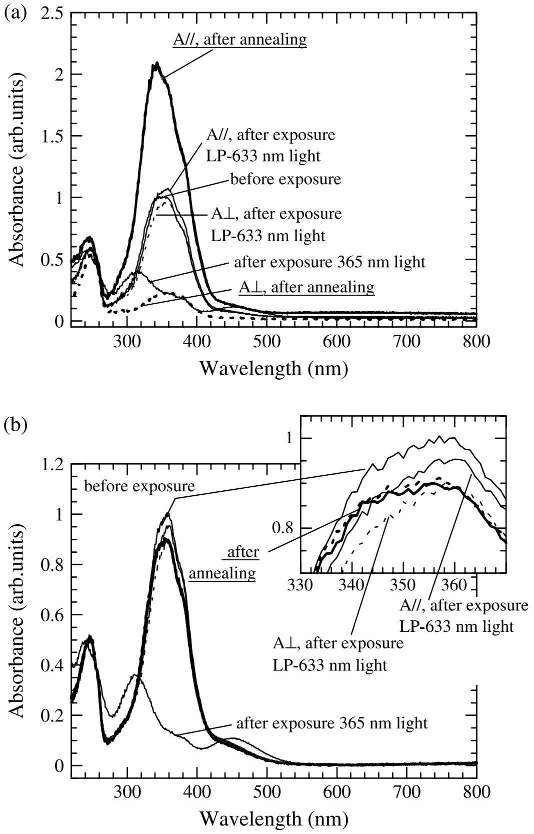

Fig. 7. UV–vis polarization spectrum of **PAz** films before photoirradiating, after irradiating with NP 365 nm light for 1.5 J cm^{-2} doses followed by irradiating with LP 633 nm light (thin lines), and after subsequent annealing (thick lines). $A_{\parallel}$ is the solid lines and $A_{\perp}$ is the dotted lines. (a) **PAz(90)** with 372 J cm^{-2} doses, annealed at 90 °C for 10 min. (b) **PAz(50)** with 24 J cm^{-2} doses, annealed at 90 °C for 10 min.

Table 2
Thermally amplified DR values of copolymer films

	Conversion (%)[a]	$DR_{irradiated}$[b]	$DR_{annealed}$[c]
PAz(4)	79	0.046	0
PAz(10)	79	0.038	0
PAz(20)	82	0.048	0
PAz(50)	77	0.042	0
PAz(80)	100	0.049	0.78
PAz(90)	99	0.056	0.82
PAz(100)	97	0.065	0.88

[a] Conversion of *Z*-to-*E* photoisomerization. Conversion was estimated by Eq. (1).

[b] DR values after exposure to LC 633 nm light.

[c] DR values after annealing irradiated films at 90 °C.

3.5. Recovering the optical anisotropy of the uniaxially oriented LC copolymer film

To further elucidate the axis-selective photoreaction of the *Z*-isomers of the 4MAz groups, the photoreaction of a uniaxially oriented **PAz(100)** film was performed. The photoorientation process based on *E*-to-*Z* photoisomerization using LP 365 nm light and subsequent thermal amplification was used to obtain a uniaxial oriented film (initial DR value was 0.75) [20]. Fig. 8 shows the polarization absorption spectrum of the uniaxially oriented **PAz(100)** film after exposure to NP 365 nm light for 1.5 J cm^{-2} and after storing the exposed film for 4 days. After irradiating with NP 365 nm light, the optical anisotropy of the film was disappeared due to the *E*-to-*Z* photoisomerization. When this *Z*-isomer film is stored at room temperature, the optical anisotropy recovers.

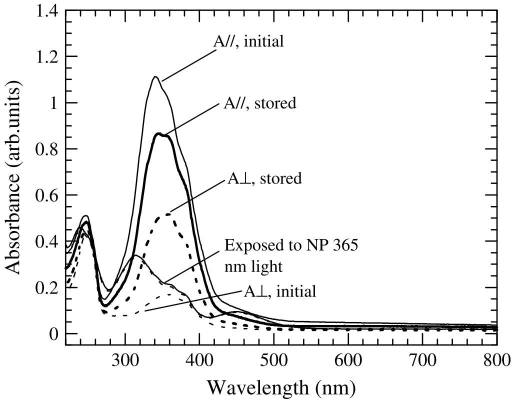

Fig. 8. UV-vis polarization absorption spectrum of uniaxially oriented **PAz(100)** film (thin lines), after exposure to NP 365 nm light for 1.5 J cm^{-2} (thin lines), and after storing the exposed film for 4 days (thick lines). $A_{\parallel}$ is the solid lines and $A_{\perp}$ is the dotted lines.

