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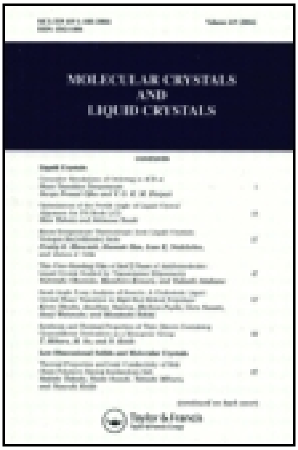

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Synthesis and Photoinduced Alignment of Photo-Cross-Linkable Copolymer Liquid Crystals Containing Tolane Side Groups

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Synthesis and Photoinduced Alignment of Photo-Cross-Linkable Copolymer Liquid Crystals Containing Tolane Side Groups

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Methacrylate copolymer liquid crystals (CPLCs) comprising photo-cross-linkable 4-(4′-methoxycinnamoyloxy)biphenyl (4MCB) side groups and 4-cyano- or 4-methyl-tolane side groups were synthesized. Thermally enhanced molecular reorientation behavior of CPLC films was investigated by irradiating with linearly polarized ultraviolet (LPUV) light and subsequent annealing. The exposure to LPUV light generated an axis-selective photoreaction of the 4MCB groups for all CPLC films. Thermally enhanced cooperative in-plane reorientation was observed for CPLC copolymerized with a 4-methoxytolane side groups and the generated birefringence was 0.25. However, out-of-plane reorientation was predominant when a comonomer with a 4-cyanotolane group was copolymerized.

Keywords: optical anisotropy; photocrosslinking; photoinduced orientation; polymer liquid crystal; tolane

INTRODUCTION

Irradiating with a linearly polarized (LP) light to photosensitive polymeric films generates an optical anisotropy due to an axis-selective photoreaction of the photoreactive groups [1–3]. To generate a large optical anisotropy of the film, a molecular reorientation is necessary.

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Several types of photoreactive polymeric materials that exhibit photoinduced reorientation have been investigated, including azobenzene containing polymers and photocrosslinkable polymers [1–6]. Among them, we have been studying thermally enhanced molecular reorientation of photo-cross-linkable polymer liquid crystal (PPLC) films using LP ultraviolet (LPUV) light and subsequent annealing [4,5,7–9]. The resultant film can be used as optical devices such as holographic and optical memories, and a birefringent film applicable to a phase retarder in liquid crystal displays [8,9].

In order to obtain a thin holographic element with high diffraction efficiency, large photoinduced birefringence of a film is required. We reported that a high degree of in-plane reorientation was achieved in a methacrylate PPLC with a 4-(4′-methoxycinnamoyloxy)biphenyl (4MCB) side group [5]. An irradiating with LPUV light generated an axis-selective photocrosslinking reaction of the film, and the annealing enhances the photoinduced optical anisotropy because the photo-cross-linked mesogenic groups act as the command groups in bulk. Cooperative reorientation of a non-photoreactive mesogenic group on the reorientation behavior of PPLC was also reported [10].

It is known that a tolane moiety exhibits large optical birefringence and several LC monomers and polymers containing tolane groups were synthesized [11,12]. Okano et al. reported that a polymer liquid crystal containing an azobenzene group directly attached with a tolane moiety induced large photoinduced birefringence [12].

This paper describes synthesis and thermally enhanced photoinduced reorientation behavior of copolymer liquid crystals (CPLCs) comprising photo-cross-linkable 4MCB side groups and 4-cyano- or 4-methyltolane side groups. An axis-selective photoreaction was investigated using LPUV light, and the reorientational behavior was estimated by polarization UV-vis spectroscopy. The cooperative reorientation was observed for all CPLCs, while the reorientation direction depended on the composition and type of the end-group of the tolane moiety.

