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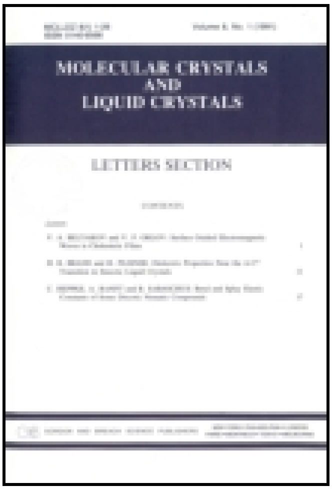

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Molecular Reorientation Behavior of Photocrosslinkable Liquid Crystalline Copolymer Films Composed of 4-(4-Methoxycinnamoyloxy)biphenyl and Phenylester Side Groups

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Molecular Reorientation Behavior of Photocrosslinkable Liquid Crystalline Copolymer Films Composed of 4-(4-Methoxycinnamoyloxy)biphenyl and Phenylester Side Groups

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The cooperative molecular reorientation in methacrylate copolymer films comprising photoreactive 4-(4-methoxycinnamoyloxy)biphenyl and phenylester in their side chains was investigated by irradiation with linearly polarized ultraviolet light and subsequent annealing. Both cinnamate and phenylester side groups were miscible in the copolymer composition, and axis-selective photoreaction of the cinnamate groups was observed. Thermally enhanced cooperative in-plane orientation of both side groups was obtained when the irradiated films were annealed in the liquid crystalline temperature range of the copolymers.

Keywords Liquid crystalline polymer; photoalignment; phenylester

Introduction

The axis-selective photoreaction of photoreactive polymeric films with linearly polarized (LP) light induces optical and mechanical anisotropy within the films [1]. This technique has been extensively investigated as a method for preparing molecularly oriented patterned structures in a remote, precise, and rapid manner without causing mechanical damage and electrical charging. To generate a large optical anisotropy in a film, molecular reorientation is required. Several types of reactions of photoreactive polymeric materials that exhibit photoinduced reorientation have been investigated, including photoisomerization, photodimerization, and photorearrangement reactions [2]. Among these, we have examined the thermally enhanced molecular reorientation of photoreactive liquid crystal polymer (PLCP) films using LP ultraviolet (LPUV) light and subsequent annealing. The resultant film can be used in optical devices, such as holographic and optical memories, and as birefringent films acting as a phase retarder in liquid crystal displays.

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We have reported that a high degree of in-plane reorientation was achieved in a methacrylate PLCP with a 4-(-methoxycinnamoyloxy)biphenyl (MCB) side group. Irradiation with LPUV light generated an axis-selective photodimerization reaction of the film. Furthermore, annealing enhanced the photoinduced optical anisotropy due to the photocrosslinked mesogenic groups acting as command groups in the bulk. Cooperative reorientation of a non-photoreactive mesogenic groups were also reported for a PLCP [3]. In the previous work, we prepared PLCP containing phenylamide side chains as an inert mesogen (PA-PLCP), and investigated their photoresponsive behavior. Axis-selective photodimerization of the MCB unit in the polymer was preferentially induced upon exposure to LPUV light. Axis-selective photoreacted MCB side groups result in thermally enhanced photoinduced optical anisotropy [4]. In this work, we focused on phenylester (PE) group. The previous PA unit itself shows no thermal amplification of molecular alignment and it only support molecular reorientation behavior of MCB unit. In contrast, the photo-Fries rearrangement with axis-selectively photoreaction of the phenyl benzoate moiety can induced thermal amplification by annealing [5]. We have explored photoresponsive behavior of PLCP copolymer composed of cinnamic acid and phenylbenzoate, and revealed that the phorodimerization and subsequent photoinduced molecular reorientation behavior originating from cinnamic acid prefencially occurred over the same behavior based on photo-Fries rearrangement [6]. However, the effect of photoreaction of PE unit on MCB moiety has not been explored so far. Herein, we prepared PLCP containing PE group (PE-PLCP) and investigated their molecular reorientation behavior.

Experimental

Materials

All starting materials were used as received from Tokyo Kasei Chemicals. The MCB and PE methacrylate monomers were synthesized according to a previously reported method in the literature [5]. Copolymerization was performed by free radical polymerization using 2–2′-azobisisobutyronitrile (AIBN) as an initiator in a tetrahydrofuran (THF) solution.

