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# A comparative study on the thermally enhanced reorientation between random and diblock methacrylate copolymers with photo-cross-linkable mesogenic side groups by irradiating with linearly polarized ultraviolet light

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## Abstract

The thermally enhanced photoinduced reorientation behavior of random and diblock copolymer films of methyl methacrylate and methacrylate with a photo-cross-linkable 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups was investigated by irradiating with linearly polarized ultraviolet light and subsequently annealing. Random copolymers were synthesized by free radical copolymerization, while diblock ones were obtained by an atom transfer radical polymerization method with a PMMA macroinitiator. The photoinduced optical anisotropy was thermally amplified when the copolymer exhibited a liquid crystalline phase. The random copolymers with a high composition of MCB side groups reverted the orientation direction and inhibited molecular aggregation. For the diblock copolymers, the reorientation behavior was analogous to the methacrylate homopolymer with MCB side groups and transmission electron microscopy revealed a phase separation structure with molecular orientation of the MCB groups.

*Keywords:* Photoorientation; Polymer liquid crystals; Phase separation

## 1. Introduction

There is a great deal of interest in the photo-control of the molecular orientation of polymer films due to its patterned birefringent structures, which can lead to unique optical devices [1–3]. The photoinduced reorientation of numerous photoreactive materials has been studied, including polymer liquid crystals (PLCs) with azobenzene side groups [3–7] and photo-cross-linkable side groups [8–10]. Based on the axis-selective photoreaction, irradiating with linearly polarized (LP) light usually generates the molecular reorientation of these polymer films [2–4]. Azobenzene containing polymers are applicable to reversible birefringent optical storage devices since the generated molecular reorientation can be erased to the initial state [1]. In contrast, photo-cross-linkable PLCs exhibit thermally stable molecular reorientation structure [8], so that the application to the birefringent optical devices, such as optical retarders, polarization converters, and interference filters, etc. can be realized.

During the course of our systematic studies on the photoinduced reorientation of photo-cross-linkable PLCs, it was discovered that irradiating with linearly polarized ultraviolet (LPUV) light controls the reorientation direction and the orientational order of the film [8–14]. The photo-cross-linked mesogenic groups parallel to the polarization (**E**) of LPUV light play an important role in the thermally enhanced photoinduced reorientation of the mesogenic group. Additionally, cooperative molecular reorientation is feasible when a monomer with photo-inactive mesogenic groups is randomly copolymerized [10–12,15]. A high degree of in-plane reorientation and reversion of the reorientation direction was generated in a polymethacrylate with a photo-cross-linkable 4-(4-methoxycinnamoyloxy) biphenyl (MCB) side groups [13,14].

The aim of this study is to investigate the influence of monomer copolymerization without mesogenic side groups on the photoinduced reorientation behaviors of a PLC film

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with MCB side groups. Two types of methacrylate copolymers of a methacrylate with a MCB side group and methyl methacrylate (MMA) were prepared. Random copolymers of these monomers were synthesized by free radical polymerization and the diblock copolymers were synthesized by the atom transfer radical polymerization (ATRP) method. Thin films of these copolymers were irradiated with LPUV light and subsequently annealed. Then the generated optical anisotropy was measured by polarization absorption spectroscopy. The reorientation behavior of the thin films is discussed in relation to the copolymerization ratio and the liquid crystalline nature of the materials. Finally, the morphology of the diblock copolymer films was proved by transmission electron microscopy (TEM).

## 2. Experimental

### 2.1. Materials

Ethyl 2-bromoisobutyrate (EBB, Tokyo Kasei), Cu(I)Cl (Aldrich), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich), anisole (Tokyo Kasei) were used as received without further purification. The methacrylate monomer with a MCB side group (**M1** in Scheme 1) was synthesized according to the literature [13]. MMA was purified by distilling over $CaH_2$. AIBN (Tokyo Kasei) was recrystallized from ethanol. All the other solvents and materials were used as received.

