Photoinduced Cooperative Reorientation of Photoreactive Liquid Crystalline Copolymer Films Comprised of Cinnamic Acid and Phenylbenzoate Side Groups

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The cooperative molecular reorientation in methacrylate copolymer films comprised of hexamethylene spacer groups terminated with photoreactive hydrogen (H) bonded 4-oxy-cinnamic acid (CA) and 4-oxy-4′-methoxyphenylbenzoate (MBe) in their side chains was investigated by irradiating with linearly polarized ultraviolet light (LPUV) and subsequent annealing. Both CA and MBe side groups were miscible in all the copolymer composition, and axis-selective photoreaction of both side groups was observed. A thermally enhanced cooperative in-plane orientation of both side groups perpendicular to the polarization (E) of LPUV light was obtained when the exposed films were annealed in the liquid crystalline temperature range of the copolymers. The generated birefringence of the reoriented film was 0.12 – 0.16 and the processing temperature was controlled between 85 and 165 °C by adjusting the copolymer composition.

Key words: photoalignment, photo-orientation, cinnamic acid, liquid crystalline polymer, birefringence

1. Introduction

Axis-selective photoreaction of photoreactive polymeric films by the use of linearly polarized (LP) light induces optical and mechanical anisotropy of the film. [1] This technique is applicable to photoalignment layer for monomeric liquid crystal (LC) for LC displays and birefringent films, optical memories, and holographic data storage devices. [2-6] When the axis-selective photoreaction accompanies the molecular reorientation, a large optical anisotropy of the film is generated, which is not only applicable to LC photoalignment layer but also birefringent films and diffraction devices with large birefringence. [7-12]

We have been carried out systematic studies on the photoinduced molecular reorientation of photoreactive liquid crystalline polymers (PLCPs) comprised of cinnamate mesogenic side groups. [8-12] Photoinduced small optical anisotropy is amplified by heating due to the self-organization of LC mesogenic groups in the materials. [8] Additionally, we have found that a PLCP comprised of 4-oxy-cinnamic acid (CA) side groups (P1 in Fig. 1) reveals a large photoinduced molecular reorientation with a high photoreactivity towards LPUV light. [13] Because LC characteristics of P1 is due to hydrogen (H)-bonded dimer of cinnamic acid side groups, methacrylate copolymers and polymer blends having cinnamic acid and 4-oxybenzoic acid (BA) side groups show a similar LC mesomorphism to P1 with wide range of the copolymerization ratio due to the randomly-formed H-bonded LC mesogenic structures. [14] In these cases, cooperative photoinduced molecular reorientation is achieved to demonstrate a controllability of the photoinduced birefringence of the film by tuning the copolymer composition. However, plastic film substrates for a practical purpose cannot be used because the processing temperature to generate the molecular reorientation is higher than 150 °C regardless of the copolymer composition. Copolymerization to P1 with comonomers

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comprised of non-H-bonded 4-oxy-4’-methoxybiphenyl mesogenic side groups was investigated to introduce a controllability of processing temperature. [15] However, cooperative reorientation ability became low when the proportion of 4-oxy-4’-methoxybiphenyl mesogenic side groups increased, and both in-plane and out-of-plane reorientation was generated at elevated temperatures due to low miscibility of both mesogenic side groups. Therefore, new copolymers comprised of CA and non-photoactive side groups that exhibit sufficient miscibility to induce effective cooperative molecular reorientation at low processing temperature are needed.

In this paper, synthesis and thermally enhanced cooperative reorientation behavior of methacrylate copolymers comprised of CA and 4-oxy-4’-methoxyphenylenebenzoxate (MBe) in their side chains are described. Controllability of generated birefringence and processing temperature is achieved by adjusting the copolymer composition.

2. Experimental

![Chemical structure of (co)polymer used in this study.](image)

**Fig. 1.** Chemical structure of (co)polymer used in this study.

2.1. Materials

Figure 1 shows chemical structure of (co)polymer P1-P6 used in this study. Methacrylate monomers with CA and MBe side groups were synthesized according to the literatures. [13,16] (Co)polymers were synthesized by a free radical polymerization in THF solution using AIBN as an initiator. Adjusting the monomer feed ratio controlled copolymer composition. Table 1 summarizes composition, molecular weight, and thermal property of copolymers.

2.2. Photoirradiation and characterization

A thin (co)polymer film was prepared by a spin-coating method on a quartz substrate from THF solution, resulting in a 0.2 μm thick film. The film was irradiated by a 250W ultra high-pressure Hg-UV lamp (10 mW/cm² at 365 nm) equipped with Glan-Taylor polarization prisms and a cut-off filter less than 290 nm. The degree of the photoreaction of CA groups was evaluated by monitoring the absorbance at 314 nm in UV-vis spectroscopy.

