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Photoinduced orientation of liquid crystalline copolymer films containing 4-oxybenzoic acid side groups and photo-cross-linkable mesogenic side groups

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Abstract

The cooperative molecular reorientation in methacrylate copolymer films with hexamethylene spacer groups terminated with 4-oxybenzoic acid (BA) and 4-(4-methoxycinnamoyloxy)biphenyl (MCB) in their side chains was investigated by irradiating with linearly polarized ultraviolet light (LPUV) and subsequent annealing. A high degree of cooperative in-plane reorientation of both the BA and MCB groups was obtained when the composition of the BA groups was greater than 50 mol% and hydrogen (H)-bonded LC mesogenic dimers of BA molecules existed. On the other hand, the molecular reorientation was restricted when the BA groups did not form H-bonds. It was clarified that the amount of axis-selectively photoreacted MCB groups and the H-bonds of the BA groups that exhibit a LC nature play important roles in the thermally enhanced molecular reorientation.

Keywords: Liquid crystalline polymer; Photoinduced orientation; H-bonds

1. Introduction

The molecular orientation in polymeric films using a photo-exposure technique induces a large optical anisotropy of the film, which can be applied to various birefringent optical devices, optical memories, and holographic data storage devices [1]. Based on Weigert's effect, irradiating with linearly polarized (LP) light easily creates a small optical anisotropy in a photoreactive film. However, to generate a large optical anisotropy, a molecular reorientation should accompany the axis-selective photoreaction [1–6]. Various types of azobenzene-containing polymeric films have been reported as materials that generate a large photoinduced optical anisotropy based on an axis-selective *trans-cis-trans* photoisomerization where a reversible photoinduced optical anisotropy is obtained by adjusting the polarization of the writing LP light beams [2–4]. Alternatively, photo-cross-linkable polymer liquid crystalline (PPLC) films containing cinnamate groups have also been reported, which reveal a stable molecular orientation [5,6]. One merit of cinnamate derivatives is their transparency in the visible region, which is important for display applications.

During the course of our systematic study on PPLCs that show a photoinduced molecular orientation, we found that polymethacrylates with 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side groups exhibit efficient in-plane molecular reorientations [6a]. The LC nature of the material allows the axis-selective photoreaction of the MCB side groups to generate a small photoinduced optical anisotropy of the film, while a subsequent thermal treatment enhances the molecular reorientation either perpendicular or parallel to the polarization direction (**E**) of LP light, depending on the degree of the photoreaction. This reoriented film is applicable to passive optical devices such as birefringent films for liquid crystal displays, the alignment layer for liquid crystals, and polarization holographic gratings [6b,7].

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It is known that hydrogen (H)-bonded dimers of aromatic acid derivatives exhibit a LC phase [8]. A H-bonded polymer network of polyacrylates with hexamethylene or decamethylene spacer groups terminated by 4-oxybenzoic acid (BA) in their side chains reveals a LC phase [9]. Kato et al. have conducted systematic studies on supramolecular formation of polymers with H-bonded new mesogenic groups of BA and a several types of monomers [10]. These supramolecular LC materials reveal new types of LC monomers and polymers, which can induce new functions using H-bonds. Alternatively, Medvedev et al. have studied the photooptical property of polyacrylates with BA in the side chains mixed with low-molecular-mass dopants comprised of azobenzene moieties, which construct the H-bond formation with BA [11]. The photoinduced orientation of the thin film is observed based on the photoinduced reorientation of azobenzene moieties, although the films are colored in the visible region. Few studies have examined the photoinduced orientation in transparent photoreactive polymeric films with H-bonded mesogenic moieties [12].

To introduce the photoinduced reorientation ability to the polymeric film with BA side groups, copolymerization with comonomers with MCB side groups is effective. In this context, this paper describes the synthesis of methacrylate copolymers that contain BA and MCB side groups, and the characterization of their H-bonded LC properties. The influence of the copolymerization ratio on H-bonding and the photoinduced molecular reorientation behavior of the copolymer films are investigated by temperature-dependent FTIR and polarization UV spectroscopies.

2. Experimental

2.1. Materials

All starting materials were used as received from Tokyo Kasei Chemicals. Methacrylate monomers were synthesized according to the literature [6a,12]. Copolymerization was performed by a free radical copolymerization using AIBN as an initiator in THF solution. Detailed polymer synthesis is described in Supplementary data.

2.2. Photoreaction

Thin polymer films, which were approximately 0.1–0.3 μm thick, were prepared by spin-coating a chloroform or THF solution of copolymers (0.5–2 w/w%) onto quartz or KBr substrates. The photoreactions were performed using an ultra-high-pressure Hg lamp equipped with Gran-Taylor polarizing prisms and a cut-filter under 290 nm to obtain LPUV light with an intensity of 150 mW cm^{-2} at 365 nm. The degree of the photoreaction was estimated by monitoring the decrease in absorbance at 315 nm using UV spectroscopy.

