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Polymer 45 (2004) 2615–2621

polymer

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Influence of substituents on the reorientational behavior in photocrosslinkable polymer liquid crystal films with *p*-substituted cinnamoyloxybiphenyl side groups by irradiating with linearly polarized ultraviolet light and annealing

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Received 29 October 2003; received in revised form 22 January 2004; accepted 6 February 2004

Abstract

This paper describes the synthesis and influence of the substituent on the reorientation behavior of photocrosslinkable methacrylate polymer liquid crystals (PPLCs), which contain *p*-substituted cinnamoyloxybiphenyl (CB) side groups. Irradiating with linearly polarized ultraviolet (LPUV) light induced optical anisotropy of all PPLC films due to an axis-selective photoreaction of the mesogenic groups. The thermally enhanced reorientation direction depended on the substituent groups and liquid crystalline nature of the PPLC. A high in-plane reorientational order ($S > 0.6$) parallel to the polarization of LPUV light was obtained for PPLCs with *p*-methoxy-CB and *p*-methyl-CB side groups, while out-of-plane reorientation was predominant for *p*-fluoro-CB and *p*-trifluoromethyl-CB side groups.

Keywords: Polymer liquid crystals; Photoinduced reorientation; Optical anisotropy

1. Introduction

Photoinduced reorientation of photosensitive polymeric films has received considerable attention due to its potential in new photonics applications [1–4]. Several types of photoreactive polymer materials have been investigated including azobenzene containing polymers and photocrosslinkable polymers. Among them, azobenzene-containing materials have been studied for use in optical switching and storage devices when the molecular orientation was controlled by linearly polarized (LP) light based on the axis-selective *trans–cis–trans* photoisomerization [1,2]. Thermally stable molecular reorientation of photocrosslinkable polymer liquid crystal (PPLC) films was achieved using an axis-selective photocrosslinking reaction from LP ultraviolet (LPUV) light [5]. The resultant birefringent films are applicable as phase retarders in liquid crystal displays [6].

During the course of our systematic study on thermally enhanced photoinduced reorientation of photocrosslinkable PPLC films, we clarified that irradiating with LPUV light generated an axis-selective photocrosslinking reaction of the film. The resultant photocrosslinked mesogenic groups act as the command groups in bulk, which controlled the thermally enhanced reorientation of the mesogenic groups [7]. A high in-plane reorientation order was observed when a methacrylate PPLC with a 4-(4′-methoxycinnamoyloxy)-biphenyl (MCB) side group was used [5,6]. The photochemistry of the MCB group has been well-documented [5]. Additionally, the influence of a non-photoreactive mesogenic group on the reorientation behavior of a PPLC with MCB groups was investigated [8].

This study sought to evaluate the influence of the end group of the 4-cinnnamoyloxybiphenyl (CB) mesogenic side group on the thermally enhanced photoinduced reorientation behavior of the PPLC films. New PPLCs, which contain CB groups with different kinds of *p*-substituted end groups, were synthesized. The orientational behavior of the film was investigated by polarization UV

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doi:10.1016/j.polymer.2004.02.009

spectroscopy. Irradiating with LPUV light and then annealing caused either in-plane or out-of-plane reorientation of the mesogenic groups in all PPLC films, but the reorientational direction was dependent on the substituent group and the annealing temperature.

2. Experimental

2.1. Monomer synthesis

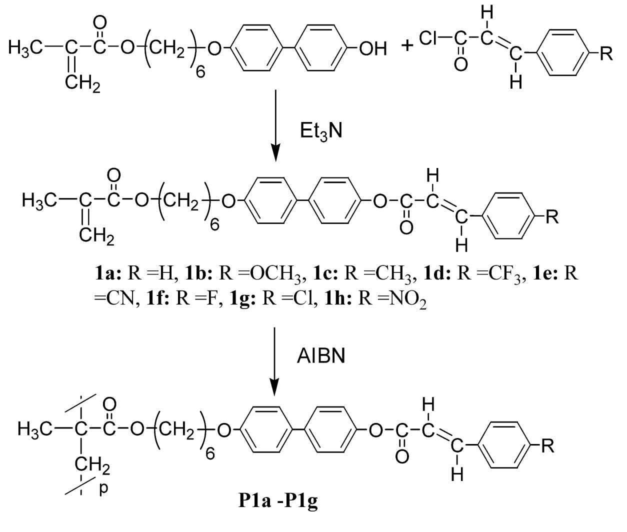
Scheme 1 outlines the synthetic route of the monomers. The methacrylate monomers **1a–1h** were synthesized according to the literature [5]. 4-Substituted cinnamoyl chloride was synthesized from the corresponding cinnamic acid and thionyl chloride. The structures of synthesized monomers were confirmed by ^{1}H NMR and FT-IR spectroscopy.

