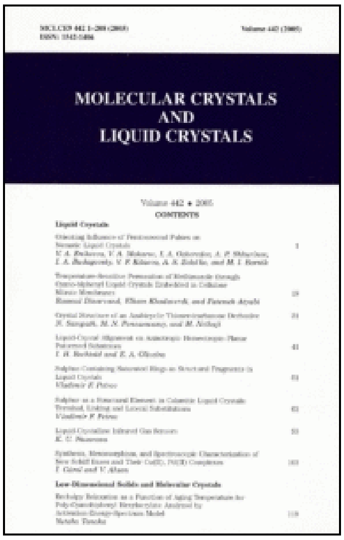

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Photoinduced Orientation of Liquid Crystalline Copolymer Films with Cinnamic Acid Side Groups Synthesized by RAFT Polymerization

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Photoinduced Orientation of Liquid Crystalline Copolymer Films with Cinnamic Acid Side Groups Synthesized by RAFT Polymerization

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Liquid crystalline (LC) polymethacrylates with hexamethylene spacer groups terminated with photoreactive hydrogen (H) bonded 4-oxycinnamic acid (CA) in the side chain were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization. The influence of the molecular weight on the thermal property, photoreactivity, and thermally enhanced photoinduced molecular reorientation behavior was investigated. All polymers exhibited a nematic LC phase, and thermally enhanced photoinduced in-plane molecular reorientation was achieved by irradiating with linearly polarized UV light and subsequent annealing. The molecular weight did not affect the photoreactivity and the axis-selectivity of anisotropic photoreaction of thin films, but effective annealing temperature and the maximum thermally enhanced in-plane order decreased as the molecular weight of the polymer decreased.

Keywords Photoinduced orientation; polymer liquid crystal; RAFT polymerization

Introduction

Photoinduced reorientation in photoreactive polymeric films has received much attention because the reoriented films are applicable to birefringent optical devices, optical and holographic data storage devices, and alignment layer for low-molecular liquid crystals [1–3]. Various photosensitive polymers were investigated to attain a large photoinduced optical anisotropy, including azobenzene-containing polymers and photo-cross-linkable liquid crystalline polymers (PLCPs) [1,4,5]. Using a linearly polarized (LP) light, a small optical anisotropy is generated based on the polarization axis-selective photoreaction of the photoreactive groups. When the molecular reorientation accompanies the axis-selective photoreaction, large optical anisotropy can be induced in the film [5]. Because the molecular reorientation involves the molecular motion, the reorientation behavior is affected by type of the polymer

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Address correspondence to Nobuhiro Kawatsuki, Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2201, Japan. Tel.: +81-792-67-4886; Fax: +81-792-67-4885; E-mail: kawatuki@eng.u-hyogo.ac.jp backbone, type and the length of the spacer between the polymer backbone and the photoreactive side groups, and molecular weight of the polymer, even if the photoreactive moiety is the same. Several studies on the influence of the spacer length on the photoinduced molecular reorientation behavior have been reported on azobenzene-containing polymers [6–8] and photo-cross-linkable polymers [9], while studies on the influence of the molecular weight are few. Kurihara and colleagues studied holographic recording of azobenzene telomer with different molecular weight [10]. The influence of the molecular weight on thermally enhanced photoinduced reorientation of LC polymethacrylates comprised of 4-methoxyazobenzene side groups, which were synthesized by atom-transfer radical polymerization (ATRP) method, was investigated [11].

Generally, isotropization temperature (T_i) and LC temperature range of LC polymers decreased as the mass-average degrees of polymerization decreased lower than approximately 50 and less [12,13]. During a course our systematic study on the thermally enhanced molecular reorientation of PLCP films, polymethacrylate with hexamethylene spacer groups terminated with photoreactive hydrogen (H) bonded 4-oxycinnamic acid (CA) in the side chain (P6CAM) revealed high photoreactivity and efficient molecular reorientation [14]. However, the influence of the molecular weight of P6CAM on the thermally enhanced photoinduced molecular reorientation behavior has not yet been explored.