2.3. Characterization

The molecular weight of a polymer was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluant, chloroform or THF), which was 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 FTIR spectra were recorded through a JASCO FTIR-410/IRT-3000 system with a Linkam TH600PM heating and cooling stage.

The thermally enhanced molecular reorientation was conducted by annealing an exposed film at an elevated temperature for 10 min. The in-plane order was evaluated using the dichroism, D, and the order parameter, S, which are expressed as in Eqs. (1) and (2), respectively [12]. Eq. (2) means that the reorientation direction is parallel to **E** of the LPUV light for $S > 0$ and perpendicular for $S < 0$.

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \tag{1}$$

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

where $A_{\parallel}$ and $A_{\perp}$ (2) are the absorbances parallel and perpendicular to **E**, respectively, and $A_{(\mathrm{large})}$ is the larger value of $A_{\parallel}$and $A_{\perp}$, while $A_{(\mathrm{small})}$ is the smaller one. D and S values are estimated at the absorption maxima of each copolymer film.

3. Results and discussion

3.1. Thermal and spectroscopic properties of copolymers

All copolymers shown in Fig. 1 were synthesized by free radical copolymerization. Adjusting the feed ratio of the two methacrylate monomers controlled copolymerization ratio. Table 1 summarizes the molecular weights and thermal properties of synthesized copolymers. Fig. 2 shows the UV–vis absorption spectra of the copolymer films on quartz substrates. It reveals two absorption maxima, 262 nm and around 320 nm, which correspond to the absorption bands of the BA and MCB groups, respectively.

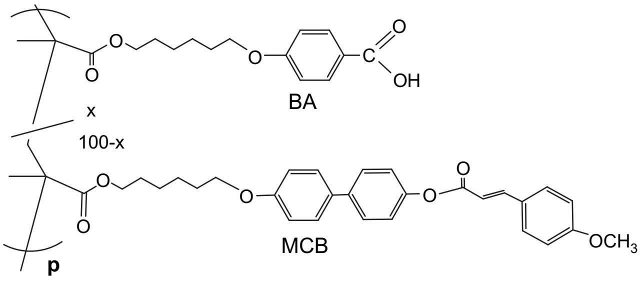

Fig. 1. Copolymers used in this study.

Table 1
Molecular weight and thermal property of synthesized copolymers

Polymer	x[a]	Molecular weight		Thermal property[c] (°C)
		$M_n \times 10^{-4}$ [b]	M_w/M_n	
P1a	100	1.53	1.8	G 157 N 179 (31.1) I
P1b	95	2.32	1.8	G 165 N 181 (28.5) I
P1c	80	2.69	1.7	G 160 N 184 (18.4) I
P1d	50	2.27	1.6	G 105 N_1 165 (0.5) N_2 220 (1.7) I
P1e	20	6.86	1.4	G 118 N 278 (2.7) I
P1f	10	3.46	2.1	C 116 N 301 (2.9) I
P1g	0	9.50	1.9	C 114 N 312 (3.4) I

[a] mol% of monomer with BA units. Determined by ^{1}H NMR.

[b] Polystyrene standards. THF as eluant.

[c] G: glass, C: crystalline, N: nematic, I: isotropic. Determined by DSC. Parentheses show transition enthalpy (J/g).

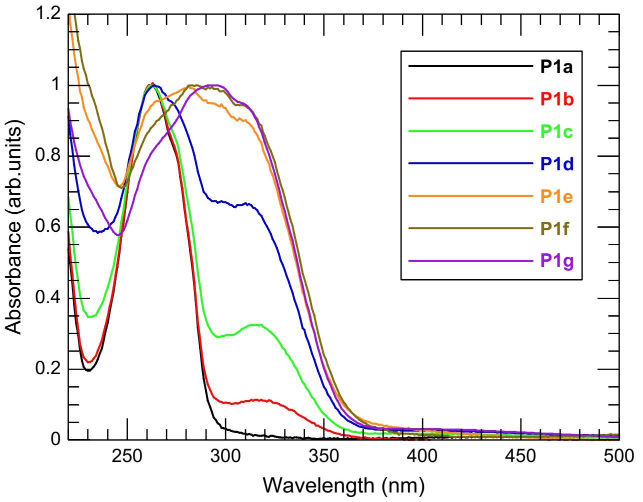

Fig. 2. UV–vis absorption spectra of copolymer films on quartz substrates.