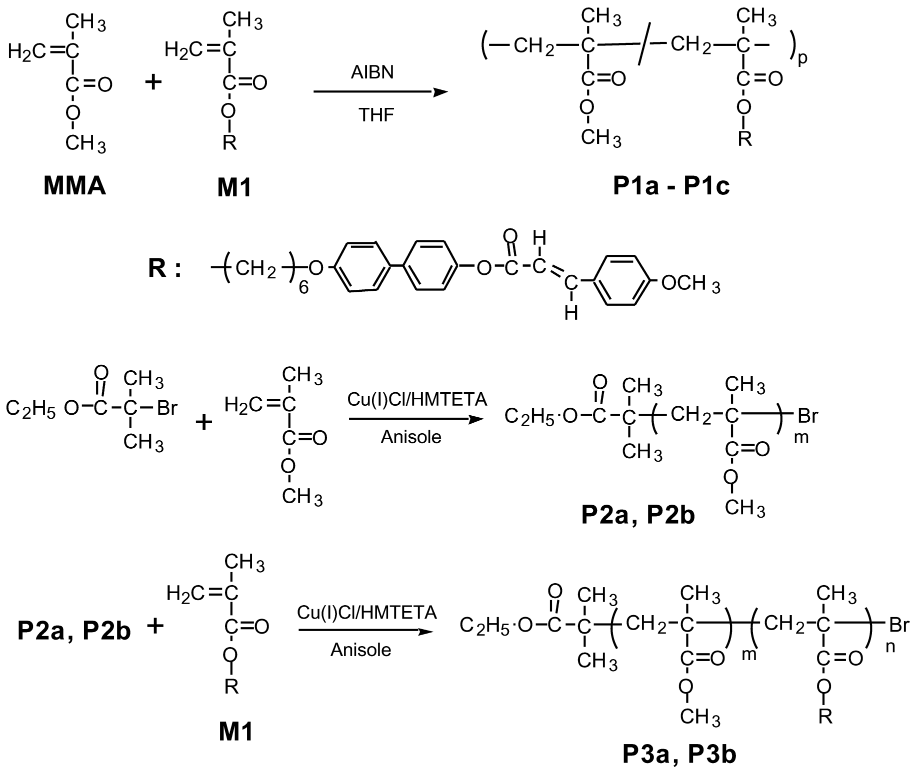
### 2.2. Random copolymer synthesis

Random copolymers **P1a–P1c** were synthesized by a radical solution copolymerization of **M1** and MMA in THF at 53 °C using AIBN as initiator. The monomer and AIBN concentrations were 10 wt %, and 2 mol/l, respectively. Table 1 summarizes the monomer feed ratio, the composition, and the molecular weight of the synthesized random copolymers.

### 2.3. Macroinitiator synthesis

The PMMA macroinitiators, **P2a** and **P2b**, were synthesized using the ATRP method [16] as shown in Scheme 1. The synthetic procedure for **P2a** is described below.

A solution of 73 μl (0.5 mmol) of 2-bromoisobutyrate, 165 μl (1.5 mmol) of HMTETA, 150 mg (1.5 mmol) of Cu(I)Cl, and 5.0 g (50 mmol) of dry MMA in 10 ml of anisole was bubbled with dry argon to remove the air from the solution. After bubbling for 30 min, the ample was sealed and the solution was heated at 80 °C for 5 h. The solution was poured into diethyl ether, and the precipitated polymer was dissolved in chloroform. To remove the catalyst the solution was passed through a neutral $Al_2O_3$ column with chloroform as eluent. The colorless solution



Scheme 1.

Table 1
Feed, composition and molecular weight of random copolymers

| Polymer | Feed (mol %) | | Composition (mol %)[a] | | Yield (%) | Molecular weight[b] | |
|---|---|---|---|---|---|---|---|
| | MMA | **M1** | MMA | **M1** | | $M_n \times 10^{-4}$ | $M_w/M_n$ |
| **Pla** | 50 | 50 | 53 | 47 | 45 | 3.1 | 2.3 |
| **P1b** | 70 | 30 | 73 | 27 | 50 | 4.4 | 2.0 |
| **P1c** | 90 | 10 | 90 | 10 | 49 | 3.6 | 1.8 |

[a] Determained by $^1$H NMR.
[b] Determained by GPC with polystyrene standards and $CHCl_3$ eluent.

was concentrated under reduced pressure and precipitated twice into diethyl ether. The polymer was collected and dried under vacuum for two days. Yield 1.95 g (39 %). $M_n$ (GPC) = 8200, $M_w/M_n = 1.09$.

**P2b** was synthesized using the same method. Table 2 summarizes the detailed experimental conditions.

### 2.4. Diblock copolymer synthesis

Diblock copolymers **P3a** and **P3b** were synthesized by the ATRP method using the PMMA macroinitiators (Scheme 1). The synthetic procedure is similar to the synthesis of the PMMA macroinitiators and the detailed experimental conditions are summarized in Table 2.