To control the molecular weight of the polymer with narrow molecular distribution, living free radical polymerization, such as ATRP and reversible addition fragmentation chain transfer (RAFT) polymerization [15,16], is known as a conventional method. Among them, RAFT polymerization is available for the monomers with carboxylic acid side groups [17]. In this paper, to clarify the influence of the molecular weight on the thermally enhanced molecular reorientation of P6CAM films, P6CAMs with various molecular weights were synthesized by the RAFT polymerization. Thermal property, photoreactivity, and photoinduced reorientation behavior were investigated in detail.

Experimental

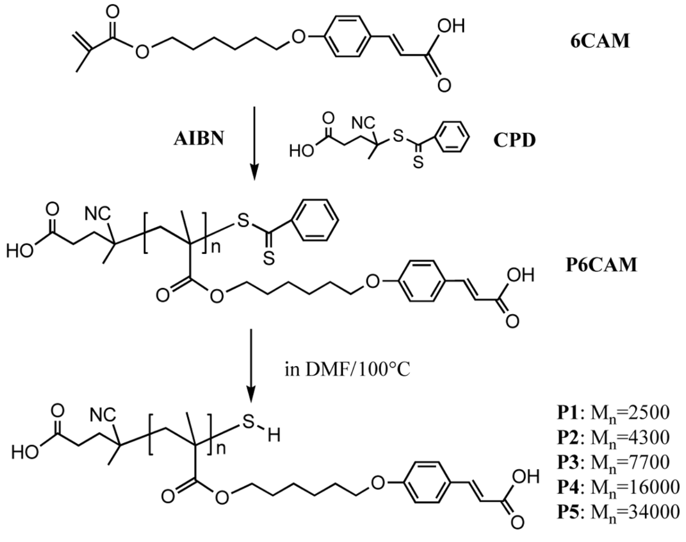
Materials

All starting materials were used as received from Tokyo Kasei Chemicals, Kanto Chemicals, and Kishida Chemicals. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored below 0°C. Methacrylate monomer with cinnamic acid (CAM) and a chain transfer agent of 4-cyanopentanoic acid dithiobenzoate (CPD) were synthesized according to the literatures [14,15].

Polymer Synthesis

Synthetic route of polymer (P6CAM; **P1**–**P5**) is outlined in Scheme 1. Typical procedure for the synthesis of **P1** is described below:

0.5 g (1.51 mmol) of 6CAM, 210 mg (0.75 mmol) of CPD, and 49.5 mg (0.3 mmol) of AIBN were dissolved in 4 ml of THF. Under the nitrogen atmosphere, the mixture was placed at 60°C for 5 h. The polymer was precipitated into diethyl ether, and purified by the reprecipitation from THF solution to diethyl ether for several times. After drying under the reduced pressure, pink-colored polymer



Scheme 1. Synthetic route of polymers **P1**–**P5**.

(PCAM-CPD) was obtained. Yield, 0.18 g (36 wt%). Thereafter, the polymer was dissolved in 4 ml of DMF, and heated at 100°C for 12 h. The colorless polymer **P1** was obtained by precipitating into diethyl ether, and purified by the reprecipitation from THF solution to diethyl ether for several times.

Other polymers (**P2**–**P5**) were synthesized by the similar method with adjusting 6CAM/CPD ratio to control the molecular weight. Table 1 summarizes experimental condition, molecular weight, and thermal property of polymers.

Characterization

Thermal properties were examined using a polarization optical microscope (POM) and a differential scanning calorimetry (DSC) analyzer. Polarization UV-vis spectra

Table 1. Experimental condition, molecular weight and thermal property of polymers

Polymer	Feed ratio[a] [M]/[I]/[C]	Molecular weight[b] $M_n \times 10^{-4}$	M_w/M_n	Thermal property[c] (°C) (ΔH, J/g)
P1	2/0.4/1	0.25	1.60	G 79 N 128 (2.1) I
P2	7/0.4/1	0.43	1.60	G 95 N 139 (2.5) I
P3	15/0.4/1	0.77	1.60	G 100 N 154 (3.8) I
P4	90/0.4/1	1.60	1.50	G 117 N 175 (15.9) I
P5	211/0.4/1	3.40	1.65	G 124 N 188 (19.5) I

[a] [M]/[I]/[C]; mol feed ratio of 6CAM/AIBN/CPD.