All the copolymers exhibit LC phases as summarized in Table 1. Fig. 3 shows the DSC scan of the copolymers. For **P1a**, **P1b**, and **P1c**, a nematic-like LC phase is observed between ∼160 and ∼180 °C under the POM observation (see Supplementary data). In these cases, the enthalpy for T_i (ΔH_{T_i}) is greater than 18 J g^{-1} and larger for copolymers with a larger BA unit content. The nematic-like LC phase is due to the H-bonded BA units, which act as LC mesogenic moieties, and the large ΔH_{T_i} is due to the disassociation of the H-bonds, which construct the LC phase. A detailed LC phase determination of the copolymers requires X-ray analysis because several polyacrylates with BA in the side chain exhibit a smectic LC phase [9a].

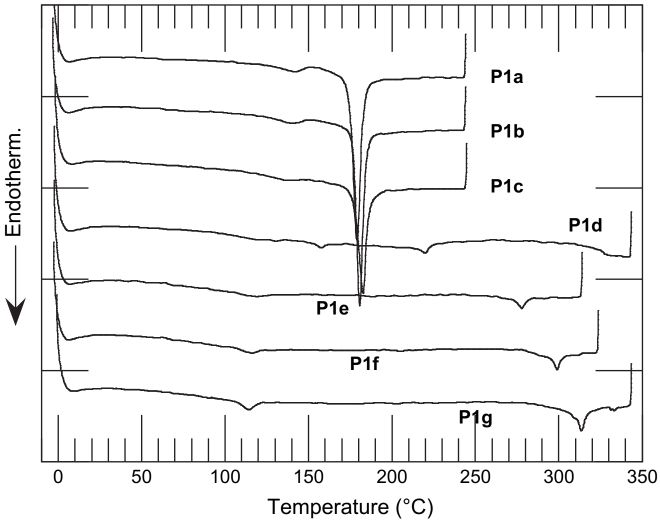

Fig. 3. DSC second heating curves of copolymers.

In contrast, **P1d** shows a wider range between 105 and 220 °C for the nematic LC phase due to the larger MCB unit content where homopolymer **P1g** exhibits a nematic LC phase between 114 and >300 °C. However, the DSC curve of **P1d** reveals two endothermic peaks at 165 °C and 220 °C as shown in Fig. 3, while the textures under the POM observation between 105 and 220 °C are similar (see Supplementary data). Additionally, **P1d** becomes softer when the temperature of the specimen is above 165 °C. These results suggest that **P1d** exhibits a nematic LC phase between 105 and 165 °C due to both the H-bonded BA groups and the MCB mesogenic groups, and the disassociation of H-bonds occurs above 165 °C. However, a sufficient amount of the MCB groups is still available to exhibit the nematic LC phase of the material. The small transition enthalpy at 165 °C should be a consequence of H-bonding of the BA groups, which gradually decompose as the temperature increases above 165 °C. For **P1e** and **P1f**, a nematic LC phase is observed and the DSC curves are similar to that of **P1g**.

3.2. FTIR study

To elucidate the H-bonding of the copolymers at elevated temperatures, temperature-dependent FTIR spectroscopy was performed. Fig. 4a shows the FTIR spectra of a **P1c** film spin-coated on a KBr substrate at various temperatures. A broad absorption between 3300 and 2500 cm^{-1}, and an absorption band at 1683 cm^{-1} are seen at r.t., which are ascribed to H-bonded OH and C=O groups of BA, respectively. When the film is heated at 170 °C (LC phase), the absorption band for BA group at 1683 cm^{-1} shifts slightly, but the absorption intensity does not change. This is due to the stable formation of the LC structure of H-bonded BA groups. However, when the film is heated at 200 °C, the absorbance of these bands decreases, but the absorbance at 1725 cm^{-1} increases. The absorption around 1725 cm^{-1} corresponds to the C=O of methacrylate, MCB, and free BA groups. The dissociation of the H-bonds occurs in the isotropic temperature range. Additionally, when the film is cooled to r.t., the spectrum returns to the initial one.

For **P1d**, the absorption bands for the H-bonded BA groups are detected at r.t. and 140 °C (N_1 phase) as shown in Fig. 4b. However, the broad absorption between 3300 and 2500 cm^{-1}, and the absorption band at 1683 cm^{-1} for the H-bonded BA groups decrease when the film is heated to 200 °C (N_2 phase) and 220 °C (isotropic phase), respectively. This means that the H-bonds of the BA groups dissociate in the N_2 LC and isotropic temperature ranges, which agrees with the DSC data described in Section 3.1. In this case, the absorption around 1725 cm^{-1} becomes broad and decreases at elevated temperatures because