2.2. Polymer synthesis

All PPLCs were synthesized by a radical solution polymerization from the corresponding monomers using AIBN as an initiator in THF at 53 °C for 1 day. The monomer and AIBN concentrations were 10 wt%, and 2 mol l^{-1}, respectively. Table 1 summarizes the molecular weight, thermal properties, and spectroscopic data of the synthesized polymers.

2.3. Photoreaction

Thin films were prepared by spin-coating a methylene chloride solution of the polymers (1.0 wt%) onto a quartz substrate, which resulted in a 200 nm-thick film. The film was irradiated with light from a 250 W high-pressure Hg-UV lamp that was passed through Glan–Taylor polarizing prisms with a cut-off filter below 290 nm. The light intensity at 313 nm was approximately 50 mW cm^{-2}. The exposed film was annealed at elevated temperatures on a Linkam TH600PM heating stage and then cooled to room temperature. The optical anisotropy of the film was measured by polarizing microscopy and polarization UV–VIS spectroscopy. The degree of the photoreaction of the PPLC was determined by monitoring the decrease in the –C=C– bond of the cinnamoyl group at 1630–1640 cm^{-1} by FT-IR.



1a: R =H, **1b:** R =OCH$_3$, **1c:** R =CH$_3$, **1d:** R =CF$_3$, **1e:** R =CN, **1f:** R =F, **1g:** R =Cl, **1h:** R =NO$_2$

P1a -P1g

Scheme 1.

2.4. Characterization

The ^{1}H NMR spectra from a Bruker DRX-500 FT-NMR system were used to identify the monomers and polymers. Gel permeation chromatography, (GPC) (Tosoh HLC-8020 GPC system with a Tosoh TSKgel column; eluent, chloroform) which was calibrated using polystyrene standards, was used to determine the molecular weights. The thermal properties were examined by differential scanning calorimetry (DSC) (Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 K min^{-1}. A polarization optical microscope (POM) (Olympus BX51) equipped with a Linkam TH600PM heating and cooling stage was also employed. Polarization UV–VIS spectra were measured using a Hitachi U-3010 spectrometer equipped with Glan–Taylor polarizing prisms. The in-plane order parameter, S, and the out-of-plane order parameter, Sh, are expressed in the form of Eqs. (1) and (2), respectively;

$$S = \frac{A_\mathrm{p} - A_\mathrm{s}}{A_{(\mathrm{large})} + 2A_{(\mathrm{small})}} \tag{1}$$

$$\mathrm{Sh} = 1 - \frac{A_{(\mathrm{annealed})}}{A_{(\mathrm{irradiated})}} \tag{2}$$

where A_p and A_s are the absorbances parallel and perpendicular to E, respectively. $A_{(\mathrm{large})}$ is the larger value of A_p and A_s, and $A_{(\mathrm{small})}$ is the smaller one. A_annealed and $A_\mathrm{irradiated}$ are the average absorbances of A_p and A_s from the annealed film and the initial irradiated film, respectively.

3. Results and discussion

3.1. Synthesis and thermal property of PPLCs

All PPLCs were synthesized from the corresponding monomers by radical polymerization in THF at 53 °C for one day. PPLCs **P1b–P1e** were precipitated when the solution was cooled to room temperature and polymer **P1g** was precipitated during the polymerization. For monomer **1h** (R = NO$_2$), a polymer was not obtained since the nitro group inhibited the radical polymerization. Repeatedly precipitating from a chloroform solution for **P1a–P1c**, **P1e** and **P1f**, and from a NMP solution for **P1d** and **P1g**

Table 1
Molecular weight, thermal property and spectroscope data for synthesized PPLCs