### 2.5. Photoreaction

Copolymer 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 by light from a 250W 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.

### 2.6. Characterization

The copolymer composition was determined by $^1$H NMR spectra with a Bruker DRX–500 FT–NMR system. 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. Additionally, the molecular weight of diblock copolymers was calculated by the peak intensities of MMA at 3.59 ppm ($COOCH_3$) and **M1** at 3.76 ppm ($PhOCH_3$) in the $^1$H NMR spectrum, using the molecular weight of the PMMA macroinitiators. The thermal properties were examined by differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 K/min. A polarization optical microscope (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. Eq. (1) expressed the in-plane order parameter, $S$.

$$S = \frac{Ap - As}{A(\text{large}) + 2A(\text{small})} \tag{1}$$

where $A_p$ and $A_s$ are the absorbances parallel and perpendicular to **E**, respectively. $A_{(\text{large})}$ is the larger value of $A_p$ and $A_s$, and $A_{(\text{small})}$ is the smaller one. Therefore, a negative $S$ value indicates that the orientational direction is perpendicular to **E**, and positive $S$ means a parallel orientation.

The thin film for the morphology observation was prepared by casting a chloroform solution of the polymer on a distilled water surface. The resultant thin film was transferred to a Cu-mesh for TEM measurement (JEOL JEM200CX).

Table 2
Experimental conditions composition and molecular weight of polymers synthesized by ATRP method

| Polymer | Init[a] | Monomer | $[M]_0/[I]_0$[b] | Time (h) | Conv. (%) | Yield (%) | Composition[c] (mol %) | | Molecular weight | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | MMA | **M1** | By NMR × $10^{-4}$ | By GPC[d] | |
| | | | | | | | | | | $M_n \times 10^{-4}$ | $M_w/M_n$ |
| **P2a** | EBB | MMA | 100 | 5 | 81 | 39 | 100 | 0 | – | 0.82 | 1.09 |
| **P2b** | EBB | MMA | 250 | 24 | 97 | 38 | 100 | 0 | – | 2.4 | 1.12 |
| **P3a** | **P2a** | **M1** | 240 | 45 | 45 | 25 | 52 | 48 | 5.5 | 3.9 | 1.26 |
| **P3a** | **P2b** | **M1** | 90 | 45 | 43 | 27 | 77 | 23 | 6.1 | 4.9 | 1.18 |

[Initiator]/[HMTETA]/[Cu(I)Cl] = 1:3:3. Reaction temperature was 80 °C for **P2a** and **P2b** synthesis, and 100 °C for **P3a** and **P3b**.
[a] Initiator, EBB; ethyl 2 bromoisobutyrate.
[b] Feed molar ration of the monomer to initiator.
[c] Determined by $^1$H NMR.
[d] Determinted by GPC with polystyrene standards and $CHCl_3$ eluent.

## 3. Results and discussion

### *3.1. Polymer synthesis*

Random copolymers **P1a–P1c** were synthesized in THF by the usual radial polymerization. The $M_n$ of the random copolymers were 31,000–44,000 and $M_w/M_n = 1.8$–2.3, which are summarized in Table 1. These values are similar to other previously synthesized copolymer liquid crystals using the free radical solution polymerization [11,12]. The macroinitiators **P2a** and **P2b**, and diblock copolymers **P3a** and **P3b** were synthesized in anisole by the ATRP method [16]. The catalyst system of Cu(I)Cl/HMTETA was used to prepare the PMMA macroinitiators with different molecular weights [17,18]. The resulting polymers had $M_n = 8200$ with $M_w/M_n = 1.09$ for **P2a**, and $M_n = 24000$ with $M_w/M_n = 1.12$ for **P2b**. After purifying the PMMA macroinitiators were subjected to further ATRP of **M1** using the same catalyst. In all cases, the resulting diblock copolymers **P3a** (from **P2a**) and **P3b** (from **P2b**) show monomodal GPC curves with increased molecular weight when compared to the macroinitiators. Table 2 details the polymerization conditions and molecular weights of these polymers. The increase in molecular weight without a significant increase in the $M_w/M_n$ for the diblock copolymers indicates an effective initiation of ATRP, which is also observed in other block copolymers using the ATRP method [16–20].