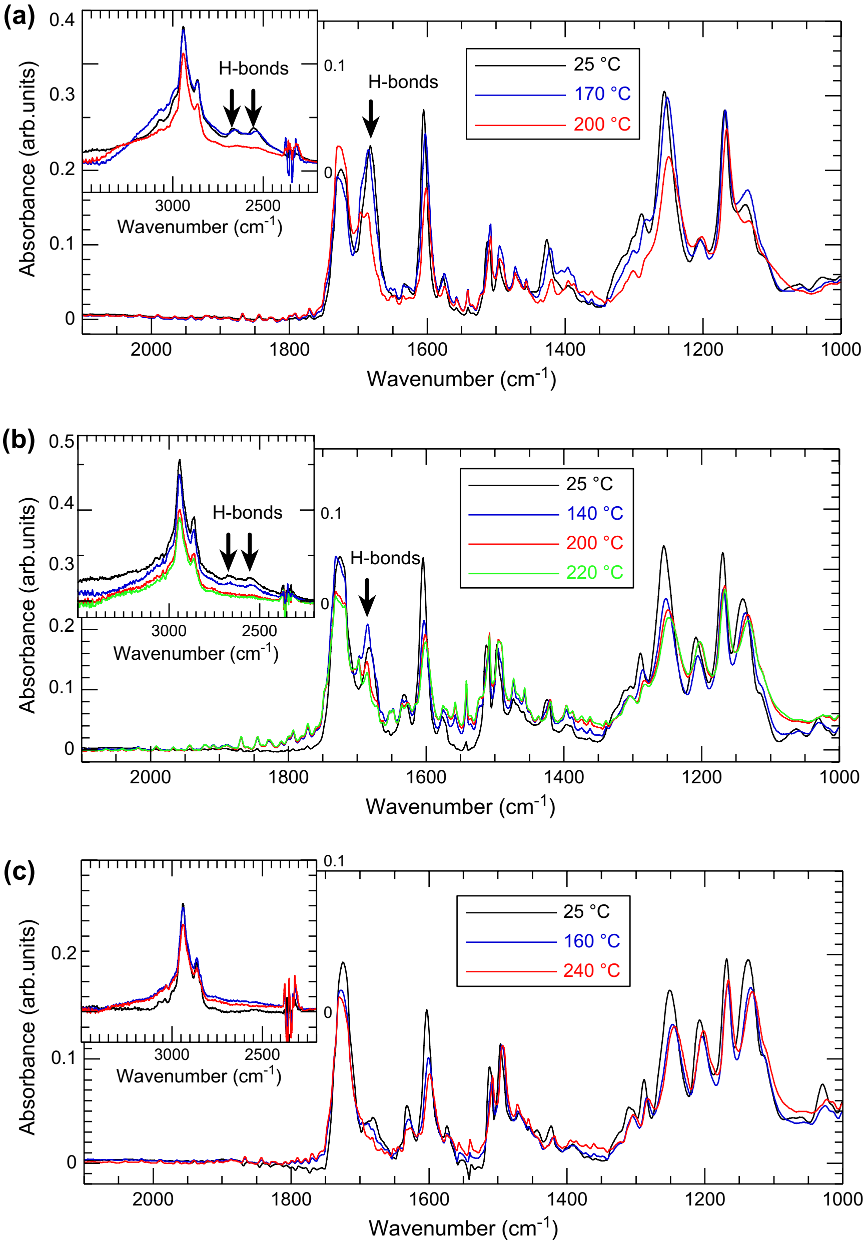

Fig. 4. FTIR spectra of copolymer films (prepared using KBr substrates) at various temperatures. (a) **P1c**, (b) **P1d**, (c) **P1e**.

the thermal aggregation of the MCB groups occurs due to the large content of MCB groups [6a]. In contrast, for **P1e**, a broad absorption between 3300 and 2500 cm^{-1} is not detected, but a small absorption at 1683 cm^{-1} is seen at r.t. as shown in Fig. 4c, indicating partial H-bonding for the as-coated film at r.t. However, the absorption band at 1683 cm^{-1} diminishes when the specimen is heated to the LC temperature. The H-bonds of the BA groups of **P1e** dissociate in the LC temperature range of the material, similar to **P1d** in the N_2 phase.

3.3. Anisotropic photoreaction of thin films

Irradiating a copolymer film with LPUV light induces an axis-selective [2+2] photo-cross-linking and a photoisomerization reaction of the MCB groups. Fig. 5a plots the degree of the photoreaction calculated by the decrease in the absorption intensity of the MCB groups as a function of exposure energy. It reveals that the rates of the photoreaction are similar to each other, and all the copolymers become insoluble after exposure, indicating the photo-cross-linking of the film. Because the photoreaction of the MCB groups in the direction parallel to **E** of LPUV light is faster than that perpendicular to **E**, a small negative optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp} < 0$) of the film is generated after the photoreaction [6,13]. Fig. 5b plots the D values at 315 nm as a function of exposure energy. The absolute D value reaches a maximum when the exposure energy is near 20–50 J cm^{-2} for all the copolymers where the degree of the photoreaction is 40–60 mol%. Because the molecular reorientation in the copolymer films rarely occurs during the exposure, the generated birefringence (Δn) of the

