Comparison Study on Thermally Stimulated Photoinduced Orientation of Liquid Crystalline Polymer with Cinnamate Side Groups using 313 nm and 365 nm Light

Hiromi Ikoma, Mizuho Kondo, and Nobuhiro Kawatsuki*

Department of Applied Chemistry, Graduate School of Engineering, University of Hyogo, 2167, Shosha, Himeji, Hyogo 671-2280, Japan
*kawatuki@eng.u-hyogo.ac.jp

Polymethacrylates with different type of cinnamate side groups (P1, P2 and P3) were synthesized, and their photochemical and photoinduced reorientation behaviors were investigated using linearly polarized (LP) 313 nm and 365 nm light. P1 and P2 exhibited liquid crystalline (LC) characteristics, but P3 did not. Thin P1 and P2 films underwent thermally stimulated photoinduced molecular reorientation using LP 313 nm or 365 nm light and subsequent annealing, where adjusting the exposure energy and the exposing light wavelength could control the reorientation direction. Type of the cinnamate side groups, resultant photoproducts, and LC characteristics of the polymer played an important role in the thermally stimulated photoinduced molecular reorientation directions and their performances.

Keywords: Liquid crystalline polymer, Cinnamate, Photo-Fries rearrangement, Photoinduced orientation, Photoalignment

1. Introduction

Photoinduced orientation of photo-responsive polymeric films can be utilized for display application such as initial alignment layer for low-molecular-weight liquid crystals (LCs) and birefringent films to improve the viewing qualities [1–6], and also be applicable to diffraction devises to control the polarization of diffraction beams [7,8]. Many kinds of photosensitive polymers comprising photo-responsive moieties have been synthesized and investigated their photo- and optical properties [9,10]. Generally, irradiating with a linearly polarized (LP) light to photosensitive polymeric films undergoes a polarization axis-selective photoreaction, which generates a small optical anisotropy of the reacted film.

When the photoreacted film exhibits LC characteristics, the photoinduced small anisotropy is occasionally amplified by annealing; the photoinduced reorientation with self-organization of LC moieties in the polymeric films has been investigated in the axis-selectively photoisomerizable and photo-cross-linkable groups of LC polymer (LCP) systems [11–14]. In these cases, a small amount of photoproducts, which is axis-selectively formed, plays an important role in the thermally stimulated molecular reorientation of the LCP films. Among them, polymeric films comprised of photo-cross-linkable LC mesogenic side groups with cinnamate or coumarin derivatives are suitable for display applications due to their transparency in the visible region.

We have systematically investigated thermal amplification of photoinduced orientation in LCPs with cinnamate or cinnamic acid side groups using LPUV light [14]. Annealing the photoreacted thin LCP films generated the self-organization of the mesogenic side groups parallel or perpendicular to the polarization (E) of LPUV light. In the previous study, we reported that a polymethacrylate with 4-methoxyphenylcinnamate (MPC) side groups (P1 in Fig. 1) exhibited an axis-selective photoreaction and the resultant small optical aniso-
tropy was significantly amplified perpendicular to $E$ of LPUV light when the films was annealed in the LC temperature range of $P_1$ [15].

It is known that phenyl cinnamate moieties undergo $[2+2]$ photo-dimerization, photo-isomerization and photo-Fries rearrangement under exposing to UV light [16,17]. Meanwhile, the wavelength of the exposing light should influence the formation of type of the photoproducts. In this context, this paper describes influence of the wavelength of the photoreaction of polymethacrylates with different type of cinnamate side groups ($P_1$, $P_2$ and $P_3$) was investigated, and their photoinduced reorientation behavior of thin films was explored. Adjusting the wavelength of the UV light controlled type of the photoproducts, and molecular reoriented direction depended on the type of the photoproducts, LC characteristics of the material and the end-substituent moieties. It was clarified that the $[2+2]$ photodimerized products played an important role in the reorientation parallel to $E$ of LP light, while the photo-Fries products preferentially generated the perpendicular molecular reorientation.

2. Experimental

2.1. Materials

All starting materials were used as received from Tokyo Kasei Chemicals. Polymethacrylates $P_1$, $P_2$ and $P_3$ were synthesized by a solution radical polymerization using AIBN as an initiator from corresponding monomers. Synthetic procedure of a methacrylate monomer possessing a hexamethylene spacer group terminated with 4-methoxyphenylcinnamate side groups ($M_1$) was synthesized according to a literature [15]. Other methacrylate monomers were synthesized by a similar method to $M_1$ using different phenol derivatives.