EXPERIMENTAL SECTION

Materials and Copolymer Synthesis

All starting materials from Tokyo Kasei Chemicals were used without further purification. The methacrylate monomer comprising 4MCB moiety (MCB6M) was synthesized according to the literature [5] and the synthetic route of monomers with a tolane moiety is shown in Scheme. All synthesized monomers were confirmed by ^{1}H-nmr and

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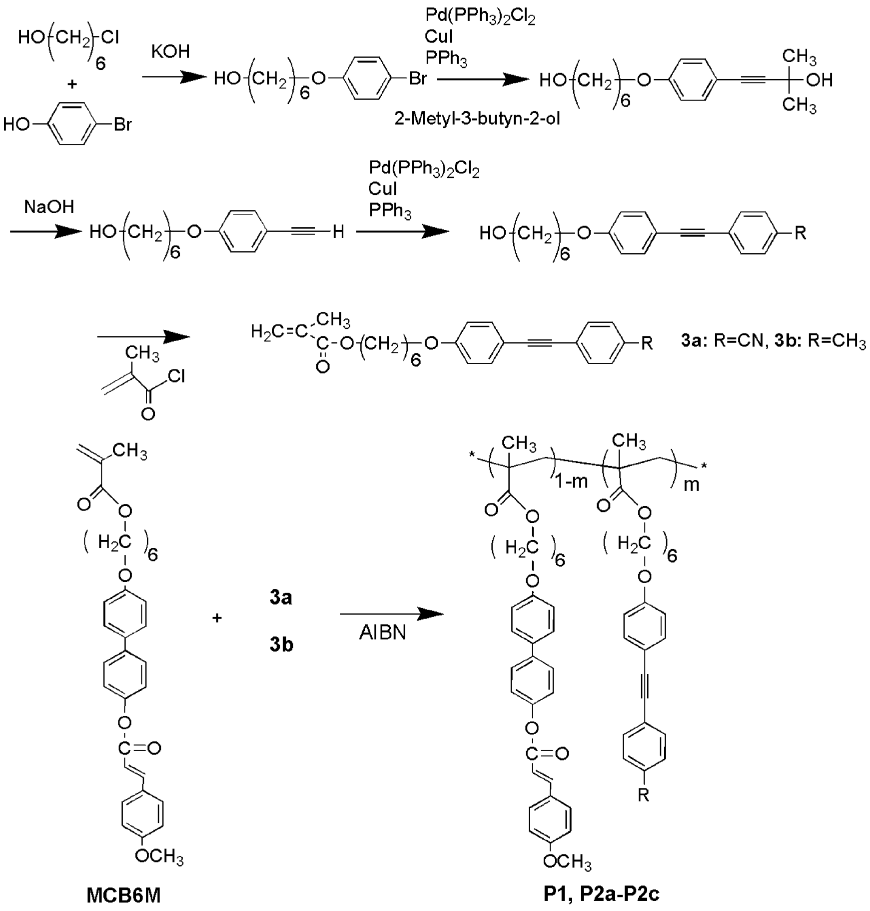

SCHEME

FT-IR spectroscopy. The radical polymerization was carried out using AIBN as an initiator in THF solution at 50–60°C for 1 day. Synthesized CPLCs were purified by washing with diethyl ether and reprecipitation method. Table 1 summarizes molecular weight and thermal properties of synthesized CPLCs.

Photoreaction

The copolymer was spin-coated on a quartz substrate from a methylene chloride solution, resulting in a 200 nm-thick film. Photoreactions were conducted by irradiating with a 250 W high-pressure mercury

TABLE 1 Composition, Molecular Weight and Thermal Property of Synthesized CPLCs

CPLC	R	m[a]	Molecular weight[b] $M_n \times 10^{-4}$	 $M_w \times 10^{-4}$	Thermal property °C[c]
P1	CN	0.5	3.2	5.6	K 108 N 234 I
P2a	CH_3	0.23	3.1	9.6	G 75 N 258 I
P2b	CH_3	0.5	1.5	3.5	G 65 N 195 I
P2c	CH_3	0.77	2.2	3.7	G 57 N 120 I

[a]Determined by 1H-NMR; [b]Measured by GPC with polystyrene standards; [c]Measured by DSC, 2nd heating data. K: crystalline, G: glass transition, N: nematic, I: isotropic, LC phase was determined by polarization optical microscope observation.

lamp attached with a cut-off filter below 300 nm. Intensity was 150 mWcm^{-2} at 365 nm. To irradiate with LPUV light, Glan-Taylor polarizing prisms were used.