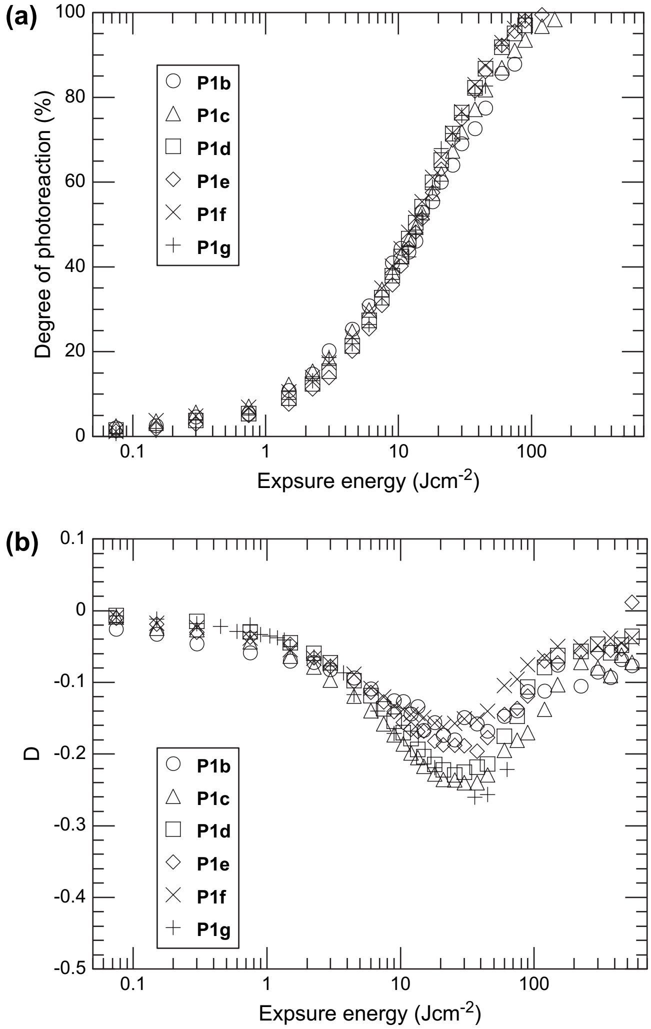

Fig. 5. (a) Degree of the photoreaction of copolymer films as a function of exposure energy. (b) Photoinduced dichroism of copolymer films as a function of exposure energy.

copolymer film is less than 0.01, like the poly(vinyl cinnamate) (PVCi) film [13b]. Additionally, when the degree of the photoreaction increases, the generated D value decreases due to the photoreaction perpendicular to **E**.

3.4. Thermally enhanced photoinduced orientation

We have previously reported that a small photoinduced ΔA of a **P1g** film was thermally enhanced both perpendicular and parallel to **E** of LPUV light by annealing the exposed film in the LC temperature range [6]. When the degree of the photoreaction is around 3 mol%, a photoinduced negative ΔA is thermally amplified perpendicular to **E**, although the aggregation of the mesogenic MCB groups is generated. In contrast, the reversion of the molecular reorientation parallel to **E** is generated when the degree of the photoreaction is around 15 mol%. However, the thermal amplification behavior of the photoinduced ΔA for copolymer films **P1b**–**P1f** drastically differs from that of **P1g**.

Fig. 6a and b plot, respectively, the changes in the UV–vis absorption spectra of **P1c** and **P1d** films before irradiating, after irradiating with LPUV light for 0.15 J cm^{-2} doses, and after subsequent annealing at 170 °C for 10 min for **P1c** and 150 °C for **P1d**. For both films, the degree of the photoreaction is approximately 3 mol%. After the LPUV photoreaction, a small negative ΔA is observed around 290–320 nm due to the axis-selective photoreaction of the MCB groups. The annealing process greatly enhances the negative ΔA in both cases. Both spectra reveal that the thermal aggregation of the MCB groups does not occur, but the mesogenic groups of a **P1g** film aggregate under the same conditions [6a]. The H-bonded mesogenic BA groups inhibit thermal aggregation of all the mesogenic groups, and the axis-selectively photoreacted MCB groups thermally induce a cooperative molecular reorientation for both the H-bonded BA and MCB side groups perpendicular to **E** of LPUV light. The S value at 262 nm is amplified from −0.001 to −0.74 for **P1c**, and from −0.002 to −0.62 for **P1d**. Additionally, the amplified S values around 310 nm (MCB group) are −0.73 for **P1c** and −0.63 for **P1d**. These values are similar to other types of PPLC films and reveal a thermally enhanced photoinduced molecular reorientation [6,12]. The **P1b** film exhibits similar results when the exposed film is annealed at 170 °C. In these cases, a very small amount of the photoproducts in the mesogenic side groups (less than 1 mol% in the MCB and H-bonded BA groups) initiates the thermally amplified cooperative molecular reorientation. The annealing procedure generates the self-organization of all the LC mesogenic groups in a perpendicular direction due to its higher LC characteristics where a small amount of photoreacted MCB groups parallel to **E** acts as impurities, which reduce the LC nature in the parallel direction [6,12,14].