[b] Molecular weight of methyl ester of polymers. Determined by GPC. Polystyrene standards, chloroform eluent.

[c] Determined by DSC and POM. G: glassy, N: nematic, I: isotropic.

were measured using a spectrometer equipped with Glan-Taylor polarizing prisms. The in-plane order parameter, S, is expressed in the form of Eq. (1);

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{(large)} + 2A_{(small)}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**), respectively, and $A_{(large)}$ is the larger value of $A_{\parallel}$ and $A_{\perp}$, and $A_{(small)}$ is the smaller one [14]. S was calculated by polarized UV-vis spectroscopy using wavelengths of 314 nm.

Photoirradiation

Thin films were prepared by spin-coating a THF solution of polymers (1.4 wt/wt.%) onto a quartz substrate. The film thickness was approximately 0.2 µm. The film was irradiated by light from a 250 W high-pressure Hg-UV lamp that was passed through Glan-Taylor polarizing prisms with a cut-off filter below 290 nm. The light intensity was 10 mW/cm^2 at 365 nm. Degree of the photoreaction (DP) was estimated by monitoring an absorption band at 314 nm (CA groups) of the UV spectra. For the thermally enhanced molecular reorientation, the irradiated film was annealed at elevated temperatures for 10 min. The generated optical anisotropy of the film was measured by polarizing microscopy and polarization UV-vis spectroscopy.