Polyer	R	Molecular weight[a]		Thermal property (°C)[b]	λ_{max} (nm)[c]	ε (μm^{-1})[c]	
		$M_n \times 10^{-4}$	M_w/M_n			313 nm	365 nm
Pla	H	2.8	2.6	K144 S 157 N 219 I	272	2.48	0.29
P1b	OCH_3	2.2	3.1	K116 N 315 I	294	4.95	0.45
P1c	CH_3	4.5	2.4	K 129 N 285 I	281	3.19	0.26
P1d	CF_3	6.5	2.2	K 145 S or N 303 I	268	1.01	0.19
P1e	CN	2.8	2.3	G 171 N > 320 I	276	2.42	0.41
Plf	F	3.5	2.5	K 139 N 297 I	271	1.98	0.19
Plg	Cl	–[d]	–[d]	K 150 S > 320 I	–[e]	–[e]	–[e]

[a] Determined by GPC, polystyrene standards, CHCl3 eluent.

[b] Determined by DSC and POM observations. G: Glass transition, K: crystalline, N: nematic, S: smectic and I: isotropic phases.

[c] On quartz substrate.

[d] Insoluble in CHCl3

[e] Not measured because of low solubility in slovents at r.t.

into diethyl ether purified the PPLCs. Table 1 summarizes molecular weight, thermal and spectroscopic properties of synthesized PPLCs. All PPLCs exhibited a nematic or smectic liquid crystalline phase.

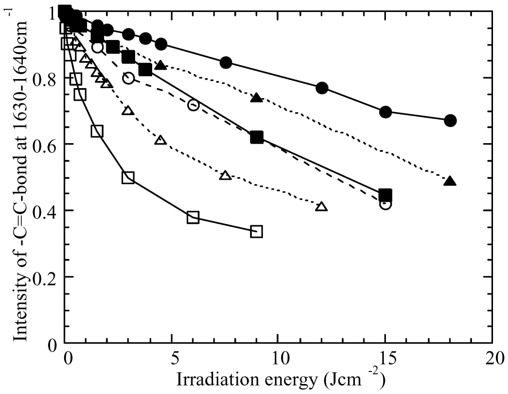


Fig. 1. Intensity of −C=C− absorption at 1630–1640 cm^{-1} of films **P1a** (open circle), **P1b** (open square), **P1c** (open triangle), **P1d** (closed circle), **P1e** (closed square) and **P1f** (closed triangle), as a function of exposure energy.

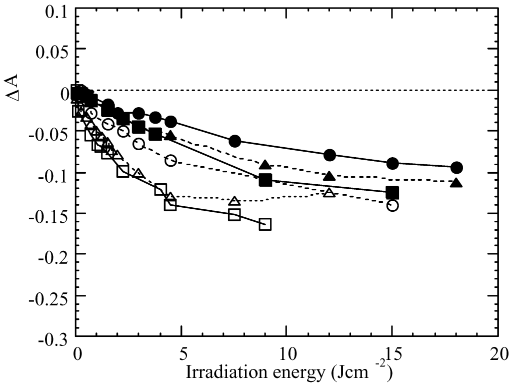


Fig. 2. Normalized photoinduced dichroism (ΔA) of films at λ_{max} of **P1a** at 272 nm (open circle), **P1b** at 294 nm (open square), **P1c** at 281 nm (open triangle), **P1d** at 268 nm (closed circle), **P1e** at 276 nm (closed square) and **P1f** at 271 nm (closed triangle), as a function of exposure energy.

3.2. Photoreaction of PPLC films

The thin PPLC films except **P1g**, which were prepared by a spin-coating method from a methylene chloride solution, were transparent and amorphous as determined by POM observations. A uniform **P1g** film was not obtained because of its low solubility in chloroform and NMP at room

