Linearly Polarized Ultraviolet Photoreaction of Poly[6-(4'-cinnamoylbiphenyl-4-yloxy)hexyl methacrylate] and Alignment Behavior of Liquid Crystals on the Resultant Photoreacted Films

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ABSTRACT: Linearly polarized (LP)-ultraviolet (UV) photoreaction of side-chain liquid crystalline polymer of poly[6-(4'-cinnamoylbiphenyl-4-yloxy)hexyl methacrylate] (SLCP **1**) and low-molecular-weight (LMW)-LC alignment behavior on photoreacted SLCP **1** film were studied. LP-UV photoreacted film showed large negative dichroism and aligned LMW-LC with the direction perpendicular to the direction of electric vector (*E*) of incident LP-UV light. It was clarified that the unphotoreacted and non-aggregated mesogenic group played an important role to control the direction of LMW-LC alignment.

KEY WORDS Liquid Crystalline Polymer / Polarized Ultraviolet Photoreaction / Photo-Crosslinking / Cinnamic Ester / Photo-Alignment /

In recent years, much attention has been focused on photo-regulation of low-molecular-weight (LMW) liquid-crystal (LC) alignment on photosensitive polymer surface because it is a clean and photo-patternable technique for the alignment of LMW-LC.¹ Several kinds of materials for photo-alignment have been studied based on anisotropic [2 + 2] photoreaction or photoisomerization using linearly polarized (LP) light.^{2–17} Anisotropic [2 + 2] photo-crosslinking of poly(vinyl cinnamate) (PVCi) film can induce irreversible LMW-LC alignment and several photo-crosslinkable cinnamate derivatives have been synthesized.^{3–9} Side-chain liquid crystalline polymers (SLCPs) containing biphenyl mesogen attached with cinnamoylalkyloxy group have been also studied for LMW-LC alignment.^{10,11} Reversible photo-alignment can be achieved using *E/Z* photoisomerization of azobenzene containing polymer films^{12–15} and spiro-pyran molecules.^{16,17}

For PVCi derivatives, LMW-LC alignment is determined by unphotoreacted cinnamic group, photo-dimerized cinnamic group and *E/Z* photoisomerization of cinnamate side-chain.^{3–8} On the other hand, LMW-LC alignment can be changed by controlling the interaction between the photoreacted mesogenic group and LMW-LC for SLCPs containing biphenyl mesogen attached with cinnamoylalkyloxy group.^{10,11} In addition, photo-crosslinkable materials have a possibility for a practical alignment layer of LC display because of thermal stability caused from their crosslinked structure.^{9,18}

We have recently synthesized photoreactive SLCPs comprising 6-(4'-cinnamoylbiphenyl-4-yloxy)hexyl side group and studied their isotropic (non-LP) photoreaction.^{19,20} Since this side group displays a long chemical structure and the polymer shows liquid crystallinity, anisotropic photoreaction and photo-induced LMW-LC alignment on its anisotropically photoreacted film can be expected to occur effectively.

The purpose of this paper is to study LP-UV photoreaction of poly[6-(4'-cinnamoylbiphenyl-4-yloxy)hexyl-methacrylate] (SLCP **1**) and to clarify the origin of LMW-LC alignment on photoreacted SLCP **1** film. LP-UV photoreaction and optical anisotropy of the film were investigated by polarized UV and FT-IR spectroscopic analyses. The LMW-LC cell was fabricated using SLCP **1** films photoreacted under various reaction conditions and the LMW-LC alignment behavior was evaluated.

EXPERIMENTAL

Materials

Photoreactive SLCP **1**, which was synthesized according to the literature,¹⁹ and the photoreaction of it are shown in Figure 1. This SLCP melts at 144°C, shows smectic phase between 144°C and 157°C, and changes to nematic phase between 157°C and 219°C, respectively. The number average molecular weight was 26800 g mol⁻¹ and the weight average molecular weight 55800 g mol⁻¹. LMW-LC used for fabricating LC cells was a nematic LMW-LC mixture (E7 from Merck, Japan) doped with 0.3 wt% of disperse blue 14.

Figure 1. Chemical structure and photoreaction of SLCP **1**.

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Thin film was prepared on a quartz or CaF_2 substrate by spin-coating from 0.5 w/w% of polymer in methylene chloride solution. Film thickness was controlled between 0.05–0.1 μm . Quartz substrate was used for UV spectroscopy and LMW-LC cell fabrication, and CaF_2 substrate was used for IR measurements.