Characterization

The optical anisotropy of the film was estimated by polarization optical microscopy (POM) and polarization UV-vis spectra (Hitachi U-3000 spectrometer equipped with Glan-Taylor polarizing prisms). The in-plane order parameter, S, is expressed in Eq. 1;

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

where $A_{//}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**) of LPUV light, respectively, while $A_{(\mathrm{large})}$ is the larger of $A_{//}$ and $A_{\perp}$, while $A_{(\mathrm{small})}$ is the smaller. These values were calculated by polarized UV-vis spectroscopy at 315 nm of the film.

RESULTS AND DISCUSSION

Thermal and Spectroscopic Properties of PPLCs

CPLCs were synthesized from the corresponding monomers by radical polymerization in THF solution. Table 1 summarizes the composition, molecular weight and thermal property of the synthesized CPLCs. All CPLCs showed nematic LC phase, and were soluble in organic solvents such as chloroform and toluene. The copolymerization of 4-methyltolane groups resulted in decreasing transition temperatures and narrowing the LC temperature range.

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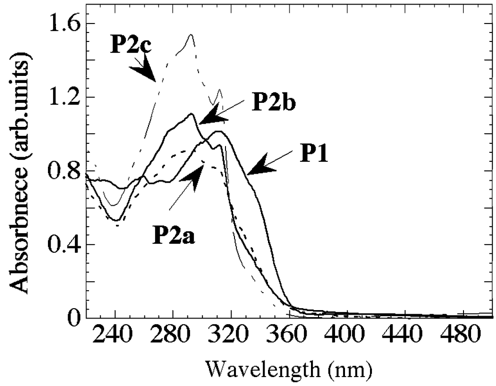
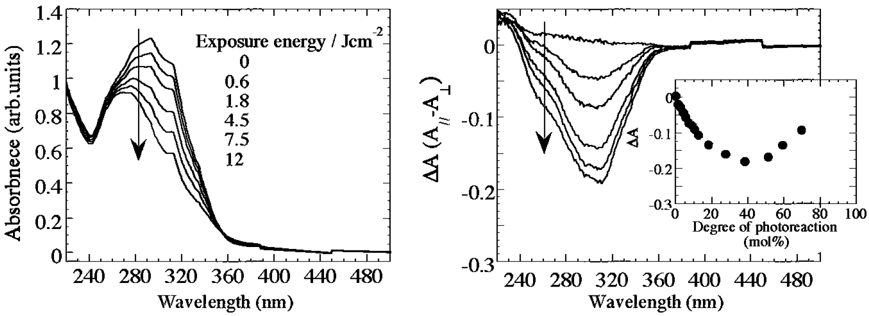


FIGURE 1 Absorption spectra of CPLC films on quartz substrate.

All spin-coated films were transparent and amorphous in nature. Figure 1 shows absorption spectrum of CPLC film on quartz substrate. It exhibits that the absorption bands of 4-cyanotolane groups around 340 nm, 4MCB groups around 315 nm and 4-methyltolane groups around 290 nm.

Photoreaction

Photoreaction of a CPLC was carried out using a thin film. Figures 2a and 2b plot change in absorption spectrum and photoinduced dichroic spectrum of a **P2a** film, respectively, which were used to monitor the



(a) (b)

FIGURE 2 (a) Change in absorption of **P2a** film irradiating with LPUV light. (b) Change in photoinduced optical anisotropy of **P2a** film. The inset exhibits the photoinduced ΔA at 315 nm as a function of degree of photoreaction.

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photoreaction of the film exposed to LPUV light. The resultant films became insoluble in organic solvents because of a photocrosslinking reaction of the mesogenic groups. Figure 2b reveals that irradiating with LPUV light generates a small negative optical anisotropy ΔA ($=A_{//} - A_{\perp} < 0$) around 310 nm due to an axis-selective photoreaction of 4MCB groups [5]. The ΔA increased as the photoreaction proceeded but decreased when the degree of the photoreaction became greater than 50 mol% as plotted in the inset of Figure 2b. Other CPLC films showed the similar spectrum change.