On the other hand, when the irradiated **P1d** film (degree of the photoreaction = 3 mol%) is annealed at 180 °C (N_2 LC phase), thermal amplification of the negative ΔA is very small as shown in Fig. 6c. The thermally amplified S value is less than −0.1. At this annealing temperature, the H-bonds of the BA groups decompose, but the material exhibits a LC nature as described in Section 3.1. The free BA groups without H-bonding restrict the thermally amplified in-plane molecular reorientation of the mesogenic MCB groups. A detailed temperature dependency is discussed in Section 3.6.

Similar to the **P1d** film annealed in the N_2 LC temperature range, thermal amplification of the photoinduced ΔA in the early stage of the photoreaction is not generated for the **P1e** and **P1f** films due to the free BA groups. For these copolymers, reversion of the photoinduced ΔA parallel to **E** is observed when the degree of the photoreaction is approximately 15 mol%. Fig. 6d plots the changes in the UV–vis absorption spectra of a **P1f** film before irradiating, after irradiating with LPUV light in 1.5 J cm^{-2} doses, and after subsequent annealing at 160 °C. The S values are enhanced from −0.002 to +0.13. However, this enhancement is much smaller than that for a homopolymer **P1g** film under similar irradiating and annealing conditions where an S value greater than +0.6 is obtained. The smaller positive S values for the