For the molecular reorientation, the exposed film was annealed at elevated temperatures for 10 min. The photoinduced and thermally enhanced optical anisotropies of the film were measured by polarizing optical microscopy (POM) and polarization UV-vis spectroscopy.

The in-plane order parameter, S, is expressed in the form of equation 1:

$$S = \frac{A_1 - A_2}{A_1 + 2A_2}$$  (1),

where $A_1$ and $A_2$ are the absorbances parallel and perpendicular to $E$, respectively. $S$ is calculated at 314 nm and 259 nm.

The birefringence ($\Delta n$) of the reoriented film was evaluated using a polarimeter (Shintech OPTIPRO 11-200A) at 547 nm.

3. Results and discussion

3.1. Thermal and spectroscopic properties of copolymers

All the synthesized copolymers exhibit a nematic LC phase between the LC temperature range of homopolymers P1 and P6. POM observation revealed no phase separation in the LC texture. DSC curves show clear Tg and isotropic transition as shown in Fig. 2, indicating the

![DSC second heating curves of copolymers.](image)

**Fig. 2.** DSC second heating curves of copolymers.
effective miscibility of both CA and MBe side groups. Because the LC temperature range of P6 is much lower than that of P1, random copolymerization of P6 units controls the LC temperature range of the copolymers.

Figs. 3a and b show absorption spectra of copolymers in THF solution and films on quartz substrates, respectively. Absorption maxima ($\lambda_{\text{max}}$) at 259 nm and 314 nm are observed, which correspond to absorption of MBe and CA side groups, respectively, and their absorbance is proportional to the copolymerization ratio.

![Fig. 3. UV absorption spectra of copolymers (a) in THF solution, and (b) on quartz substrates.](image)

3.2. Photoreaction of copolymer films

It is known that UV light exposure induces [2+2] photodimerization of CA groups and photo-Fries rearrangement of MBe groups. [13, 17] Figure 4 shows change in the absorption spectrum of a P3 film under exposure to UV light. The absorption bands at 314 nm and 259 nm decreased and that around 370 nm increased. The decrease at 314 nm is due to [2+2] photodimerization of CA groups, while decrease at 259 nm includes both photo-Fries rearrangement of MBe groups and dimerization of CA. The appearance at 370 nm is due to photo-Fries products (formation of phenyl ketone). Other copolymer films showed similar photoreaction behavior. Figs. 5a and b plot absorbances at 314 nm, 259 nm and 370 nm as a function of exposure energy, respectively. It reveals that the photo-Fries rearrangement is slower than the photodimerization due to smaller absorption coefficient of MBe groups to the UV light source. Additionally, the photoreaction rates of the [2+2] photodimerization decreased when the content of MBe groups increased. This is because that the dimerization becomes difficult when the content of CA groups decreases due to the increased distance between two cinnamic acids. [14, 15]

Irradiating a copolymer film with LPUV light induced the axis-selective [2+2] photodimerization and photo-Fries rearrangement to generate a small negative optical anisotropy $[\Delta A(=A_c-A_t)<0]$ of the film. [13, 18] Inset figures of Figs. 5a and b plot photoinduced $\Delta A$ at 314 nm and 259 nm, where the

![Fig. 4. Change in UV absorption spectrum of a copolymer P3 film upon exposure to UV light.](image)

![Fig. 5. Absorbances at 314 nm, 259 nm and 370 nm of copolymer films as a function of exposure energy. Inset shows photoinduced optical anisotropy ($\Delta A$) at 314 nm and 259 nm as a function of exposure energy. Open triangle: P1, open circle: P2, closed square: P3, closed triangle: P4, closed circle: P5.](image)
absorbance of the initial film was normalized one, as a function of exposure energy. The photoinduced negative optical anisotropy of the mesogenic side groups is the same as other PLCPs in previous studies, which is caused by axis-selective photoreaction. [13-15,18] Because the photoreaction of MBe groups was slower than that of CA groups, required exposure energy for maximum ΔA at 259 nm [ΔA_{max}(259)] was greater than that for ΔA_{max}(314). The ΔA_{max}(314) was obtained when degree of the photoreaction of CA groups was approximately 30-50 mol% for all the films because the molecular reorientation in the copolymer films rarely occurred during the exposure.