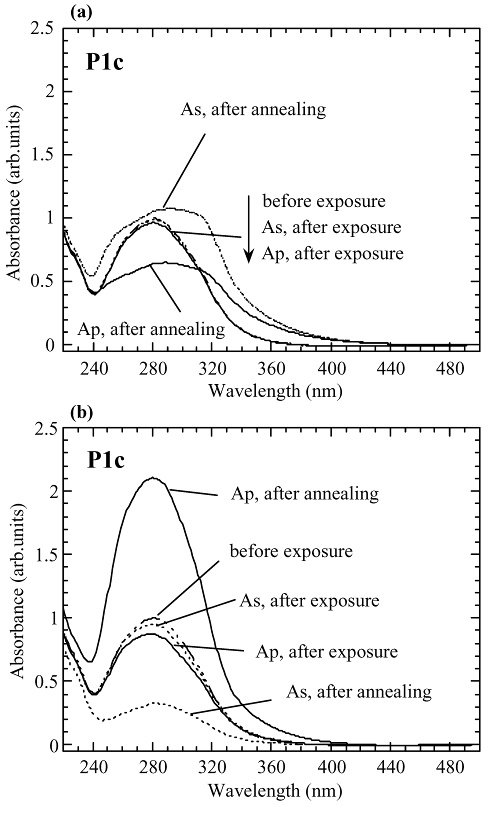


Fig. 3. UV polarization spectra of a **P1c** film before irradiation (dash-dot line), after irradiation with LPUV light (thin lines), and after subsequent annealing (thick lines) at 180 °C for 10 min. Exposure doses were (a) 150 mJ cm^{-2}, and (b) 1.2 J cm^{-2}. A_p is shown as the solid lines, and A_s is shown as the dotted lines.

temperature. Irradiating the films with UV light induced a [2 + 2] photo-cycloaddition reaction of the cinnamoyl group and the resultant films were insoluble in organic solvents. Fig. 1 plots intensity of –C=C– absorption band at 1630–1640 cm^{-1} for the polymer films as a function of exposure dose for estimating the degree of photoreaction. It indicates that the photoreaction rates of **P1b**, **P1c**, **P1a**, **P1e**, **P1f** and **P1d** decrease in the order listed, which is consistent with the magnitude of the absorption coefficient at 313 and 365 nm of the PPLC film (Table 1).

When the films were exposed to LPUV light, all the films exhibited negative optical anisotropy ($\Delta A = A_p - A_s < 0$). Fig. 2 plots the normalized photoinduced ΔA of the films at $\lambda_{\max}$ as a function of exposure energy. It shows that ΔA increased as the exposure doses increased and a larger ΔA was obtained in the early stage of irradiation as the photoreaction rate increased. These results indicate that all the PPLC films resulted in an axis-selective photocrosslinking reaction of the mesogenic side groups.

3.3. Thermally enhanced photoinduced reorientation of the PPLC film

We reported that annealing a **P1b** film, which was exposed to LPUV light, generated an in-plane reorientation of mesogenic side groups [6]. During the early stages of the photoreaction, the negative optical anisotropy was thermally amplified and the orientation direction was reverted when the degree of photocrosslinking was approximately 10–20 mol% [5]. The influence of the substituent end groups of the PPLCs was evaluated by irradiating the films with LPUV light and subsequently annealing in the LC temperature range of the polymer.

Fig. 3(a) shows polarized UV–VIS spectral differences between a **P1c** film irradiated with 150 mJ cm^{-2} doses of LPUV light and the same film subsequently annealed at 180 °C for 10 min. The degree of the photoreaction was about 3 mol%. After exposure, a small negative ΔA was generated. The annealing process amplified the orientational order parameter S from -0.011 to -0.18 and the enhanced reorientation direction of mesogenic groups perpendicular to **E** of LPUV light [9]. The spectrum exhibits a red shift in the absorption band, suggesting that annealing causes J-aggregation of the mesogenic groups. In contrast, the reorientation direction reversed, parallel to **E**, when the irradiation dose was 1.2 J cm^{-2}, as shown in Fig. 3(b). The degree of the photoreaction was about 17 mol% and the aggregation of the mesogenic groups was suppressed. S was amplified from -0.04 to $+0.66$, which is attributed to the thermally enhanced reorientation of the unreacted mesogenic groups along the photocrosslinked mesogenic groups parallel to **E** [7]. These behaviors are quite similar to that of the **P1b** film as previously reported [5].