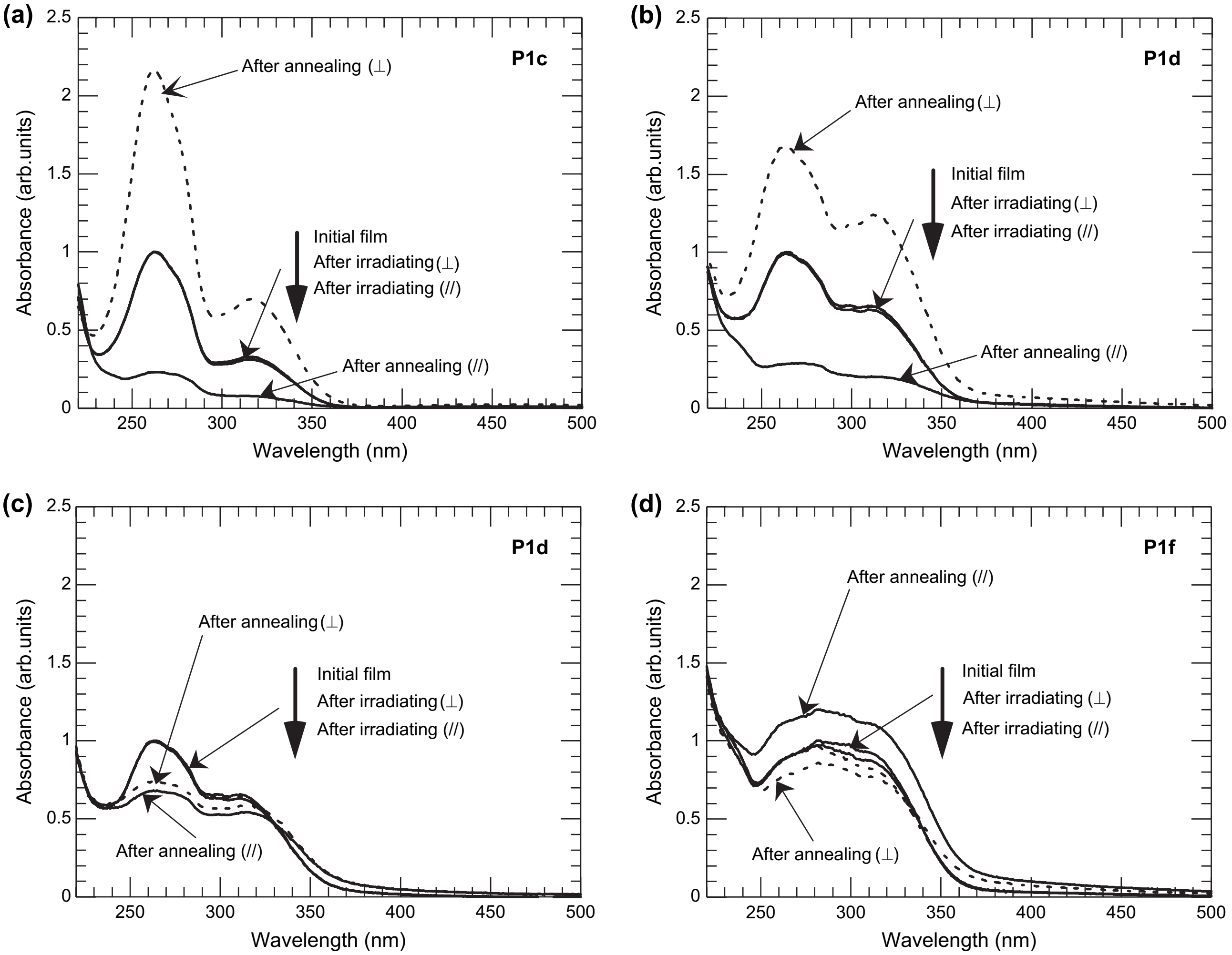

Fig. 6. Changes in the UV–vis absorption spectra of copolymer films before irradiating (thin line), after irradiating with LPUV light (thin lines), and after subsequent annealing (thick lines). Solid lines exhibit the absorption parallel to **E** and dotted lines are perpendicular to **E**. (a) **P1c** irradiated with 0.15 J cm^{-2} doses and annealed at 170 °C. (b) **P1d** irradiated with 0.15 J cm^{-2} doses and annealed at 150 °C. (c) **P1d** irradiated with 0.15 J cm^{-2} doses and annealed at 180 °C. (d) **P1f** irradiated with 1.5 J cm^{-2} doses and annealed at 160 °C.

copolymer films **P1e** and **P1f** are attributed to the small amount of free BA groups, which inhibit the in-plane reorientation of the MCB side groups.

3.5. Influence of the exposure energy

The thermally enhanced molecular reorientational order depends on the degree of the photoreaction. Fig. 7 plots the thermally enhanced *S* values as a function of exposure energy of LPUV light when the irradiated films are annealed at elevated temperatures. The annealing temperature is 150 °C for **P1a**, **P1d**, and **P1g**, 170 °C for **P1b** and **P1c**, and 180 °C for **P1e** and **P1f**. For copolymers **P1b**–**P1d**, ΔA perpendicular to **E** is greatly amplified when the exposure doses are between 0.1 and 2.5 J cm^{-2}, and the degree of the photoreaction is 2–18 mol%. On the other hand, the **P1e** and **P1f** films do not reveal a thermal amplification of ΔA in the early stage of the photoreaction. The annealing process only generates a molecular aggregation for these copolymers. In contrast, a small amplification perpendicular to **E** and MCB group aggregation are observed for homopolymer **P1g**. For copolymers **P1e** and **P1f**, the small amount of free BA groups inhibits the thermally enhanced in-plane molecular reorientation of the MCB groups even though the film has a small photoinduced optical anisotropy.

In contrast, when the exposure doses are between 1 and 8 J cm^{-1} and the degree of the photoreaction is around 15 mol%, a reversion of ΔA parallel to **E** is observed for **P1e**, **P1f**, and **P1g**. However, the thermally enhanced *S* values for **P1e** and **P1f** are much smaller than that of **P1g** because the free BA groups inhibit the in-plane reorientation as described in the previous section. Furthermore, for **P1b**–**P1d**, thermal amplification parallel to **E** is not detected, although the H-bonded BA groups reveal the LC nature. In these cases, the amount of the axis-selectively reacted MCB groups parallel to **E** in the total mesogenic groups, including the H-bonded BA groups, is insufficient to act as a photo-cross-linked anchor, which initiates the thermally enhanced reorientation in all the mesogenic side groups parallel to **E** because the content of the BA groups is too large. A similar phenomenon has been

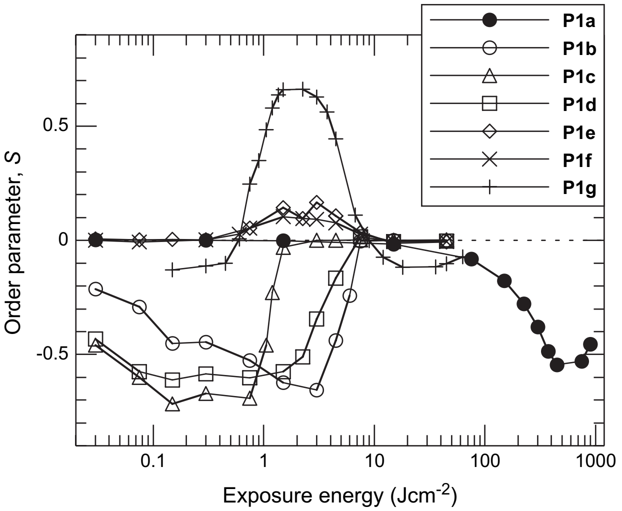

Fig. 7. Thermally enhanced S values as a function of exposure energy of LPUV light when the irradiated films are annealed at elevated temperatures. S values are determined at 262 nm for **P1a–P1d**, at 282 nm for **P1e** and **P1f**, and at 295 nm for **P1g**.

reported for copolymer films containing MCB and a large amount of unphotoreactive mesogenic side groups [15].