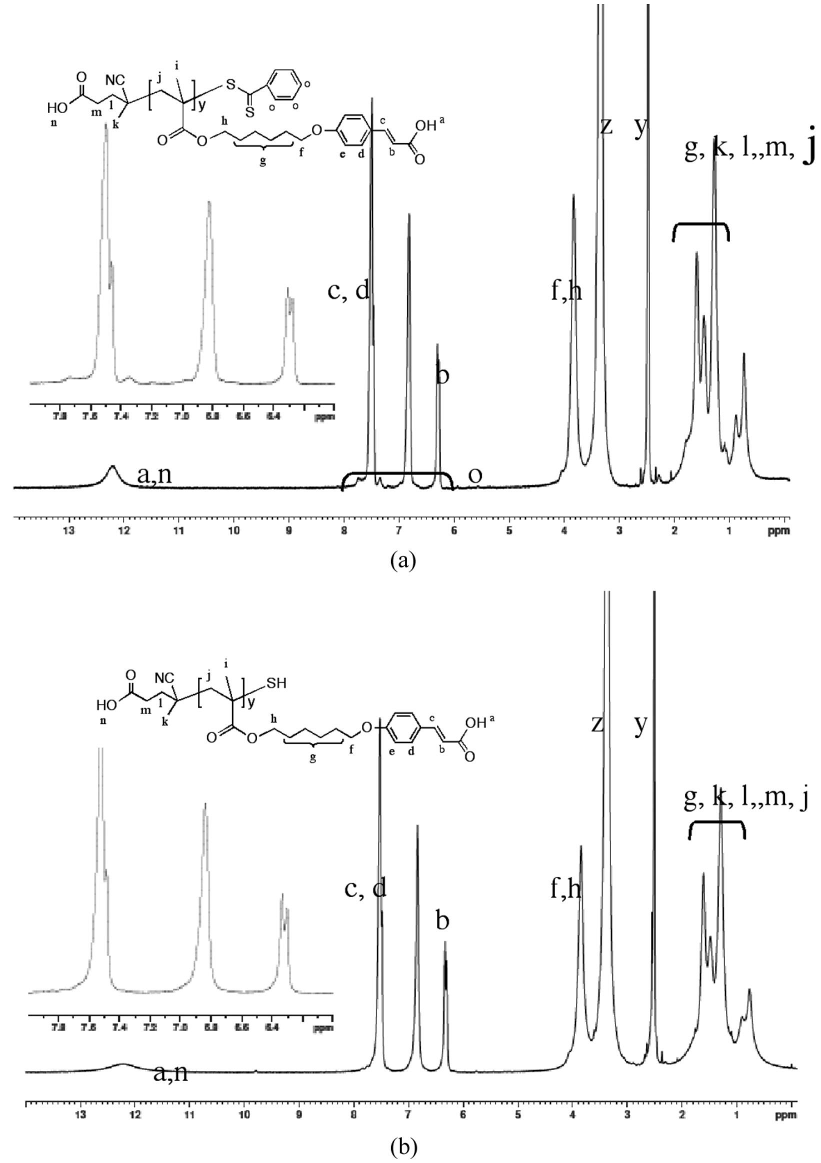
Results and Discussion

Polymer Synthesis

Polymers were synthesized by the RAFT polymerization method using CPD and AIBN in THF solution. After the polymerization, polymers were slightly pink-color due to the dithiobenzoate end groups. The dithiobenzoate groups were thermally decomposed to SH groups by treating in DMF solution at 100°C. After decomposing, polymers became colorless. Figures 1a and b show ^{1}H-nmr spectra of P6CAM with CPD end groups (P6CAM-CPD) and that after the heat treatment. The signals around $\delta = 7.3$–8.0 ppm (Fig. 1a), which were assigned to be the phenyl protons of dithiobenzoate end group, were diminished after the thermal decomposition (Fig. 1b).

Molecular weights of the polymers were measured after modifying the aromatic acid groups to the methyl ester [18]. Figure 2 shows GPC trace of polymers, which reveals monomodal curves that suggest the controlled molecular weight by adjusting the monomer/CPD ratio.

All polymers showed a glass transition followed by a nematic LC phase. Figure 3 plots the transition temperatures of the polymers as a function of number average of molecular weight (M_n). The LC temperature range increased as the molecular weight increased, and the transition temperatures were close to the P6CAM synthesized by the free radical polymerization when the molecular weight was larger than 15,000 [14]. In contrast, T_i for **P1** was 60°C lower than that of **P5** because it consisted of only 6–8 monomer units. Additionally, transition enthalpy (ΔH for T_i) became smaller when the molecular weight of the polymer decreased as summarized in Table 1.



(a)

(b)

Figure 1. ^{1}H NMR spectrum of (a) P6CA-CPD and (b) treated P6CA in DMSO-d6. (y: DMSO, z: H_2O).

LC mesomorphism of the material is influenced by not only the molecular weight of the polymer but also the COOH group at the end of the polymer main chain.

Axis-Selective Photoreaction of Polymer Films

A transparent film was fabricated by a spin-coating method from THF solution. Irradiating a polymeric film with LPUV light induces an axis-selective [2 + 2] photodimerization and a photoisomerization reaction of the CA groups to generate a

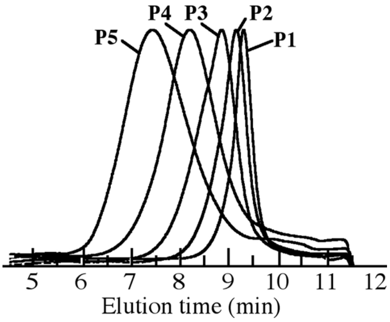


Figure 2. GPC trace for **P1**–**P5** after esterification (COOH to $COOCH_3$). Eluent; chloroform.

negative optical anisotropy ($\Delta A_{\parallel} - A_{\perp} < 0$). Figures 4a and b plot the DP and the photoinduced ΔA at 314 nm, where the absorbance of the initial film was normalized one, as a function of exposure energy, respectively. The rates of the photoreaction and the photoinduced ΔA were similar among the polymers, indicating that there was not any molecular weight dependency in both the photoreactivitiy and axis-selectivity of the photoreaction. Additionally, maximum ΔAs were obtained when the DP was approximately 30–50 mol% for all the films. These behaviors were similar to that of P6CAM synthesized by the free radical polymerization [14,18].