2.2. Photoreaction

Thin polymer films were prepared by spin-coating a methylene chloride solution of polymers onto quartz or CaF$_2$ substrates. The film thickness was approximately 200 nm to evaluate the reorientation behavior using spectroscopic methods. Photoreactions were performed using an ultrahigh-pressure Hg lamp equipped with Glan-Taylor polarizing prisms and band-pass filter at 313 nm or 365 nm to obtain monochromic LPUV light.

2.3. Characterization

$^1$H-NMR spectra using a Bruker DRX-500 FT-NMR and FT-IR spectra (JASCO FTIR-410) confirmed the monomers and polymers. The molecular weight of the polymers was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, chloroform) calibrated using polystyrene standards. The thermal properties were examined using a polarization optical microscope (POM; Olympus BX51) equipped with a Linkam TH600PM heating and cooling stage in addition to differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 °C min$^{-1}$. The polarization absorption spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms.

The photoinduced optical anisotropy, $\Delta A$, which was evaluated using the polarization absorption spectra, is expressed as Eq. 1,

$$\Delta A = A_{\parallel} - A_{\perp} \quad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to $E$ of LP light, respectively. Annealing an exposed film at an elevated temperature for 10 min induced thermally enhanced molecular reorientation. The in-plane dichroic ratio, $DR$, was evaluated using equation expressed as Eq. 2, where positive (negative) $DR$ values mean perpendicular (parallel) reorientation to $E$.

$$\Delta A = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + A_{\parallel}} \quad (2)$$

3. Results and discussion

3.1. Thermal properties of polymers and photoreaction of films

Table 1 summarizes molecular weight and thermal property of synthesized polymers. $P_1$ and $P_2$ exhibit a nematic LC phase, while $P_3$ does not.
Type of the end-group affects the thermal property of the material.

Figures 2a–c show changes in UV–vis absorption spectra of P1–P3 films upon irradiating with LP 313 nm light, respectively. The absorption band at 313 nm decreased when the exposure energy increased for all films, while new absorption around 360 nm appeared for P1 and P2. This new absorption band was not seen for P3. The decrease in the absorption is due to the [2+2] photo-dimerization of the cinnamate side groups, and the new absorption band at longer wavelength is attributed to photo-Fries rearrangement (Scheme 1). Because P3 possesses methyl substituent at \( \sigma \)-position, inhibiting the rearrangement. Additionally, photoinduced negative optical anisotropy (\( \Delta A < 0 \)) was observed for all films due to the axis-selective photoreaction (insets of Figs. 2).

In contrast, photo-Fries rearrangement for P1 and P2 films was restricted when exposing to LP 365 nm light and the photoreaction required larger exposure energy due to small absorbance for the initial film (Figs. 3a–c). This case also exhibited the photoinduced negative optical anisotropy for the cinnamate side groups (insets of Figs. 3). Because phenoxy moiety may not respond to the absorption at 365 nm, the photo-Fries rearrangement could not occur.

Difference in the photoreaction was confirmed by FT-IR spectroscopy for a P1 film. New absorption bands at 3500, 1690 cm\(^{-1}\) appeared for the 313 nm light irradiation could be assigned to the photo-Fries products (Fig. 4a), while these bands did not seen for the 365 nm light irradiation.

Fig. 2. Changes in UV–vis absorption spectra of (a) P1, (b) P2, and (c) P3 films upon irradiating with LP 313 nm light. Insets plot photoinduced optical anisotropy at 314 nm and 360 nm.

Fig. 3. Changes in UV–vis absorption spectra of (a) P1, (b) P2, and (c) P3 films upon irradiating with LP 365 nm light. Insets plot photoinduced optical anisotropy at 314 nm and 360 nm.

Scheme 1. Type of photoreaction of side groups

Fig. 4. Changes in FT-IR spectra of P1 films upon irradiating with (a) 313 nm and (b) 365 nm light. Inset figures indicate the identifications of absorption bands in each product.

3.2. Thermally stimulated photoinduced molecular reorientation

As previously reported, small photoinduced optical anisotropy of a P1 film was amplified when the exposed film was annealed in its LC temperature range. Figures 5a–c plot changes in polarization absorption spectra of P1–P3 films before and after irradiating with LP 313 nm light, and after subsequent annealing. In all cases, degree of the photoreaction (DP) was approximately 3%,
where the photoinduced optical anisotropy was less than 0.05. Thermal treatment amplified the photoinduced DR values from 0.01 (0.01) to 0.76 (0.69) for (P1 (P2), but no-change was observed for P3 when annealed at any temperatures. The axis-selectively formed photo-products (dimers and photo-Fries products) acted as impurities in the parallel direction to E of LP 313 nm light, inducing the thermally stimulated self-organization of the mesogenic side group perpendicular to E; the LC characteristics in perpendicular direction was larger than that in parallel direction. Additionally, thermal reorganization could not occur for P3 because it did not show LC characteristics.