Characterization and Photoreaction

^{1}H nuclear magnetic resonance (NMR) spectra of synthesized compounds were measured on a Bruker DRX500 spectrophotometer. Thin films (ca. 0.1–0.3 μm thick) of the copolymers were prepared by spin-coating polymer solutions (0.5–2 w/w% in dichloromethane) onto a quartz substrate. The film was irradiated with UV light from a high-pressure Hg-UV lamp (Ushio, Spot Cure UIS 20102) that was passed through a Glan-Taylor polarizing prism with a cut-off filter below 290 nm. After exposure, the film was annealed at elevated temperatures for 10 min. The optical anisotropy of the film was evaluated using a polarizing microscope (POM: Olympus, BX-51P) and polarized absorption spectroscopy (Hitachi, U3010). The thermodynamic properties of the polymers were analyzed using differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C) at heating and cooling rates of 10°C/min. The mesophase of the polymers was determined by X-ray diffractometry (XRD; Rigaku, SmartLab). The molecular weight of the polymer was determined by gel permeation chromatography calibrated with polystyrene standards (GPC; Jasco UV-2075, RI-8020, Tosoh TSKgel 4000H, TSKgel α5000; chloroform eluent). The in-plane order

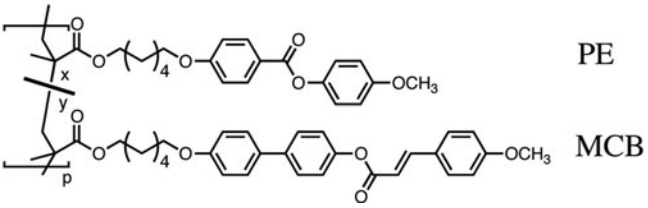

Figure 1. Chemical structure of the polymers used in this study.

parameter, S, is expressed as:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{large} + 2A_{small}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ represent the absorbance parallel and perpendicular to the polarization direction of the LPUV light (***E***), respectively; A_{large} is the larger value of $A_{\parallel}$ and $A_{\perp}$; and A_{small} is the smaller value. These values of the film were calculated using polarized UV-vis spectroscopy at 315 nm.

Results and Discussion

Characterization

All copolymers shown in Fig. 1 were synthesized by free radical copolymerization. The copolymerization ratio was controlled by adjusting the feed ratio of the two methacrylate monomers. The molecular weight, polydispersity index, and thermal properties of the synthesized copolymers are summarized in Table 1. DSC thermograms are presented in Fig. 2. POM observations revealed that all the copolymers exhibit LC phases without obvious phase separation between the LC temperature range of homopolymers **P1** and **P7**. Additionally, glass transition temperature and the clearing point show low value in comparison to the PA-PLCP. The XRD profile of the copolymers, show broad peak around $2\theta = 20^\circ$ without any reflection at small angle range, indicating that the polymers used

Table 1. Nomenclature, feed ratio of monomers, molecular weight, polydispersity index and mesomorphic properties of the polymers

Nomenclature	Feed ratio (PE/MCB (mol/mol))	(M_n) Molecular weight	Polydispersity index	Mesomorphic properties [a] (°C)
P1	10/0	53,000	2.5	G 41 N114 I
P2	8/2	31,000	2.2	G 53 N 150 I
P3	6/4	30,000	1.9	G 76 N 187 I
P4	5/5	40,000	1.9	G 77 N 214 I
P5	4/6	38,000	1.6	G 80 N 225 I
P6	2/8	35,000	2.1	G91 N 285 I
P7	0/10	39,000	2.1	G115 N 315 I

[a] G, glassy; N, nematic; I, isotropic.

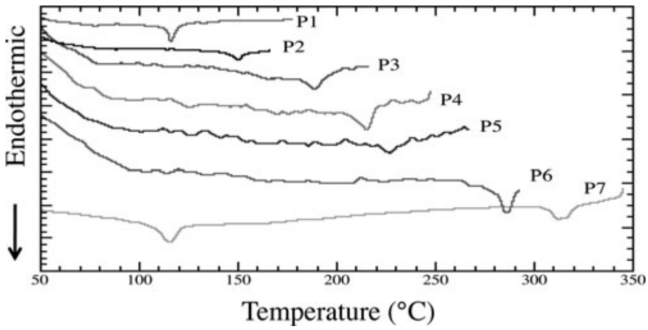

Figure 2. DSC second heating curves of the polymers.

in this study possess a nematic phase (Fig. 3). Figure 4 shows the UV absorption spectra of the copolymers in a dichloromethane solution. Two absorption maxima are evident at 260 nm and at approximately 315 nm. These bands correspond to the absorption of the PE and MCB groups, respectively. The calculated PE content in the copolymer is almost proportional to the feed ratio of the monomers.