Thermal Amplification of the Photoinduced Optical Anisotropy

We previously reported that a small photoinduced ΔA of a P6CAM film was thermally amplified perpendicular to **E** of LPUV light by annealing the exposed film in the LC temperature range when the DP was around 2–4 mol%, and the efficient molecular reorientation was obtained when the annealing temperature was close to the clearing point of the material [14]. The molecular weight influenced this thermal amplification behavior. Figures 5a and b show the UV-vis polarization spectra of **P1** and **P5** films before and after photoirradiating, and after subsequent annealing at 110°C for **P1**, and 160°C for **P5**, respectively. The DP of the films was 1.5 mol%

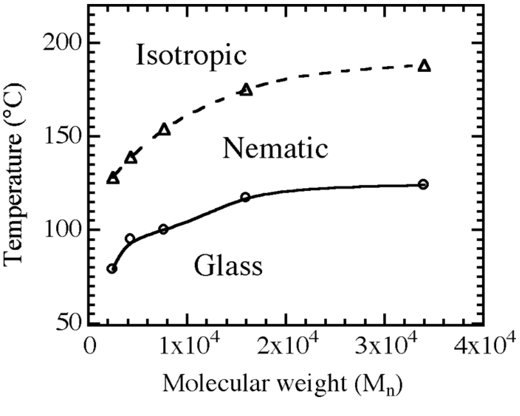
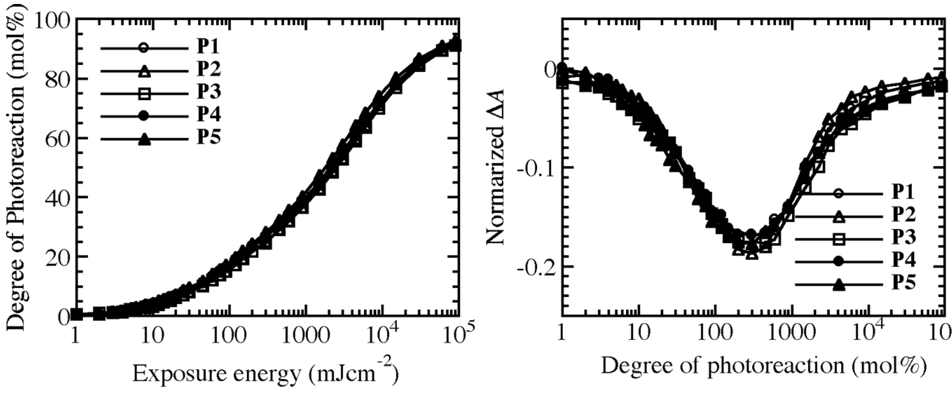


Figure 3. Thermal property of polymers as a function of number average of molecular weight.

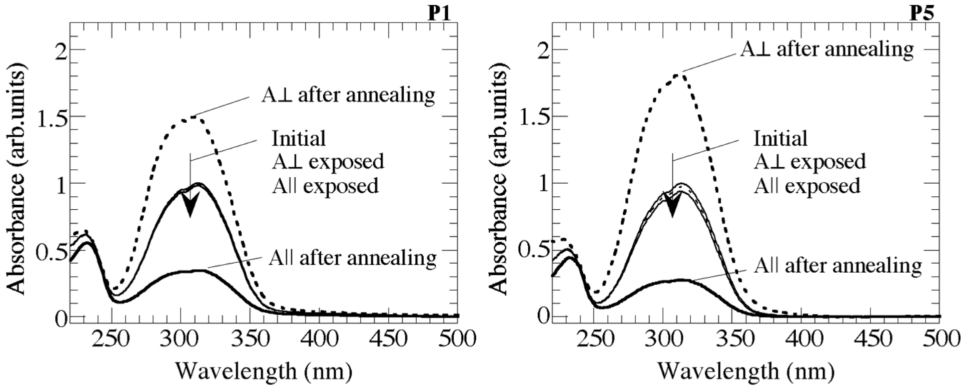


(a) (b)