For **P1a** and **P1e** films, the photoinduced negative optical anisotropy was not thermally amplified in the early stages of the photoreaction as shown in Fig. 4(a) and (c). The

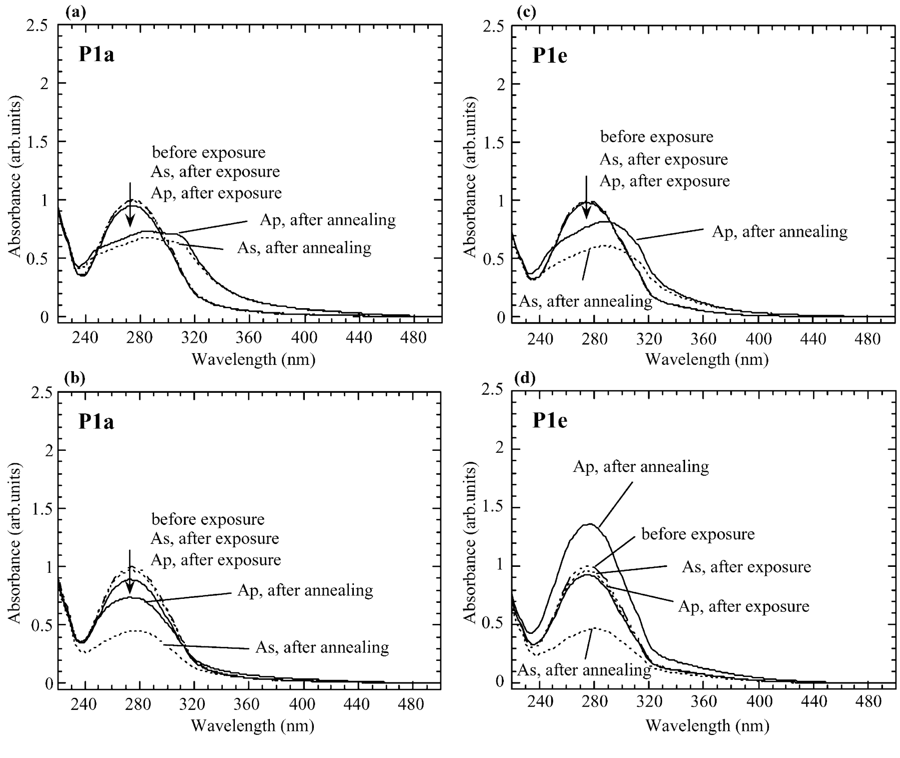


Fig. 4. UV polarization spectra of **P1a** and **P1e** films before irradiation (dash-dot line), after irradiation with LPUV light (thin lines), and after subsequent annealing (thick lines) at 180 °C for **P1a**, and 220 °C for **P1e**, respectively. Exposure doses were (a) 750 mJ cm^{-2} for **P1a**, (b) 2.5 J cm^{-2} for **P1a**, (c) 500 mJ cm^{-2} for **P1e** and (d) 2.5 J cm^{-2} for **P1e**. A_p is shown as the solid lines, and A_s is shown as the dotted lines.