Photoresponsive Behavior of Copolymer Films

Figure 5 shows the change in the UV absorption spectrum of the PE copolymer containing 50% MCB (**P4**) under UV irradiation. Absorption bands at 315 and 260 nm decreased after a lower energy dose ($<10^3$ mJ/cm^2), while the band at approximately 370 nm increased upon exposure to high energy ($>10^3$ mJ/cm^2) UV light. The decrease in the peak at 315 nm results from the [2 + 2] photodimerization of the MCB group, and the increase at 370 nm is due to the photo-Fries rearrangement. The decrease in the peak at 260 nm is caused by photodimerization and photorearrangement reactions. Figure 6 plots the change in copolymer absorbance at 315 nm and 370 nm as a function of exposure energy. The extent

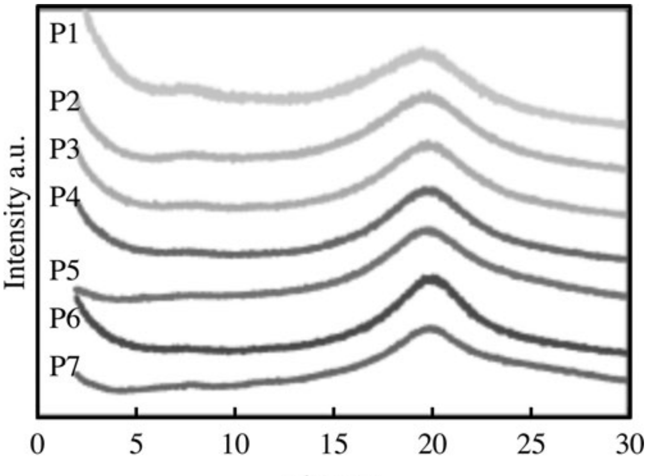

Figure 3. XRD profile of the polymers coated on a glass substrate.

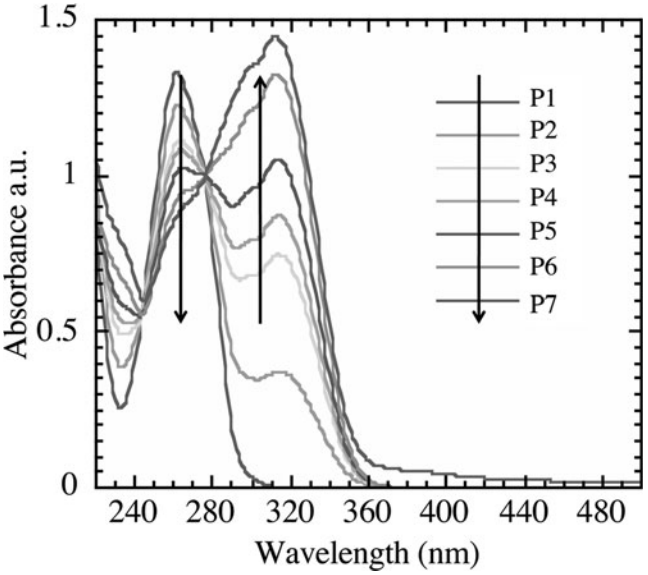

Figure 4. UV absorption spectra of the copolymers in dichloromethane solution.

of the photodimerization reaction decreased with lower MCB content and is evident from the increased distance between two cinnamates. In addition, small change was observed at 370 nm when the exposure energy was less than 10^3 mJ/cm^2. This observation suggests that the photodimerization occurs preferentially over the photo-Fries rearrangement in the corresponding energy range.

Figure 7 summarizes the photoinduced optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp}$) from the absorbance at 315 nm and 370 nm for the polymers as a function of the exposure energy.

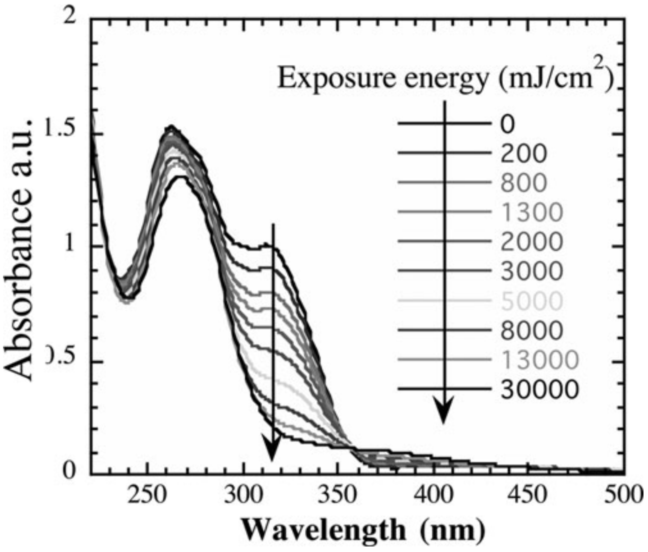

Figure 5. Change in the UV absorption spectrum of **P4** film under UV irradiation.