### *3.2. Thermal and spectroscopic properties of the polymers*

Table 3 summarizes the thermal and spectroscopic properties of the synthesized copolymers and the homopolymer of **M1** (**P4**). For the random copolymer series, nematic LC phase is observed for **P1a** and **P1b**, but **P1c** does not exhibit a LC phase. **P1a** and **P1b** show one glass transition ($T_g$) and a clearing point ($T_i$), and $T_i$ decreases as the MMA composition increases. Additionally, the enthalpy for the LC-isotropic phase transition ($\Delta H_{NI}$) is much smaller than that of **P4**, which implies that the MMA unit lowers the liquid crystalline nature of these copolymers. In contrast, the diblock copolymers **P3a** and **P3b** show nematic phase similar to the homopolymer **P4** after melting, which implies the phase separation between PMMA and LC blocks. The LC transition temperatures of **P3a** and **P3b**, however, are slightly lower than that of **P4**, suggesting that the LC structures are disordered near the microphase interface as observed in other LC block copolymers [21,22].

Table 3
Thermal and spectroscopic properties of copolymers

| Polymer | Thermal property[a] | | | | | $\lambda_{max}$ (nm) | |
|---|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_i$ (°C) | $\Delta H_{NI}$ (J/g) | Film[b] | Solution[c] |
| **Pla** | 78 | – | – | 215 | 0.9 | 292 | 314 |
| **Plb** | 92 | – | – | 178 | 0.7 | 298 | 314 |
| **Plc** | 98 | – | – | – | – | 314 | 314 |
| **P3a** | 101 | 113 | 2.3 | 315 | 1.2 | 292 | 314 |
| **P3b** | 100 | 108 | 1.8 | 319 | 1.1 | 293 | 314 |
| **P4** | 105 | 116 | 2.2 | 326 | 3.5 | 292 | 314 |

[a] Determained by DSC.
[b] On quartz substrate.
[c] In methylene chloride solution.

The absorption spectra of the copolymer films are shown in Fig. 1. It reveals that the absorption spectrum of the films is similar when the copolymer exhibits a LC phase, and the absorption maximum ($\lambda_{max}$) is shifted to a shorter wavelength compared to the solution (Table 3). Additionally, the absorption band of **P1b** shifted slightly to a longer wavelength when compared to other LC copolymers as shown in inset of Fig. 1. In contrast, the absorption spectrum of the **P1c** film is similar to that of the solution. The difference in absorption spectrum between the film state and the solution for the LC copolymers results from the head-to-head (H–H) association of the mesogenic cinnamoyloxybiphenyl groups in the film state [23,24].

### *3.3. Thermally enhanced photoinduced reorientation of random copolymers*

The photoreaction of the copolymer films was conducted by irradiating with UV light. After exposure all the copolymer films became insoluble because the [2 + 2] photo-cycloaddition reaction, the main photoreaction of the MCB group, proceeded [13]. We previously reported how to enhance thermally the photoinduced optical anisotropy and how to control the reorientation direction of the MCB groups for **P4** [13,14]. Applying this knowledge to investigate the reorientation behavior of the copolymers, thin films were exposed to LPUV light and then annealed at elevated temperatures.

Fig. 2 shows the polarized absorption spectral differences between a **P1a** film with exposure to LPUV light and the same film after annealing at 175 °C for 10 min, where the

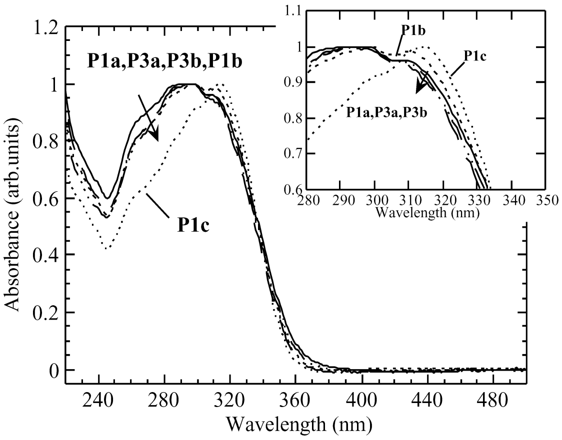


Fig. 1. Absorption spectra of the copolymer films. The inset magnifies the figure.