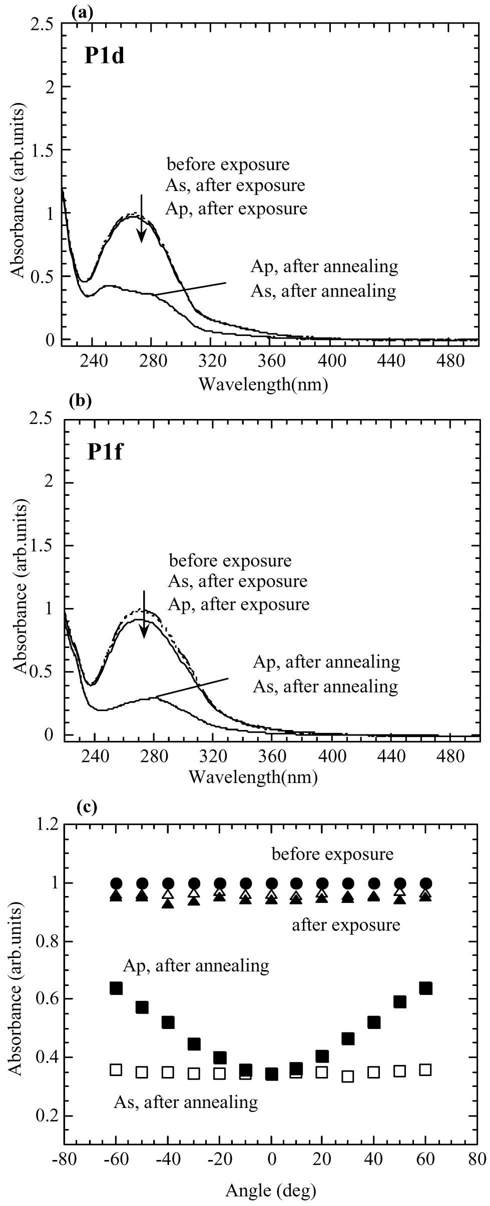


Fig. 5. (a), (b) UV polarization spectra of **P1d** and **P1f** films before irradiation (dash-dot line), after irradiation with LPUV light (thin lines), and after subsequent annealing (thick lines) at 180 °C. Exposure doses were (a) 1.5 J cm^{-2} for **P1d** and (b) 1.0 J cm^{-2} for **P1f**. (c) Angular dependence of UV absorption spectrum of **P1d** film at 268 nm before exposure (circle points), after exposure to 1.5 J cm^{-2} (triangle points) and after annealing (square points). A_p is shown as the closed points, and A_s is shown as the open points.

exposure doses were 750 mJ cm^{-2} for **P1a** and 500 mJ cm^{-2} for **P1e**. The degree of the photoreaction was about 5 mol% for both films. After annealing the exposed films, small positive optical anisotropies ($\Delta A > 0$) were thermally generated and were accompanied by a red-shift due to aggregation. Additionally, when the degree of the photoreaction was less than 3 mol%, thermal aggregation was generated without thermally enhanced optical anisotropy. When the exposure doses were sufficient, this aggregation was suppressed and reorientation parallel to **E** was generated, as shown in Fig. 4(b) and (d). The exposure doses were 2.5 J cm^{-2} for both films and the degree of the photoreaction was about 17 mol% for **P1a** and 15 mol% for **P1e** film. The generated S values for **P1e** and **P1a** were $+0.42$ and $+0.20$, respectively. For **P1a**, the absorption intensities in both directions decreased after annealing, suggesting simultaneous out-of-plane reorientation. The out-of-plane reorientation was confirmed by measuring the angular dependence of the absorption spectrum.

On the other hand, in-plane reorientation was not generated for **P1d** and **P1f** films regardless of exposure dose. Annealing decreased the absorption intensity as a result of out-of-plane reorientation of the mesogenic groups. Fig. 5(a) shows polarized UV–VIS spectra of a **P1d** film irradiated with 1.5 J cm^{-2} doses (5 mol% of photoreaction) and after annealing at 180 °C for 10 min. Similar spectral changes were observed when the degree of the photoreaction was less than 30 mol%. **P1f** exhibited spectral changes similar to that of **P1d** as shown in Fig. 5(b). The absorption intensity decreased when the films were annealed before exposing to LPUV light. A small change in the spectrum shape will be due to the small amount of aggregates in the as-coated film, which do not thermally reorient. Furthermore, Fig. 5(c) plots the angular dependence of the absorption for the **P1d** film and reveals that the absorbance increased as the angle of the monitoring p-polarized light increased, indicating out-of-plane reorientation. The generated Sh was 0.62. These results suggest that the out-of-plane reorientation is the main component for the **P1d** and **P1f** films.

3.4. Influence of annealing temperature

The influence of the annealing temperature was evaluated by annealing the irradiated films at various temperatures for 10 min and then cooling to room temperature. The degree of the photoreaction for all the films was set about 17 mol%, where the largest in-plane reorientation was observed for films **P1a**–**P1c** and **P1e**. Fig. 6(a) plots the thermally enhanced S and Sh values for the **P1c** film as a function of the annealing temperature. When the annealing temperature was below T_m, out-of-plane reorientation (Sh > 0) was observed although the reason for the reorientation below T_m is currently unclear. When the annealing temperature increased above T_m, in-plane reorientation parallel to **E** was generated and reorientational order increased as the annealing temperature increased. This phenomenon is attributed to the thermally enhanced reorientation of the unreacted mesogenic groups along the photocrosslinked mesogenic groups parallel to **E**, similar to **P1b** [5]. The generated S value was 0.65, which is similar to **P1b**. It is noteworthy that the Sh value was negative when a large in-plane reorientation was observed, which means that the mesogenic groups along the propagation of the LPUV light incidence also homogeneously reoriented parallel to **E**. When the annealing temperature was above 200 °C, the film