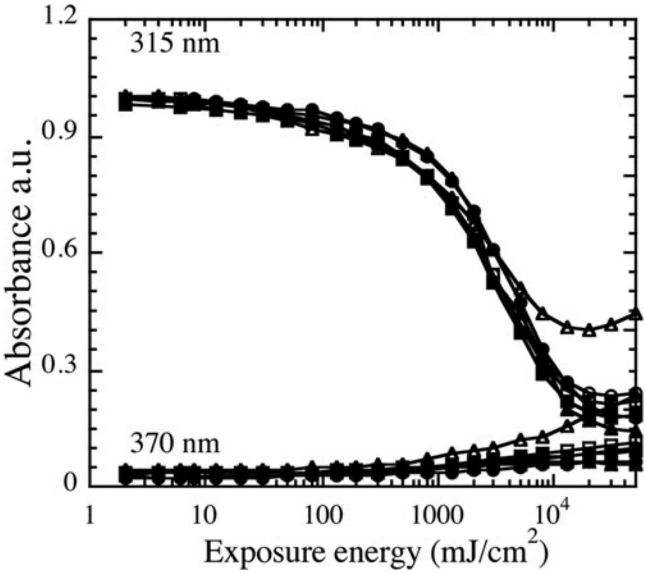

Figure 6. Change in absorbance of the copolymers at 315 nm and 370 nm as a function of the exposure energy. Open triangle; **P2**, open circle; **P3**, open square; **P4**, closed square; **P5**, closed circle; **P6**, closed triangle; **P7**.

The irradiated films exhibited negative optical anisotropy ($\Delta A < 0$) after exposure to LPUV light. Additionally, no axis-selectivity was observed at 370 nm. These results suggest that the axis-selective photodimerization of cinnamate moieties is stimulated in the copolymers under irradiation with UV light at $<10^3$ mJ/cm^2.

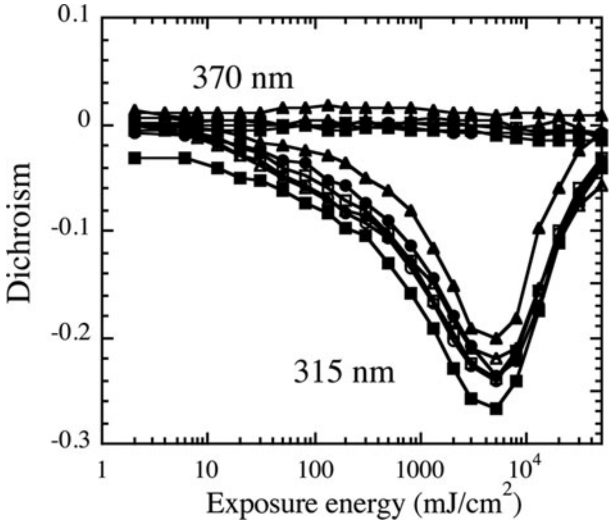

Figure 7. Change in optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp}$) of the polymers at 315 nm and 370 nm as a function of the exposure energy. Open triangle; **P2**, open circle; **P3**, open square; **P4**, closed square; **P5**, closed circle; **P6**, closed triangle; **P7**.