Thermally Enhanced Reorientation of the Exposed PPLC Films

It is known that the annealing process enhanced the photoinduced optical anisotropy of a homopolymer of MCB6M film [5,8]. When the degree of the photoreaction was approximately 10–20 mol%, the photoinduced negative optical anisotropy was reversed and enhanced by annealing the exposed film at the LC temperature range of the PPLC. This is because that the photocrosslinked mesogenic groups act as the "command in bulk", which controls the direction of molecular reorientation.

Figures 3a–3d show the absorption spectra of CPLC films before and after irradiating with LPUV light, and after the subsequent annealing at the LC temperature of each CPLCs. The degree of the photoreaction was adjusted approximately 15 mol%. In all cases, negative optical anisotropy was generated after exposing to LPUV light, and annealing procedure changed the spectrum. For **P2a** and **P2b** (Figs. 3b and 3c), reversion of the photoinduced optical anisotropy was observed. The increase of $A_{//}$ and decrease of $A_{\perp}$ after annealing mean the reorientation of the mesogenic groups parallel to the photocrosslinked 4MCB groups, which were parallel to **E** [5]. The enhanced in-plane order parameters, S, at 315 nm were +0.71 for **P2a** and +0.44 for **P2b**. The S values around 290 nm were similar to these values, suggesting that the cooperative reorientation of 4-methyltolane groups. However, for **P1** (Fig. 3a), absorption for both directions decreased after annealing, indicating an out-of-plane reorientation of the mesogenic groups occurred. Annealing process will induce the out-of-plane reorientation of 4-cyanotolane moieties, followed by cooperative out-of-plane reorientation of 4MCB groups. For **P2c** (Fig. 3d), annealing process scarcely changed the spectrum. The composition of photoreacted 4MCB groups in the total amount of mesogenic groups was too small to act as the command in bulk for the thermally enhanced reorientation parallel to **E**.

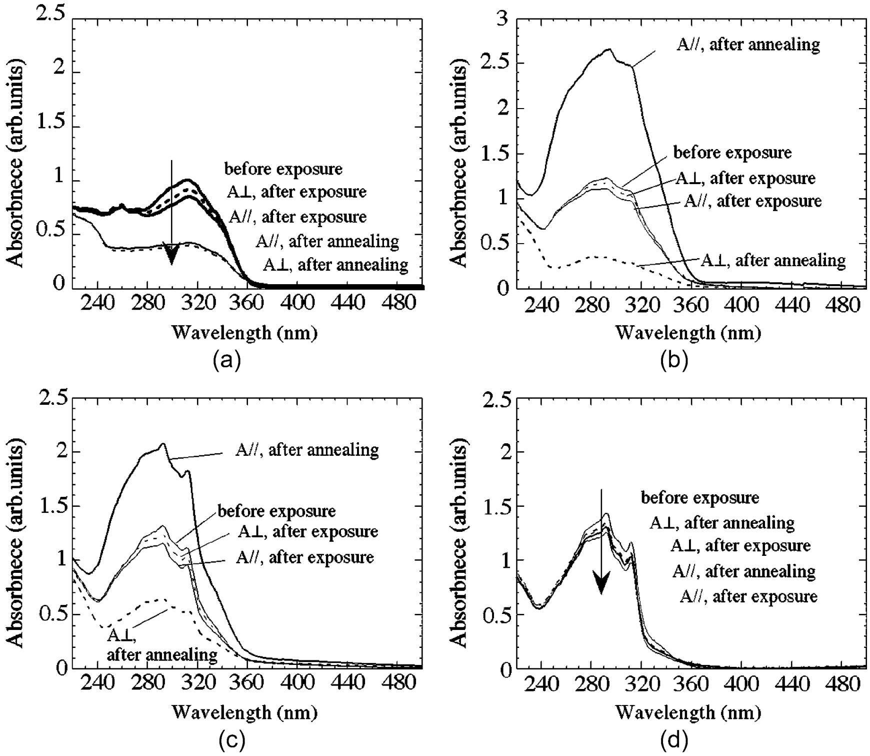

FIGURE 3 UV polarization spectrum of CPLC films before photoirradiation, after irradiation (thin lines), and after subsequent annealing (thick lines). $A_{//}$ is shown as the solid lines and $A_{\perp}$ is shown as the dotted lines. The degree of photoreaction was approximately 15 mol%. (a) **P1** film, annealed at 140°C for 10 min. (b) **P2a** film, annealed at 150°C for 10 min. (c) **P2b** film, annealed at 140°C for 10 min. (d) **P2c** film, annealed at 90°C for 10 min.