3.3. Thermal enhancement of photoinduced optical anisotropy

We have previously reported that annealing an exposed P1 film in the LC temperature range amplifies the photoinduced small ΔA of the film perpendicular to the polarization of LPUV light. [13] For copolymers P2-P5, thermally amplified cooperative reorientation of both CA and MBe side groups was observed. For example, Fig. 6 plots change in the UV polarization spectra of a P3 film before and after exposing to LPUV light for 4 mJ/cm², and subsequent annealing at 115 °C for 10 min, when the maximum molecular reorientation was obtained. The degree of the photoreaction of CA groups was 5 %. The irradiating with LPUV light caused a small negative ΔA. After the annealing, the thermal enhancement of the photoinduced ΔA was observed. The in-plane order was changed from 0.02 to 0.60 at 314 nm, and 0.02 to 0.55 at 259 nm. The generated Δn was 0.15. This means that a small amount of the photoreacted CA groups initiated the thermally amplified cooperative molecular reorientation for both CA and MBe side groups.

The annealing procedure generates the self-organization of all the LC mesogenic groups in a perpendicular direction due to its higher LC characteristics. Namely, a small amount of photoreacted CA and MBe groups parallel to the polarization of LPUV light acted as impurities, which reduced the LC mesophorism in the parallel direction. [13] Other copolymer films also exhibited sufficient cooperative molecular reorientation as summarized in Table 2, where the maximum order parameter of both CA and MBe mesogenic groups are greater than 0.45, indicating effective cooperative molecular reorientation.

The exposure energy affected the efficiency of the thermal enhancement of the molecular reorientation because degree of the photoreaction influenced on the self-organization ability of both

![Fig. 6. UV-vis polarization spectra of a P3 film before photoirradiation, after irradiation (thin lines), and after subsequent annealing (thick lines) for 10 min. Solid line represent A0, while dotted lines show A⊥.](image)

Table 2. Thermally enhanced in-plane order parameter and generated birefringence of copolymer films

| copolymer | Annealing temperature (°C) | In-plane order, S|B| (°) | Birefringence (a) | n |
|-----------|---------------------------|------------------|------|------------------|---|
| P1        | 165                       | 0.67             | 0.15 |                  |
| P2        | 140                       | 0.65             | 0.16 |                  |
| P3        | 115                       | 0.60             | 0.15 |                  |
| P4        | 95                        | 0.55             | 0.12 |                  |
| P5        | 85                        | 0.48             | 0.16 |                  |

(a) Determined by polarized absorption spectrum. b) at 547 nm.

![Fig. 7. Thermally enhanced in-plane order, S, at (a) 314 nm and (b) 259 nm of copolymer films as a function of exposure energy. Open triangle: P1, open circle: P2, closed square: P3, closed triangle: P4, closed circle: P5. Annealing temperature: P1: 165°C, P2: 140°C, P3: 115°C, P4: 95°C, P5: 85°C.](image)
mesogenic side groups. Figs. 7a and b plot thermally enhanced S values at 314 nm and 259 nm of copolymer films as a function of exposure energy when the irradiated film is annealed at LC temperature range of the copolymers. For all the copolymers, large cooperative reorientation (S>0.45) was obtained when the exposure energy was 1-10 mJ/cm², where the degree of the photoreaction of CA groups was around 3-7 %. These phenomena are similar to other PLC copolymers comprised of CA side groups that exhibit photoinduced cooperative reorientation. [14,15]

Finally, influence of the annealing temperature on the thermal enhancement of the optical anisotropy was evaluated. Figs. 8a and b plot thermally enhanced S values at 314 nm and 259 nm of copolymer films as a function of annealing temperature. Unlike the PLC copolymers comprised of CA and 4-oxy-4'-methoxybiphenyl side groups, [15] sufficient in-plane cooperative molecular reorientation was achieved when the annealing temperature was LC temperature range of the copolymers, and out-of-plane reorientation was not observed. This is due to effective miscibility of CA and MBe side groups as described in section 3.1.

4. Conclusion

Photoreactive LC copolymers comprised of CA and MBe mesogenic side groups were synthesized and thermally enhanced molecular reorientation behavior of the thin films was investigated. Sufficient cooperative reorientation of both side groups was achieved for all the copolymer films when they were annealed at the LC temperature range of the material after the axis-selective photoreaction of the CA and MBe side groups at the initial stage of the exposure. The generated in-plane order parameter was greater than 0.45 and birefringence was around 0.15. The processing temperature was between 85 °C and 165 °C, which can be controlled by adjusting the copolymer composition. The reoriented films are applicable not only to photoalignment layer for curable LCs, but also to birefringent films by themselves using plastic substrates for a practical purpose.

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References