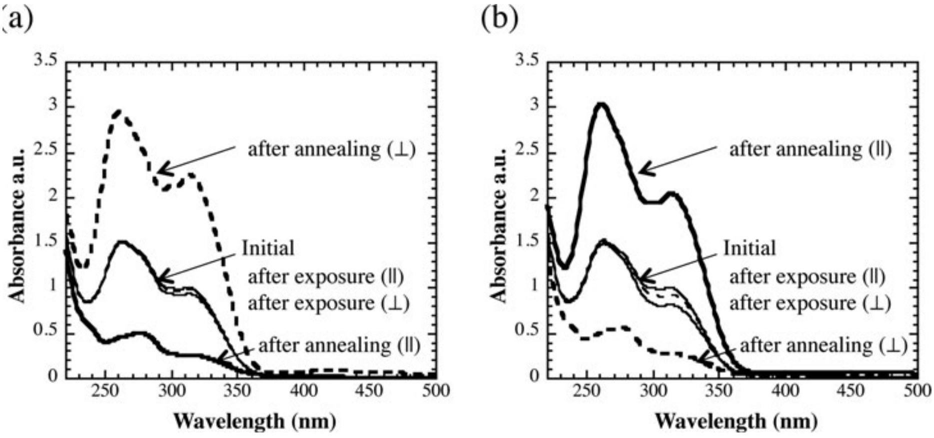

Figure 8. Polarized absorption spectra for **P4** before (thin lines) and after UV exposure (middle), and after annealing for 10 min (thick lines). Solid and dashed lines indicate $A_{\parallel}$ and $A_{\perp}$ for each stage, respectively. Exposure energies and annealing temperatures for the samples are 100 mJ/cm^2 and 150°C for (a) and 700 mJ/cm^2 and 150°C for **(b)**, respectively.

Thermal Enhancement of Photoinduced Optical Anisotropy

The photoinduced small optical anisotropy was amplified when the photoirradiated PLCP film was annealed above glass transition temperature. In contrast to the PA-PLCP films, all the (co)polymer of PE-PLCP enhanced the molecular alignment in two direction by changing the exposure energy; the optical anisotropy perpendicular to ***E*** was enhanced during the early stage of photoirradiation, while the molecular alignment parallel to ***E*** was enhanced at the latter stage of photoirradiation, and the maximum value of S is larger than that of PA-PLCPs, presuming that the cooperative molecular reorientation behavior is induced more effectively by using PE as a photo-inert moiety.

Figure 8 displays polarized absorption spectra of the **P4** copolymer film before and after irradiation with LPUV light for 100 mJ/cm^2 (a) and 700 mJ/cm^2 (b), and after subsequent annealing at the LC temperature. It is clearly observed that the amplified optical anisotropy reverted by changing exposed energy. The enhanced in-plane order parameter, S, at 315 nm was −0.65 for Fig. 8 (a) and 0.70 for Fig.8 (b), respectively. The S values at approximately 260 nm were similar, which suggests that the cooperative reorientation of PE groups is activated. This result is due to a small amount of photodimerized cinnamate parallel to ***E*** acting as an impurity and reducing the LC mesomorphism in the parallel direction at early stage while the photocrosslinked mesogenic groups act as the "command in bulk", which controls the direction of molecular reorientation at latter stage, similar to that for MCB copolymer films containing non-photoreactive mesogens [3a].

Figure 9 summarizes the effect of the exposure energy on the thermally enhanced reorientation behavior of the copolymers. The PLCP films were annealed in the LC temperature range after a 10 min irradiation; the annealing temperatures were 120°C for **P2**, 140°C for **P3,** 150°C for **P4**, 160°C for **P5**, 170°C for **P6,** and 170°C for **P7**. The molecular orientation was evaluated using the in-plane order parameter (S). The molecular reorientation behavior is induced over a wide range as the MCB content is reduced. The PE copolymers enable alignment perpendicular to ***E*** through the formation of photodimers, which suppresses the photoreaction of cinnamate units due to an increase in the distance between two cinnamate

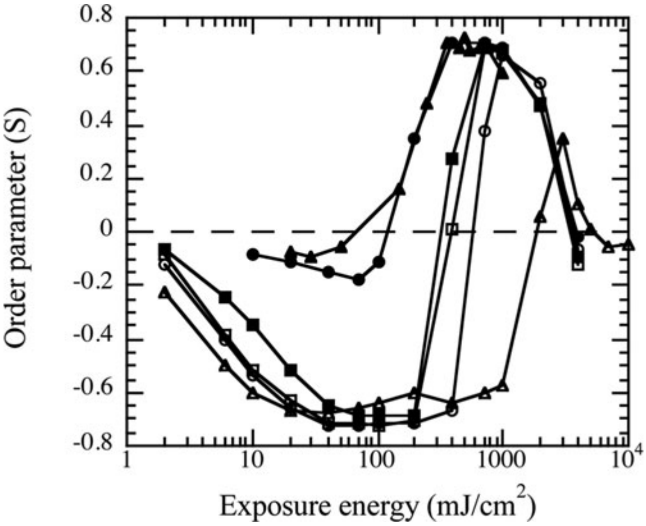

Figure 9. Thermally enhanced in-plane order, S, as a function of LPUV exposure energy with subsequent annealing at elevated temperatures. Open triangle; **P2**, open circle; **P3**, open square; **P4**, closed square; **P5**, closed circle; **P6**, closed triangle; **P7**. Annealing temperatures: **P2**, 120°C; **P3**, 140°C **P4**, 150°C; **P5**, 160°C; **P6**, 170°C; P7, 170°C.