exposure energy is (a) 40 mJ cm$^{-2}$, and (b) 400 mJ cm$^{-2}$, respectively. Both energy doses generated small negative optical anisotropy ($\Delta A = A_p - A_s < 0$) after irradiating because of the axis-selective photoreaction of the MCB groups [13]. After annealing, for the 40 mJ cm$^{-2}$ dose, the negative optical anisotropy increased and the generated orientational order ($S$) was thermally amplified from $-0.014$ to $-0.57$. On the other hand, the orientational order reverts ($\Delta A = A_p - A_s > 0$) for the 400 mJ cm$^{-2}$ dose and the generated $S$ changed from $-0.03$ to $+0.50$ as shown in Fig. 2(b). Fig. 3 plots the induced $S$ as a function of exposure energy. The thermally enhanced reorientation direction changed from perpendicular to parallel to **E** when the exposure doses were increased. The negative anisotropy was amplified when the degree of the photoreaction was less than 12 mol %. When the degree of the photoreaction was between 15 mol % and 28 mol % the reorientation direction reverted parallel to **E**. Additionally, the molecular reorientation was barely enhanced when the exposure energy was more than 750 mJ cm$^{-2}$ because the high degree of cross-linking restricts the mobilization of the mesogenic groups. We reported that a small amount of photoproducts parallel to **E** induced the thermal amplification perpendicular (a negative $S$) of the **P4** homopolymer. This is because the photoproducts parallel to **E** lower the liquid crystalline nature and the reversion of the orientation direction is caused by the command effect of the photo-cross-linked MCB groups parallel to **E**. Additionally, reorientation perpendicular to **E** is accompanied by a red-shift in the absorption band after annealing due to the head-to-tail (H–T) aggregation of the mesogenic MCB groups and the resulting $S$ was less than $-0.3$ [13]. In contrast, a high reorientational order for **P1a** was obtained for both in-plane reorientation directions and the absorption bands after annealing are similar to that before exposure as shown in Fig. 2a, suggesting that H–T aggregation of the mesogenic groups is suppressed by the randomly copolymerized MMA units.

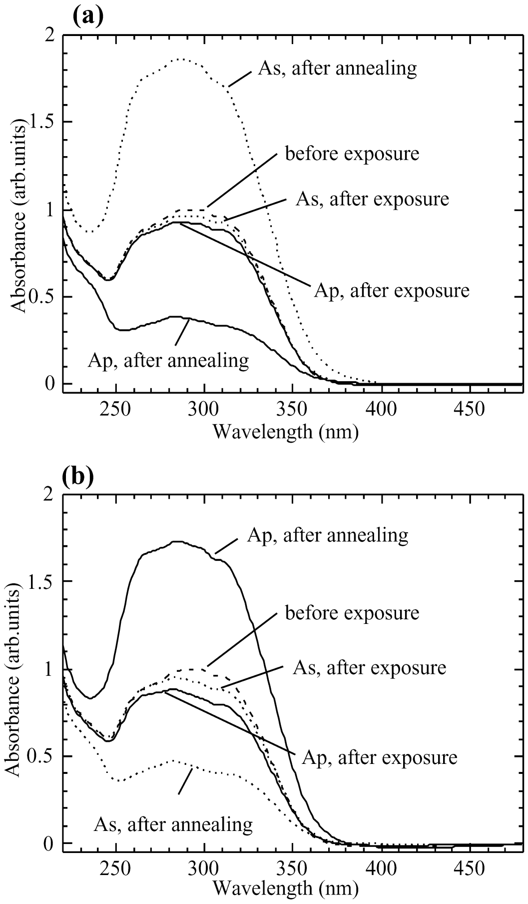


Fig. 2. UV polarization spectrum of **P1a** film before photoirradiation, after irradiating, and after subsequent annealing at 175 °C for 10 min. $A_p$ is the solid lines, and $A_s$ is the dotted lines. (a) 40 mJ cm$^{-2}$ doses; (b) 400 mJ cm$^{-2}$ doses.

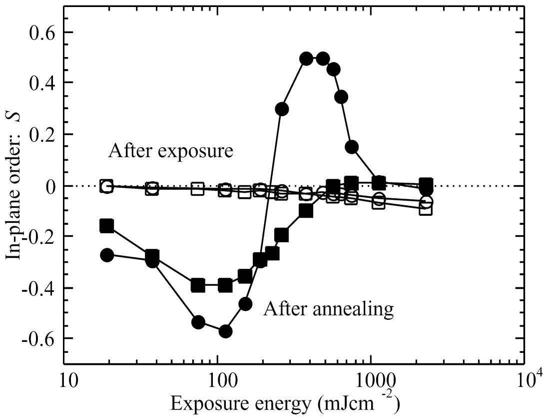


Fig. 3. Order parameter $S$ of **P1a** and **P1b** films after irradiating with LPUV light (open points) and after subsequent annealing (closed points) as a function of the exposure energy. The circles and squares denote $S$ for **P1a** and **P1b** films, respectively.