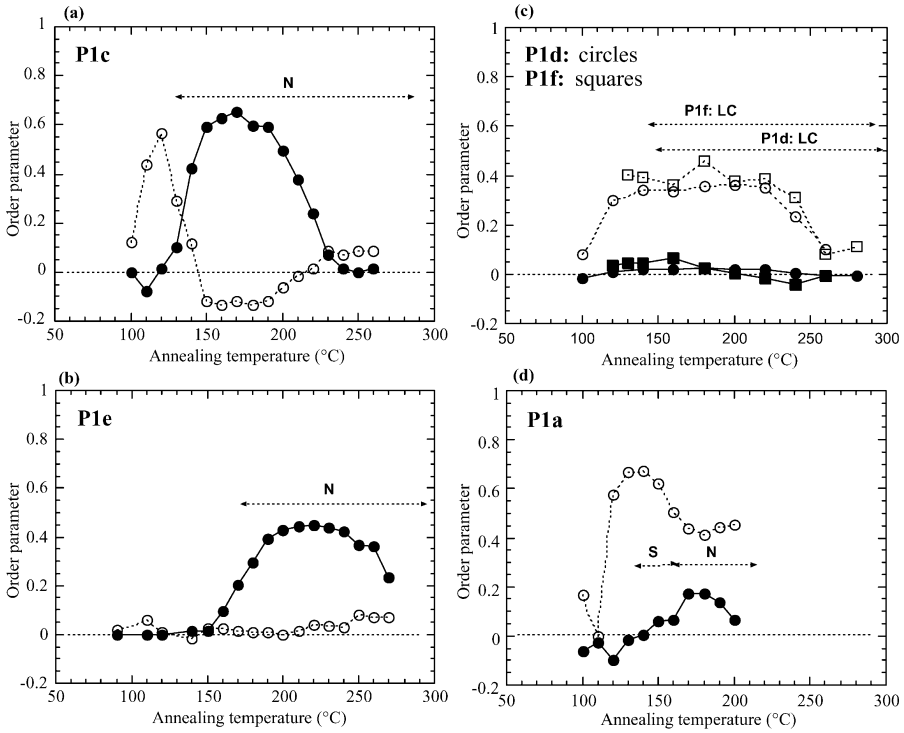


Fig. 6. Change in in-plane order parameter *S* and out-of-plane order parameter Sh of PPLC films as a function of annealing temperature. Exposure doses were (a) 1.2 J cm^{-2} for **P1c**, (b) 2.5 J cm^{-2} for **P1e**, (c) 3.0 J cm^{-2} for **P1d** (circle points) and 2.5 Js cm^{-2} for **P1f** (square points), and (d) 2.5 J cm^{-2} for **P1a**. Closed points indicate *S* values, and open plots Sh ones.

partially degraded, which resulted in a decrease in the orientational order.

In-plane reorientation parallel to **E** was also generated when annealing **P1e** in the LC temperature range (Fig. 6(b)). The *S* values above 240 °C also decreased due to the partial degradation of the film. For **P1d** and **P1f**, out-of-plane reorientation was the major component as plotted in Fig. 6(c). Thermally enhanced out-of-plane reorientation of azobenzene-containing PLC films was also reported [10, 11]. The interaction between the substrate and the mesogenic groups with fluorine atom will cause the out-of-plane reorientation. Furthermore, Fig. 6(d) indicates that for **P1a** out-of-plane reorientation was generated, but not in-plane reorientation when the annealing temperature was between 130 and 160 °C. Both in-plane and out-of-plane reorientations were induced when the film was annealed in the nematic temperature range (160–200 °C), which suggests that the type of the LC nature affects the reorientation direction.

4. Conclusions

The influence of the substituent end group on the reorientation behavior of photocrosslinkable methacrylate PPLCs, which contained *p*-substituted CB side groups, was investigated. All the synthesized PPLCs exhibited liquid crystalline nature. Exposing the films to LPUV light led negative optical anisotropies ($\Delta A < 0$) and the resultant films were insoluble in organic solvents due to photocrosslinking. Subsequent annealing generated in-plane reorientation for films **P1a**, **P1b**, **P1c**, and **P1e**, which exhibited a nematic LC phase. For **P1b** and **P1c**, the reorientation direction was reversed, depending on the exposure dose. For **P1d** and **P1f**, out-of-plane reorientation was dominant. It was concluded that annealing in the LC temperature range after irradiating with LPUV light caused the molecular reorientation for all PPLC films, but the reorientation direction was strongly affected by the substituent group and the type of the LC phase.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the JSPS of the Japanese Government.

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