moieties. It was also observed that the polymers exhibited positive optical anisotropy at the latter stage of photoirradiation and the maximum in-plane order was reduced with an increase in PE. This behavior is a result of the decrease in the number of initial cinnamate units, leading to a reduction in photoreactivity and thus, a reduction in photoreaction

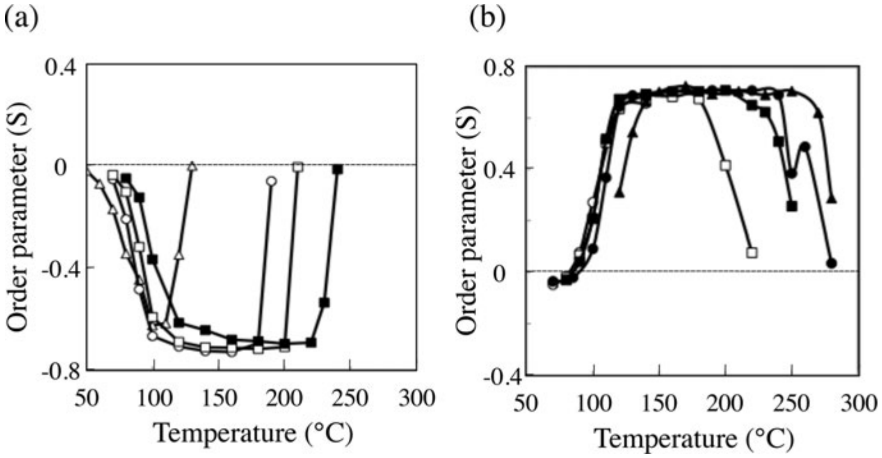

Figure 10. Thermally enhanced S values for copolymers annealed at various temperatures that induce (a) negative and (b) positive anisotropy. Open triangle; **P2**, open circle; **P3**, open square; **P4**, closed square; **P5**, closed circle; **P6**, closed triangle; **P7.** The exposure energies were 40 mJ/cm^2 for **P2**, 70 mJ/cm^2 for **P3**, 70 mJ/cm^2 for **P4**, 1000 mJ/cm^2 for **P5** to induce optical anisotropy perpendicular to ***E*** while 1000mJ/cm^2 for **P3**, 700 mJ/cm^2 for **P4**, **P5**, **P6** and 500 mJ/cm^2 for **P7** to induce optical anisotropy parallel to ***E***.

products. In comparison to previous PA-PLCPs, the maximum in-plane order parameter is larger and exposure energy for the reversion of the direction of molecular reorientation is almost the same. These results indicate that the photoinduced molecular reorientation of MCB unit takes over that of PE unit and the PE side chain only work as a non-photoreacted mesogen at relevant range.

The effect of the annealing temperature on the thermally enhanced molecular order of the copolymers is summarized in Fig. 10. The exposure energies that induce the largest S for each copolymer were 40 mJ/cm^2 for **P2**, 70 mJ/cm^2 for **P3**, 70 mJ/cm^2 for **P4**, 1000 mJ/cm^2 for **P5** to induce optical anisotropy perpendicular to ***E*** while 1000mJ/cm^2 for **P3**, 700 mJ/cm^2 for **P4**, **P5**, **P6** and 500 mJ/cm^2 for **P7** to induce optical anisotropy parallel to ***E***. The generated optical anisotropy was stable at the respective LC-isotropic transition temperatures. Unlike the PLCP copolymers composed of PE and cinnamic acid [6], a small amount of molecular reorientation was induced in the copolymers below 110°C, even if the polymers were heated above their glass transition temperature. This temperature corresponds to the glass transition temperature for the MCB homopolymer (**P7**). Therefore, it is presumed that the molecular mobility of the cinnamate unit plays an important role for the thermally enhanced molecular reorientation behavior.

Conclusion

Photoreactive liquid crystalline copolymer films containing PE side chains as an inert mesogen were prepared, and their photoresponsive behavior was investigated. Axis-selective photoreacted MCB side groups result in thermally enhanced photoinduced optical anisotropy. The PE copolymer exhibited effective molecular orientation behavior.

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