Similar thermal stimulations perpendicular to E for P1 and P2, and no-changes in P3 were observed when films were exposed to LP 365 nm light with similar degree of the photoreaction (Figs. 6a–c). A small amount of axis-selectively formed photodimerized products also initiated the molecular reorientation. Interestingly, a reversion of the molecular reorientation direction was observed for P1 for the use of LP 365 nm light when DP was approximately 10 % (Fig. 7a). This phenomenon was not observed for the use of LP 313 nm light. A certain amount of axis-selectively formed photodimerized side groups parallel to E without photo-Fries products act as photo-cross-linked anchor for the thermally stimulated reorientation along their direction. The similar reversion behavior of the thermally stimulated photoinduced molecular reorientation direction was reported in LCPs with 4-oxybiphenyl-cinnamate mesogenic side groups, where the formation of the photo-Fries products was restricted [14].

However, for P2, reorientation parallel to E was not detected when DP was 10% (Fig. 7b). In this case, absorbance in both directions decreased, suggesting the out-of-plane motion of the side groups. Thermal treatment induced the molecularly self-organization in a direction where the unreacted mesogenic side groups mostly remained. This motion could not be generated when using LP 313 nm light, because the photo-Fries products inhibit both parallel and out-of-plane motion of the mesogenic side groups in the higher degree of photoreaction.

Fig. 5. Polarization absorption spectra of P1–P3 films before and after irradiating with LP 313 nm light, and subsequent annealing. (a) P1 exposed for 0.01 J/cm2 and annealed at 120 °C. (b) P2 exposed for 0.003 J/cm2 and annealed at 100 °C. (c) P3 exposed for 0.01 J/cm2 and annealed at 100 °C.

Fig. 6. Polarization absorption spectra of P1–P3 films before and after irradiating with LP 365 nm light, and subsequent annealing. (a) P1 exposed for 0.02 J/cm2 and annealed at 120 °C. (b) P2 exposed for 0.02 J/cm2 and annealed at 100 °C. (c) P3 exposed for 0.01 J/cm2 and annealed at 100 °C.

Fig. 7. Polarization absorption spectra of P1 and P2 films before and after irradiating with LP 365 nm light, and subsequent annealing. (a) P1 exposed for 1.0 J/cm2 and annealed at 120 °C. (b) P2 exposed for 0.2 J/cm2 and annealed at 100 °C.
3.3. Influence of exposure energy on thermally stimulated photoinduced molecular reorientation

Figures 8a–c plot changes in absorbance when irradiating with LP 313 nm light, and after subsequent annealing for P1–P3 films, respectively, and Fig. 8d plots the resultant DR values, as a function of exposure energy. Significant thermally stimulated reorientation perpendicular to E (DR > 0.4) was observed for P1 and P2 films when the exposure energy was between 1 and 30 mJ/cm², where the DP was less than 5 %. Further exposing resulted in negligible molecular motion after annealing due to formation of large amounts of photo-Fries products, which reduced LC characteristics of the material. Additionally, no-molecular motion was detected for P3 due to lack of LC characteristics.

In contrast, different thermally stimulated reorientation behavior for P1 and P2 films was observed when using LP 365 nm light (Figures 9a–d). For P1, thermally stimulated reorientation perpendicular to E (DR > 0.4) was observed in the low exposure doses (DP = 1–5 %), but it reversed to parallel to E when DP was 8–15 %. As described in the above section, the [2+2] photodimers parallel to E effectively acted as the photo-cross-linked anchor to thermally stimulate the mesogenic side groups along their direction sufficiently due to no photo-Fries products. However, reversion of the in-plane reorientation direction was not detected for P2 at higher exposure doses. The methyl end moiety inhibited the in-plane motion parallel to E even though the formation of photo-Fries products was restricted.

4. Conclusion

Photoreaction and thermally stimulated photoinduced reorientation of polymethacrylates with cinnamate side groups were investigated using LP 313 nm and 365 nm light. The 313 nm light exposure underwent both photo-Fries rearrangement and [2+2] photodimerization, but the 365 nm light restricted the photo-Fries rearrangement. When the polymer exhibited LC characteristics, thermally stimulated molecular reorientation was generated; a small amount of axis-selectively formed photo-Fries products induced perpendicular reorientation to E of LP light, while [2+2] photodimerized products acted as photo-cross-linked anchor to reorient parallel to E for P1 when the formation of photo-Fries products was inhibited. The reoriented films can be utilized for birefringent films and LC photoalignment layer for display applications.

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