The thermally enhanced *S* values at 315 nm as a function of exposure energy are plotted in Figure 4. The **P1** film did not exhibit any in-plane reorientation, while out-of-plane reorientation was observed regardless of the exposure energy. This means that 4-cyanotolane side groups tend to reorient in the out-of-plane direction under elevated temperatures, and MCB side groups cooperatively reorient to the same direction. Similar thermally enhanced cooperative out-of-plane reorientation of 4MCB groups was observed when 4MCB monomer was copolymerized with the large amount of methacrylate monomers comprising 4-methoxybiphenyl side groups [10].

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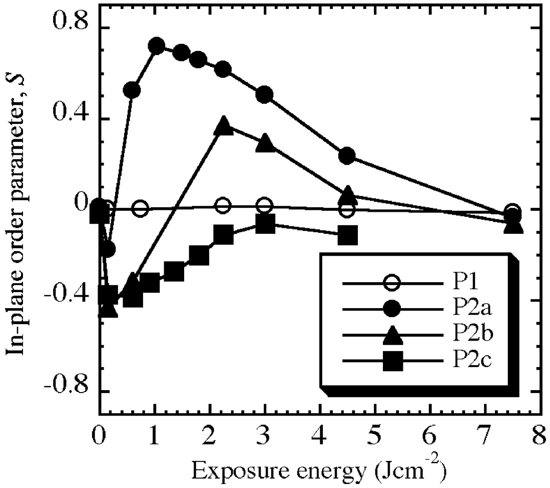

FIGURE 4 Thermally enhanced in-plane order parameter, S, as a function of exposure energy. Annealing temperature: **P1** 140°C, **P2a** 150°C, **P2b** 140°C, **P2c** 90°C.

On the other hand, **P2a–P2c** exhibited in-plane reorientation after annealing the exposed film. For **P2a**, a large positive order parameter ($S > +0.5$) was obtained when the exposure energy was between 0.5 and 3 Jcm^{-2}, where the degree of photoreaction was 10–25 mol%. The generated S values at 290 nm are similar to that at 315 nm. This result indicates a cooperative reorientation both 4MCB and 4-methyltolane mesogenic groups. The generated birefringence at 633 nm is 0.25 when the order parameter is +0.70. This birefringence value is comparable to that obtained by the PMCB6M homopolymer. To attain larger birefringence value, larger in-plane reorientation or copolymerization of LC monomer with the larger inherent birefringent value will be required.

Alternatively, at an early stage of the photoreaction, thermal amplification of the photoinduced negative optical anisotropy was observed for **P2a–P2c**. For **P2b** and **P2c**, large in-plane order of 0.4 was obtained when the degree of photoreaction was less than 10%, although the generated birefringence was less than 0.15. Since the photoreacted groups parallel to **E** reduce the LC nature of the film, the thermal treatment generates a reorientation perpendicular to **E**, in which the LC nature is greater than that in the parallel direction [5].

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CONCLUSION

Methacrylate copolymer liquid crystals comprising 4MCB and tolane moieties were synthesized. All CPLCs exhibited nematic LC nature. The exposing a CPLC film to LPUV light induced an optical anisotropy of the film due to an axis-selective photo-cross-linking reaction of 4MCB groups. Thermally enhanced out-of-plane reorientation occurred regardless of the degree of the photoreaction for CPLC comprising 4-cyanotolane groups. In contrast, for copolymers containing more than 50 mol% of 4-methyltolane groups, photoinduced optical anisotropy reversed and enhanced to parallel to **E** after annealing the exposed film at LC temperature range of the CPLC. Cooperative reorientation of both mesogenic groups was observed and the generated in-plane order parameter was 0.7. The induced birefringence at 633 nm was 0.25, suggesting that the inherent birefringence of 4-methyltolane groups is comparable to that of 4MCB groups.

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