This means that the *Z*-to-*E* thermal isomerization preserves the direction of the transition moment of the 4MAz groups. The recovered DR value is 0.28. The decrease in the DR value is due to the partial disordering during both the *E*-to-*Z* photoisomerization and the thermal *Z*-to-*E* relaxation.

The optical anisotropy is also recovered by exposure to LP 633 nm light. Fig. 9 plots the recovered DR values when the above-mentioned *Z*-isomer film is exposed to LP 633 nm light with the polarization parallel or perpendicular to the original orientation direction of the film as a function of the exposure time of LP 633 nm light. For comparison, the photoinduced DR values using a randomly oriented *Z*-isomer film (Section 3.3) are also plotted. When the polarization of LP 633 nm light is parallel to the original orientation direction, the generated DR values reach 0.3, which are much higher than the DR values when using a randomly oriented *Z*-isomer film (<0.1). The *Z*-to-*E* photoisomerization of the initially-oriented *Z*-isomer film restores the original orientation direction in addition to the molecular reorientation. That is, the direction of the transition moment for both isomers is preserved. On the other hand, the photoinduced DR values are near zero when the polarization of LP 633 nm light is perpendicular to the original orientation direction. In this case, the *Z*-to-*E* photoisomerization perpendicular to the original orientation direction preferentially occurs, which randomizes the direction of the N=N bond. Consequently, the photoinduced DR values become negative and close to zero since the generated LC nature perpendicular to the initial orientation direction may induce partial self-organization. These results indicate that the photoisomerization of the oriented 4MAz groups preserves the absorption axes of both *E*- and *Z*-isomers in the same direction.

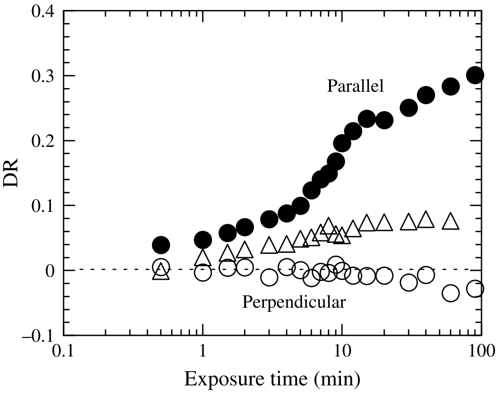

Fig. 9. Recovered DR values at 345 nm when uniaxially oriented *E*-isomer **PAz(100)** film was exposed to NP 365 nm light to form a *Z*-isomer film, and subsequently exposed to LP 633 nm light (closed circles and open circles, respectively). Polarization of LP 633 nm light is parallel (closed circles) or perpendicular (open circles) to the initial orientation direction. Photoinduced DR values when a randomly oriented *E*-isomer film was exposed to NP 365 nm light to form a *Z*-isomer film, and subsequently exposed to LP 633 nm light is also shown (open triangles).

4. Conclusion

The influence of the copolymerization ratio on the spectroscopic properties and photoinduced optical anisotropy of the LC and non-LC copolymer film with 4MAz side groups and methyl methacrylate units was investigated. The spectroscopic study reveals that the association of the 4MAz groups in the LC copolymer films is generated, while the absorption for the non-LC copolymer films is similar to the solution. The molecular association decomposes when the film is exposed to 365 nm light to form *Z*-isomers, followed by storing at room temperature or irradiating with 633 nm light to induce *Z*-to-*E* isomerization. For all the *Z*-isomer copolymer films, irradiating with LP 633 nm light generates an axis-selective *Z*-to-*E* photoisomerization, which induces a positive optical anisotropy. For the LC copolymers, the magnitude of the photoinduced ΔA of a film is greater than that of non-LC copolymers since the LC nature of the film increases upon *Z*-to-*E* photoisomerization, which induces self-organization. Furthermore, the photoinduced optical anisotropy is amplified for the LC copolymer films when the exposed film is annealed in the liquid crystalline temperature range of the material. The axis-selectivity of the *Z*-to-*E* photoisomerization creates the photoinduced optical anisotropy of the film and liquid crystallinity of the material is important for the thermal amplification of the optical anisotropy.

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