It is noteworthy that thermal amplification of the molecular reorientation perpendicular to **E** ($S > 0.5$) is observed for **P1a** films when the exposure dose is around 800 J cm^{-2}. The UV–vis absorption and FTIR spectra show an axis-selective partial decomposition of the BA groups. Similar to the axis-selective photoreaction of the MCB groups for the **P1b–P1d** films, a small amount of decomposed BA groups parallel to **E** acts as impurities, which reduce the LC nature in the parallel direction and result in the thermal amplification of ΔA. This result indicates that the axis-selectively photoreacted impurity parallel to **E** leads to the thermally amplified self-organization of the H-bonded BA mesogenic groups perpendicular to **E**.

3.6. Influence of the annealing temperature

Similar to other photo-cross-linkable LC polymeric films, the annealing temperature influences the thermal enhancement behavior of copolymer films [6]. Fig. 8 plots the S values annealed at various temperatures when the degree of the photoreaction is approximately 3 mol% for **P1b–P1d** and 15 mol% for **P1e–P1g**. For **P1b** and **P1c**, a maximum S value is attained when annealed at a temperature close to T_i. Above T_i, thermal amplification does not occur due to the H-bonds of the BA groups decomposing. For **P1d**, annealing near 165 °C generates a maximum S value. Because H-bonds of the BA groups decompose above 165 °C, the annealing procedure in this temperature range leads to a random orientation of the mesogenic moieties. In contrast, positive S values are obtained for the **P1e–P1g** films when the films are annealed in the LC temperature range of the copolymers, but the enhanced S values for the **P1e** and **P1f** films are much smaller than that for the homopolymer **P1g** film due to the free BA groups as discussed in the previous section.

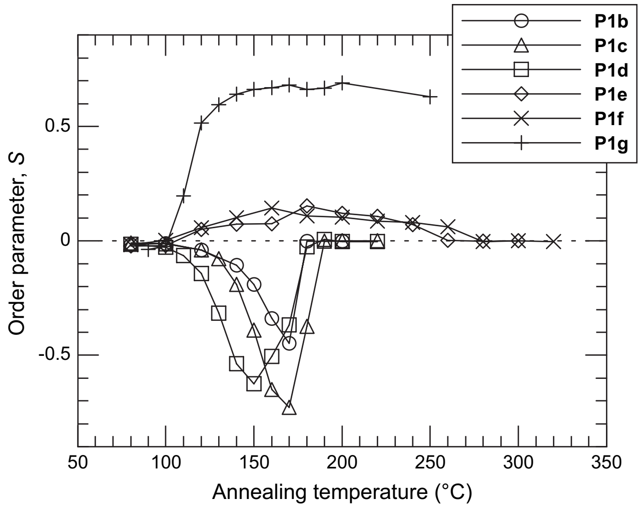

Fig. 8. Thermally enhanced S values annealed at various temperatures. Degree of the photoreaction: 3 mol% for **P1b–P1d**, and 15 mol% for **P1e–P1g**.

4. Conclusion

New liquid crystalline methacrylate copolymers, which contain BA and MCB side groups, were synthesized, and the photoinduced reorientation behavior of their thin films was investigated using LPUV light irradiation and subsequent annealing. Copolymers with a higher content of BA groups exhibit a nematic-like LC nature due to both the mesogenic H-bonded BA dimers and MCB groups. For copolymers with a lower BA composition, H-bonds of the BA groups decompose, but a nematic LC nature is revealed due to the large amount of MCB mesogens. To obtain a high thermally enhanced in-plane reorientation without the molecular aggregation, H-bonding of the BA moieties, which is the origin of the supramolecular LC nature of the material, plays important roles in the cooperative reorientation both BA and MCB side groups. A small amount of axis-selectively photoreacted MCB side groups generates the thermally enhanced small photoinduced optical anisotropy. On the other hand, free BA groups without H-bonding restrict the molecular reorientation of the mesogenic MCB side groups. These reoriented films may be applicable to birefringent films and LC alignment layers for liquid crystalline displays.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2007.04.004.

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