Fig. 3 also plots the generated $S$ for an irradiated **P1b** film that was annealed for 10 min at 125 °C as a function of exposure doses. When the exposure energy was less than 200 J cm$^{-2}$ the photoinduced negative optical anisotropy was thermally enhanced without molecular aggregation. This behavior is similar to a **P1a** film, whereas the reorientation direction did not revert ($S > 0$) regardless of the energy dose. We previously reported that approximately 15–30 mol % of the photo-cross-linked mesogenic MCB groups was required for the reversion of the reorientation direction [13,25], which confirms the results obtained with **P1a**. The liquid crystalline nature of the **P1b** film, however, was diminished after a high degree of photoreaction because the amount of non-photoreacted MCB groups was small. Thus, the photo-cross-linked MCB groups parallel to **E** cannot reorient the surrounding non-photoreacted MCB groups. Furthermore, annealing a exposed **P1c** film between 80 and 140 °C did not enhance the optical anisotropy. Fig. 4 shows spectral differences in the polarized absorption between a **P1c** film exposed to LPUV light with 180 mJ cm$^{-2}$ doses, and the same film after subsequently annealing for 10 min at 100 °C, which indicates that the annealing diminishes the photoinduced optical anisotropy.

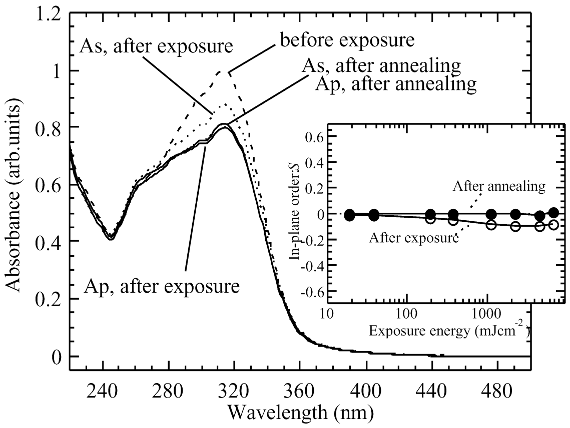


Fig. 4. UV polarization spectrum of **P1c** film before photoirradiation, after irradiating with 180 mJ cm$^{-2}$ doses, and after subsequent annealing at 100 °C for 10 min. The inset shows the order parameter $S$ of **P1c** film after irradiating with LPUV light (open points) and after subsequent annealing (closed points) as a function of the exposure energy.

This tendency is observed for all exposure doses as plotted in the inset of Fig. 4. After annealing the optical anisotropy disappeared because of the randomization of the mesogenic groups above the $T_g$ of the film. These results suggest that the liquid crystalline nature of the film plays an important role in the thermal enhancement of the photoinduced in-plane optical anisotropy.

### *3.4. Thermally enhanced photoinduced reorientation of the diblock copolymers*

Fig. 5 plots the induced in-plane order, $S$, of irradiated diblock copolymer films that were annealed at 175 °C for 10 min, as a function of the exposure doses. For a **P3a** film, the photoinduced $S$ was negatively enhanced from $-0.007$ to $-0.14$ when the exposure doses were less than 30 mJ cm$^{-2}$. For **P3a** and **P3b**, the red-shift of the absorption bands after the annealing, which resulted from the H–T aggregation, was observed similarly to homopolymer **P4**. Unlike the random copolymers the PMMA block in the copolymers cannot inhibit the molecular association of the mesogenic groups. Moreover, when the exposure doses were between 150 J cm$^{-2}$ and 900 J cm$^{-2}$ and the degree of the photoreaction was around 15–30%, the reorientation direction reverted for both diblock copolymers. The $S$ was changed from $-0.03$ to $+0.52$ for **P3a** and from $-0.03$ to $+0.21$ for **P3b**. These reorientation behaviors are the same as **P4**, which suggests that the photoreacted mesogenic MCB groups in the LC block controls the thermal amplification and the reversion of the photoinduced optical anisotropy of the film regardless of the PMMA fraction amount. Consequently, the thermal properties of the LC block are almost independent on the copolymer composition, but the induced positive $S$ decreased as the composition of the PMMA unit increased.