Figure 4. (a) Degree of the photoreaction (DP) of polymer films as a function of exposure energy. (b) Normalized photoinduced optical anisotropy (ΔA) of polymer films at 314 nm as a function of DP. Initial absorbance at 314 nm is normalized to 1.0.

for **P1**, and 3.5 mol% for **P5**. In these conditions, the maximum thermally amplified in-plane order was obtained. The photoinduced small negative ΔA was thermally enhanced from -0.003 to -0.52 for **P1**, and from -0.012 to -0.68 for **P5**. The annealing procedure generates the self-organization of the H-bonded CA mesogenic groups in a perpendicular direction due to its higher LC characteristics [14,18]. Other polymers also exhibited the similar thermal amplification of the photoinduced negative ΔA as summarized in Table 2. However, the thermally enhanced S values and the required DP for the maximum S values depended on the molecular weight of the polymer. Detailed results were described below.

Figure 6 plots the thermally enhanced S values as a function of the DP. The annealing temperatures were 110°C for **P1**, 120°C for **P2**, 135°C for **P3,**



(a) (b)

Figure 5. UV-vis polarization spectrum of polymer films before photoirradiating, after irradiating (thin lines), and after subsequent annealing (thick lines) for 10 min. Solid line represent $A_{||}$, while dotted lines show $A_{\perp}$. Key: (a) **P1**, irradiating with 4 mJ cm^{-2} doses and annealed at 110°C and; (b) **P5**, irradiating with 12 mJ cm^{-2} doses and annealed at 160°C.

Table 2. Maximum in-plane order of polymer films

Polymer	Exposure energy[a]	DP[b] (mJ cm^{-2}) (mol%)	Annealing temperature[c] (°C)	In-plane order[d]
P1	4	1.5	110	−0.52
P2	4	1.5	120	−0.49
P3	6	2.5	135	−0.58
P4	8	3.0	150	−0.65
P5	12	3.5	160	−0.68

[a] At 365 nm.

[b] Estimated by measuring absorbance at 314 nm.

[c] Annealed for 10 min.

[d] At 314 nm.

150°C for **P4**, 160°C for **P5**. For **P4** and **P5**, the thermal amplification of the photoinduced negative ΔA was generated when the DP was 2.5–5 mol%, and the enhanced $|S|$ values were greater than 0.6. Additionally, when the DP was 12–15 mol%, the photoinduced ΔA was reversely enhanced parallel to the polarization of LPUV light for **P4** and **P5** films ($S \sim +0.15$). The molecular reorientation parallel to **E** is caused by the axis-selectively photoreacted H-bonded CA-CA side groups which act as photo-cross-linked anchors to induce the in-plane molecular reorientation parallel to **E** [14]. These thermal amplification behaviors were similar to that for P6CAM synthesized by the free radical polymerization [14,18]. In contrast, a large negative S values ($S \sim -0.6$) was obtained for **P3** when the DP was 2–4 mol%, but positive S values was not obtained. Furthermore, for **P1** and **P2**, maximum $|S|$ values were around 0.5, which was obtained when the DP was 1–3 mol%, and positive S values was not obtained.

When the molecular weight was low, self-organization of the H-bonded CA groups became difficult due to the influence of COOH group at the end of the main

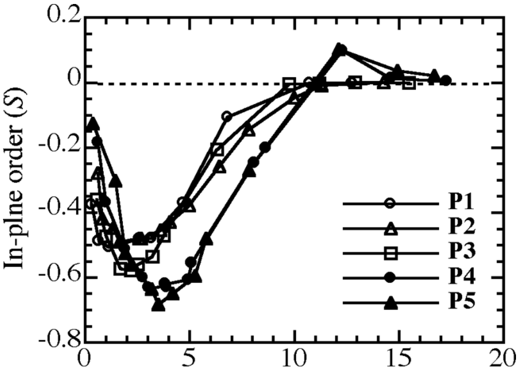


Figure 6. Thermally enhanced S values at 314 nm of the photoreacted polymer films as a function of the degree of the photoreaction. Open circles; **P1**, open triangles; **P2**, open squares; **P3**; closed circles; **P4**, closed triangles; **P5**. Annealing temperatures are 110°C for **P1**, 120°C for **P2**, 135°C for **P3**, 150°C for **P4**, 160°C for **P5**.