LP-UV Photoreaction and Techniques

LP-UV photoreaction was carried out using both as-coated and annealed films at room temperature. Annealing of the film was run at 210°C for 10 min and then cooled down slowly to room temperature before irradiation. The LP-UV photoreaction was performed by high-pressure UV light with glan taylor polarizing prisms and a cut filter under 290 nm. Intensity was 150 mW cm^{-2} at 365 nm in all cases. The progress of photoreaction was determined by FT-IR with monitoring the decrease of intensity of the $-\text{C}=\text{C}-$ vibration (1637 cm^{-1}) of cinnamoyl group in **1**.¹⁸ Polarized FT-IR was measured with JASCO FT/IR-410 system with a wire-grid polarizer. Polarized UV-Vis spectroscopy, and preparation and evaluation of an LMW-LC cell were performed as the same method as described previously.^{10,11}

RESULTS AND DISCUSSION

Photoreaction of SLCP **1** Film

It is known that UV spectra of SLCP **1** film change drastically after annealing the film in LC temperature range of the polymer as a result of strong aggregation of the mesogenic group.¹⁹ Therefore, we studied and compared LP-UV photoreaction using both as-coated and annealed films.

Figure 2 compares a progress of the reaction of as-coated and annealed SLCP **1** films under LP-UV irradiation. It exhibits that the reaction is slower for the annealed film than that for the as-coated one. Slow photoreaction for the annealed film is a consequence that the conformational change of the mesogenic group during the photoreaction is necessary due to the aggregation.²⁰

LP-UV Photoreaction and Optical Anisotropy of As-Coated SLCP **1** Film

Figure 3 shows polarized FT-IR spectra of SLCP **1** film before and after LP-UV photoreaction for 3 min, where α_b denotes the absorption before irradiation, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ denote parallel and perpendicular absorption to the direction of electric vector (E) of the incident LP-UV light, respectively. After LP-UV photoreaction, the absorbance at 1725 cm^{-1} ($-\text{C}=\text{O}$), 1637 cm^{-1} ($-\text{C}=\text{C}-$ in cinnamoyl group), 1500 cm^{-1} ($-\text{C}=\text{C}-$ in phenyl group) and 1203 cm^{-1} ($-\text{Ph}-\text{O}-\text{C}=\text{O}$) decreased for both direction, and the decreases at 1637 cm^{-1} , 1500 cm^{-1} , and 1203 cm^{-1} were larger for the parallel absorption due to anisotropic photoreaction of the cinnamoyl group. Note that there were no-change and no-difference for C–H vibration around 2800–2900 cm^{-1} and alkyl biphenyl ether ($-\text{CH}_2-\text{O}-\text{Ph}-\text{Ph}-$) at 1248 cm^{-1} for both direction. This means that the main-chain, methylene spacer and biphenyl group do not change their conformation after LP-UV irradiation.

Figure 2. Time-conversion plot of photoreaction of SLCP **1**.

Figure 3. Polarized FT-IR spectrum for as-coated SLCP **1** film. (a) before irradiation (α_b); (b), (c) after LP-UV irradiation for 3 min; (d) differential spectrum of $\alpha_{\parallel} - \alpha_{\perp}$.

The change in UV-spectrum of as-coated SLCP **1** film irradiated by LP-UV light is shown in Figure 4(a), where $A_{\parallel}$ denotes the parallel absorption and $A_{\perp}$ perpendicular to E of the incident LP-UV light. After LP-UV irradiation, negative dichroism ($\Delta A = A_{\parallel} - A_{\perp} < 0$) was observed due to the anisotropic photoreaction of the mesogenic group. In addition, absorption maximum (λ_{max}) shifted to shorter wavelength and became broader for both direction.

The dichroism ΔA at various irradiation time is plotted in Figure 4(b). The ΔA was negative and increased until 3-min irradiation due to the anisotropic photoreaction of the cinnamoyl group. Furthermore, the ΔA decreased on further irradiation since the photoreaction of the cinnamoyl group in the perpendicular direction could also occur. By means of polarized FT-IR and UV spectroscopies, the degree of photoreaction for 3-min irradiation was 51% and 26% for parallel and perpendicular direction to E , respectively. The λ_{max} of ΔA was 282 nm for the 1-min irradiated film. This wavelength is longer than that of the as-coated spectrum ($\lambda_{\text{max}} = 272 \text{ nm}$, because of the small amount of head-to-head aggregation), that is, same wavelength of the solution of SLCP **1**, where no-aggregation.¹⁹ This will be a consequence that the photoreaction of the non-aggregated mesogenic group ($\lambda_{\text{max}} = 282 \text{ nm}$) preferentially occurs in the initial stage of the photoreaction. On further LP-UV irradiation, ΔA peak shifted gradually to shorter wavelength. This blue shift is a consequence of the different amount of photoreacted and unreacted

Figure 4. (a) Change in UV absorption spectra of as-coated **1** film irradiated with LP-UV light at room temperature. (b) The dichroism ΔA in Figure 4(a). Film thickness was $0.07 \mu\text{m}$.

cinnamoylbiphenyl group between parallel and perpendicular to *E* direction.