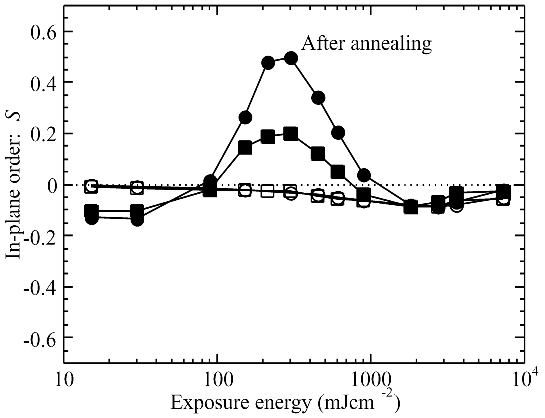


Fig. 5. Order parameter $S$ of **P3a** and **P3b** films after irradiating with LPUV light (open points) and after subsequent annealing at 175 °C (closed points) as a function of the exposure energy. The circles and squares denote $S$ for **P3a** and **P3b** films, respectively.

For homopolymer **P4**, we reported that positive $S$ values around $+0.68$ were obtained when the exposed films were annealed between 135 and 250 °C, which corresponds to the LC temperature range of the polymer [13]. The similar argument is varied with the reorientation behavior of random copolymer **P1a**,[1] but not for **P3a** and **P3b**. The induced positive $S$ value increased as the annealing temperature increased as plotted in Fig. 6. When the annealing temperature was 200 °C the maximum $S$ of $+0.61$ and $+0.31$ were obtained for **P3a** and **P3b**, respectively. In addition, unlike **P4**, which reached a maximum $S$ value of $+0.68$ in 5 min at an annealing temperature of 150 °C, the generated $S$ value at 150 °C increased with annealing time as plotted in Fig. 7. However, the generated S value of **P3b** is smaller than **P3a**, and the maximum $S$ values for the **P3a** and **P3b** films are still smaller than when annealed at 200 °C. These results suggest that during annealing the reorientation of the MCB groups is proceeded by a microphase separation between the PMMA and LC blocks and that the effective reorientation of the MCB groups during the phase separation may be inhibited as the PMMA fraction is increased.

### *3.5. TEM observation*

To investigate further the reorientation behavior of the diblock copolymer **P3b**, the thermally induced phase separation morphology was observed by TEM. Fig. 8a displays a TEM image of a **P3b** film subjected to 190 °C for 1 day. The LC block appears dark due to straining with $OsO_4$, which reveals a microphase-separated lamellar morphology with a spacing of 49 nm. This morphology is expected from a volume fraction (LC fraction, $f = 0.61$) of the PMMA and LC blocks and is similar to other diblock copolymer LCs [21,25].

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[1] The $S$ value around $+0.50$ was obtained for a **P1a** film when the film exposed for 350 mJ cm$^{-2}$ doses was annealed at between 150 and 190 °C.

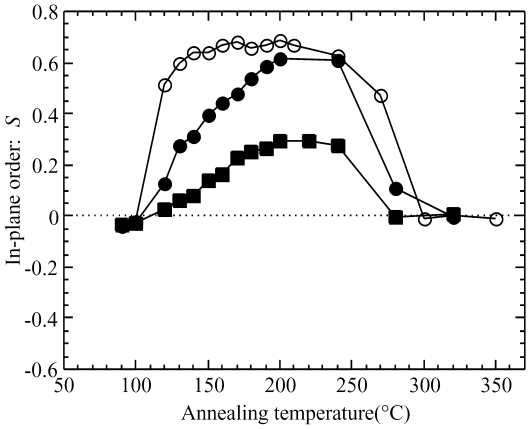

Fig. 6. Annealing temperature dependence of the in-plane order parameter $S$ of **P3a**, **P3b** and **P4** films. The exposure energy was 450 mJ cm$^{-2}$ for all films. The closed circles and squares, and open circles denote $S$ for **P3a**, **P3b** and **P4** films, respectively.