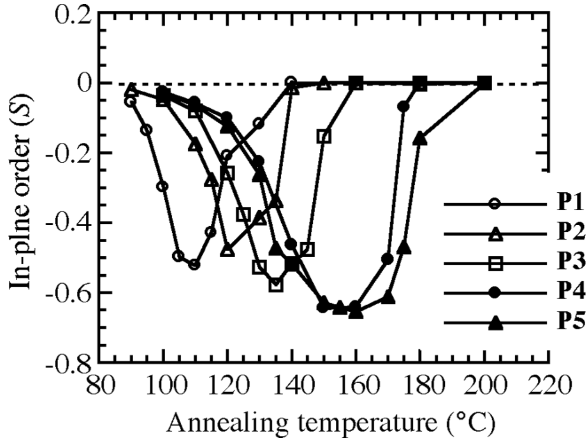


Figure 7. Thermally enhanced *S* values of the photoreacted polymer films when the annealing temperature is varied. Open circles; **P1**, open triangles; **P2**, open squares; **P3**; closed circles; **P4**, closed triangles; **P5**. Exposure energy: **P1, P2**; 4 mJ cm^{-2}, **P3**; 6 mJcm^{-2}, **P4**; 8 mJ cm^{-2}, **P5**; 12 mJ cm^{-2}.

chain, which also made H-bonds with CA groups to reduce the LC mesomorphism of the material. This caused somewhat lower thermally enhanced maximum *S* values for **P1** and **P2** films and the lower required DP for the maximum *S*, because high amount of the photoreaction further lowered the LC mesomorphism of the material.

The influence of the annealing temperature on the thermal amplification of the photoinduced negative ΔA of the film was investigated in detail. Figure 7 plots the *S* values of the polymer films annealed at various temperatures when the DPs were 1.5 mol% for **P1** and **P2**, 2.5 mol% for **P3**, 3.0 mol% for **P4**, and 3.5 mol% for **P5**. For all cases, the maximum *S* values were attained when the annealing temperature was 10–15°C lower than Ti. These results are similar to the thermal amplification of the photoinduced ΔA of polymeric films with H-bonded CA-CA side groups [14,18]. In other words, the effective annealing temperature for the amplification of the photoinduced optical anisotropy was controlled by adjusting the molecular weight of P6CAM.

Conclusions

Polymethacrylates comprised of cinnamic acid side groups with various molecular weights were synthesized by the RAFT polymerization. The molecular weight was controlled by adjusting the monomer/CPD ratio, and the dithiobenzoate end groups were thermally decomposed to obtain colorless polymers. All polymers revealed a nematic LC phase due to the H-bonded CA mesogenic side groups, but the LC temperature range decreased as the molecular weight decreased. Irradiating thin films with LPUV light generated a small negative optical anisotropy due to the axis-selective photoreaction. Both photoreactivity and the photoinduced optical anisotropy did not depend on the molecular weight of the polymer. The photoinduced optical anisotropy was thermally amplified for all the polymer films when the exposed films were annealed LC temperature range of the polymer, indicating that the effective annealing temperature for the sufficient thermally enhanced in-plane order is adjusted by the molecular weight of the polymer. The absolute values for the enhanced in-plane order were greater than 0.58 when the molecular weight of the polymer was larger than 7700, while around 0.5 when the molecular weight was smaller than 4300. The LC mesomorphism of the material and the COOH end groups in the polymer main chain affect the thermal amplification behavior.

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