LP-UV Photoreaction and Optical Anisotropy of Annealed SLCP **1** Film

On the other hand, the change in absorption spectrum for the annealed thin film was quite different from that for the as-coated one as shown in Figure 5(a). Since the mesogenic group showed strong head-to-tail aggregation, the intensity of the spectrum became small after annealing before irradiation. After LP-UV irradiation, the dichroism ΔA became negative but was small compared to that of the as-coated film as shown in Figure 5(b). For the 1–5 min LP-UV irradiated film, ΔA spectrum was very broad and the peak wavelength of ΔA was around 300–315 nm. This wavelength is compatible with the absorption of the head-to-tail aggregated mesogenic group appearing after annealing.¹⁹ Because of the anisotropic photoreaction of the aggregated mesogenic group, ΔA peak was observed in this region. This means that the aggregated mesogen that the direction is perpendicular to *E* of the incident LP-UV light remains after LP-UV photoreaction. Further irradiation resulted in blue shift of ΔA similarly to that of the as-coated one.

LMW-LC Alignment on the Photoreacted **1** Film

LMW-LC alignment behavior on the LP-UV photoreacted film was evaluated by fabricating a parallel LMW-LC cell using two substrates according to the previous papers.^{10,11} Order parameter ($S = (A_{\parallel} - A_{\perp}) / (A_{\perp} + 2A_{\parallel})$) at 653 nm was used for estimating the

Figure 5. (a) Change in UV absorption spectra of annealed **1** film irradiated with LP-UV light at room temperature. (b) The dichroism ΔA in Figure 5(a). Film thickness was $0.07 \mu\text{m}$.

Figure 6. Order parameter of homogeneous LMW-LC cell as a function of the irradiation time. As-coated film was used for the substrate.

alignment direction and efficiency.

Figure 6 plots the order parameter of the LMW-LC cell as a function of the irradiation time when using as-coated films. Analogous to LP-UV photoreaction of PVCi derivatives, homogeneous monodomain LMW-LC alignment was achieved and the alignment direction was perpendicular to *E* of the LP-UV light.^{3–5} In addition, LMW-LC alignment became distorted on 40-min irradiated film and was no longer observed on 60-min irradiated film since the optical anisotropy of the film was very small and most of the mesogenic group had reacted as shown in Figure 4.

On the other hand, LMW-LC did not align when using annealed films. This means that both remained aggregated mesogenic group and photoreacted mesogenic group (see Figure 1) cannot control LMW-LC align-

Figure 7. Dichroism of the UV-absorption of the annealed SLCP **1** film irradiated by LP-UV light for 3 min. Solid line, before re-annealing; dotted line, after heating the irradiated film at 240°C.

ment. To confirm this, an LMW-LC cell was prepared by using a film that the aggregation of the mesogenic group was decomposed. The destruction of the aggregation was carried out as follows; the LP-UV irradiated film was heated to 240°C to break the aggregation of unreacted mesogenic group and then quenched rapidly to avoid reaggregation. After this procedure ΔA became large and shifted to shorter wavelength like as-coated film (Figure 4(b)) as shown in Figure 7, although it still showed shoulder absorption around 300 nm because of remained aggregation. The LMW-LC alignment on this substrate was much better than that on non-treated one and the alignment direction of LMW-LC was perpendicular to E similarly to the as-coated film.

CONCLUSION

We clarified anisotropic LP-UV photoreaction of poly[6-(4'-cinnamoylbiphenyl-4-yloxy)hexyl methacrylate] (SLCP **1**). The dichroism of the photoreacted mesogenic group was negative and large when using as-coated films, while it was small and broad for annealed films due to the aggregation of the mesogenic group. LMW-LC can uniaxially align on the photoreacted film with the direction perpendicular to E of the incident LP-UV light, although did not align on annealed films. We conclude that LMW-LC alignment is mainly de-

termined by the direction of the unphotoreacted and non-aggregated mesogenic group.

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