Fig. 8b and 8c show TEM images of the film exposed to LPUV light for 350 mJ cm$^{-2}$ and then annealed at 170 and 190 °C for 1 day, respectively. When annealing at 190 °C the phase separation with molecular orientation was generated as shown in Fig. 8c, but the phase separation structure was unclear for the film annealed at 170 °C (Fig. 8b). This phase separation structure was not observed when the exposed film was annealed at 150 °C. Even for the film annealed at 190 °C in the reoriented film, the phase separation structure seemed partially non-uniform. The interaction of the interface between the PMMA block and the LC block including the photo-cross-linked mesogenic groups suppressed the phase separation because the photo-cross-linking forms a LC block network. Further studies on the relationship between the thermally enhanced reorientation and the phase separation behavior of the diblock copolymer LCs are in progress.

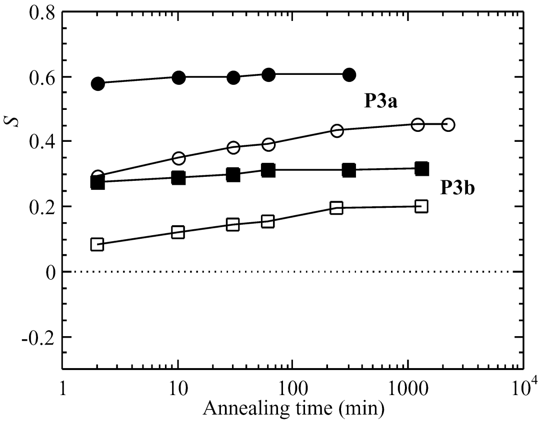

Fig. 7. Order parameter $S$ of **P3a** and **P3b** films annealed at 150 °C (open points) and at 200 °C (closed points) as a function of the annealing time. The exposure energy was 450 mJ cm$^{-2}$ for all films. The circles and squares denote $S$ for **P3a** and **P3b** films, respectively.

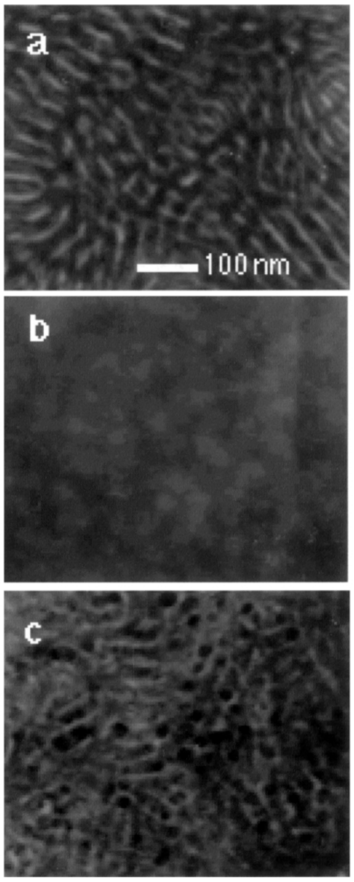

Fig. 8. TEM micrographs of the diblock copolymer **P3b**. (a) Annealed at 190 °C for 1 day, (b) irradiated with LPUV light for 350 J cm$^{-2}$ and subsequently annealing 170 °C for 1 day, (c) irradiated with LPUV light for 350 J cm$^{-2}$ and subsequently annealing 190 °C for 1 day.

## 4. Conclusions

A study comparing the reorientation behavior between random and diblock copolymers of MMA and methacrylate with a photo-cross-linkable MCB side group was conducted by exposing to LPUV light and subsequently annealing. The random copolymers were synthesized by free radical copolymerization, while the diblock copolymers were synthesized by the ATRP method with a PMMA macro-initiator. For the random copolymer series, the LC temperature range of the copolymer decreased as the MMA composition increased, but the liquid crystalline nature of the diblock copolymers is similar to the homopolymer with MCB groups. All the copolymer films exhibited small negative optical anisotropy ($\Delta A < 0$) after exposure to LPUV light, which was generated by the axis-selective photo-cross-linking reaction of the MCB side groups. For the random copolymer LC films, the negative optical anisotropy was thermally amplified and the molecular aggregation was suppressed. Additionally, the reorientation direction was reverted if the MMA composition was 53 mol %. For the diblock copolymers, the reorientation behavior was similar to the homopolymer and the orientational order decreased as the PMMA fraction increased. The differences in the thermal properties and the liquid crystalline nature among the copolymers play an important role in the thermally enhanced photoinduced optical anisotropy. In case of the diblock copolymers, nanophase separation of the thin film was observed by the TEM for the non-exposed film, but exposed film with molecular reorientation of the LC units exhibited non-uniform phase separation structures. Controlling the phase separation structures with the molecular orientation of the LC units may provide new applications in optical birefringent devices. Further studies are currently underway.

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