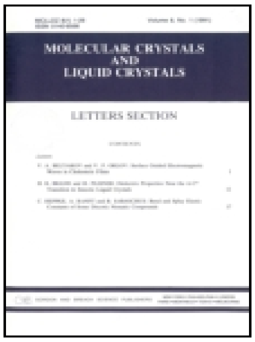

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Thermal Amplification of Photoinduced Cooperative Reorientation of Liquid Crystalline Copolymer Films Comprised of *N*-Benzylideneaniline and Benzoic Acid Side Groups

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This paper describes photoinduced cooperative molecular reorientation and its thermally stimulated amplification in liquid crystalline copolymethacrylates (LCPs) with hexamethylene spacer groups terminated with N*-benzylideneaniline (NBA) and benzoic acid (BA) in the side chain. Influence of the copolymerization ratio and annealing temperature on the molecular reorientation behavior is investigated. Both NBA and BA side groups cooperatively reorient, but the orientation order depends on the copolymerization ratio. In contrast, sufficient thermal amplification of the photoinduced optical anisotropy is achieved for all LCPs, which is controlled by adjusting the annealing temperature.*

Keywords polymer liquid crystal; benzylideneaniline; photoinduced orientation; birefringent film

Introduction

Photoinduced cooperative orientation is observed in many types of photosensitive liquid crystalline polymeric films comprised of photoalignable and non-photosensitive mesogenic side groups [1–4]. Among them, many studies have been carried out using copolymer films comprised of azobenzene and non-photoreactive side groups by means of linearly polarized (LP) light irradiation [1,5–8]. In case of the azobenzene-containing polymeric films, axis-selective trans-cis-trans photoisomerization generates the molecular reorientation perpendicular to the polarization (**E**) of LP light [1]. Additionally, thermal amplification of the photoinduced optical anisotropy of photosensitive LCP films was also reported [9].

A poly(meth)acrylate with benzoic acid (BA) side groups reveals LC characteristics due to H-bonded dimmer of BA moieties [10]. We have previously reported thermal amplification of the cooperative photoinduced orientation of a polymethacrylate films with BA and cinnamic acid side groups, where the photoinduced molecular reorientation does not occur without the annealing process [3]. Copolymethacrylates comprised of BA and 4-methoxyazobeneze side groups show photoinduced molecular orientation and its thermal

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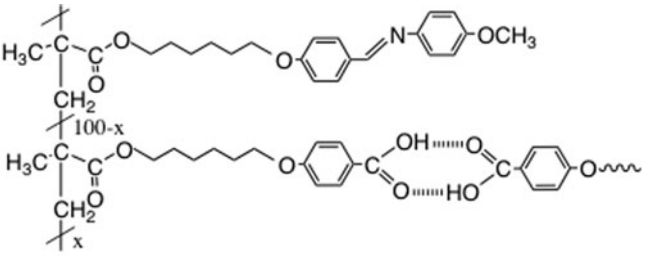

P0: x=0; **P4**: x=40; **P5:** x=50; **P6**: x=60; **P7**: x=70; **P8**: x=80

Figure 1. Chemical structure of LCPs in this study.

amplification, but the film is slightly colored because the azobenzene is not transparent in the visible region [4]. Alternatively, it is known that *N*-benzylideneaniline (NBA) derivatives are transparent in visible region and undergoes trans-cis photoisomerization likewise the azobenzene derivatives [11]. We have recently reported that a polymethacrylate with NBA-derivative side groups exhibits significant photoinduced reorientation likewise the azobenzene-containing polymeric films [12,13]. In this context, copolymerization of NBA-containing monomer as a photoalignable unit and BA-containing comonomer as a non-photosensitive mesogenic unit will attain transparent photoalignable copolymer which shows cooperative molecular orientation.

In this paper, we synthesize methacrylate copolymers with NBA and BA in the side chain (Fig. 1), and explore their photoinduced reorientation behavior using LP 365 nm light and thermally stimulated amplification of the photoinduced orientation structure. The influence of the copolymerization ratio, exposure energy, and annealing temperature on the cooperative reorientation behavior is investigated.

Experimental

Materials and Copolymer Synthesis

Methacrylate monomers with NBA and BA side groups were synthesized according to the literatures [12,13]. All copolymers (Fig. 1) were synthesized by radical copolymerization in THF using AIBN as an initiator. Copolymer composition was determined by ^{1}H-NMR. Composition, molecular weight and thermal and spectroscopic properties of synthesized copolymers are summarized in Table 1.

Characterization

Thermal properties were examined using a polarization optical microscope (POM) and a differential scanning calorimetry (DSC) analyzer. The polarized absorption UV–vis spectra was measured with a Hitachi U-3010 spectrometer equipped with Glan−Taylor polarization prisms. The photoinduced optical anisotropy, δA, in-plane order parameter, *S*, is expressed in the form of equations 1 and 2;

$$\Delta A = A_{||} - A_{\perp}, \tag{1}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively. *S* was calculated by polarized UV-vis spectroscopy using wavelengths at $\lambda_{\max}$ of the materials.

Table 1. Copolymer composition, molecular weight, and thermal properties of LCPs

LCP	$x^{a)}$	Molecular weight$^{b)}$ M_nX10^{-4}	M_w/M_n	Thermal property$^{c)}$ (°C)	Spectroscopic data λ_{max1} (nm)	λ_{max2} (nm)
P0	0	4.9	2.4	G 41 N 127 I	282	330
P4	40	2.7	2.5	G 69 N 120 I	272	333
P5	50	1.9	2.3	G 47 N 121 I	268	333
P6	60	11	1.6	G 31 N 126 I	266	334
P7	80	8.1	1.6	G 45 N 139 I	264	335
P8	80	2.6	2.5	G 70 N 143 I	263	335

a) Determined by ^{1}H-NMR. b) Determined by GPC. Polystyrene standards, THF eluent. c) Determined by DSC. 2nd heating. G: glassy, N: nematic, I: isotropic. d) On quarts substrate.

Photoirradiation

Thin films were prepared by spin-coating a THF solution of copolymers (1 wt/wt-%) onto a quartz or CaF_2 substrate. The film thickness was approximately 0.2 μm. The photoreactions were performed using a high pressure Hg lamp equipped with a glass plate placed at Brewster's angle and a band-pass filter at 365 nm (Asahi Spectra REX-250). The light intensity was 5 mW/cm^2 at 365 nm. 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 POM and polarization UV-vis spectroscopy.

Results and Discussion

Copolymer Synthesis

All synthesized copolymers are soluble in THF and revealed a LC phase, which is confirmed by POM observation. As previously reported [3,4], the introduction BA group is useful because the absorption band of BA is separated from 365 nm and the synthetic procedure is easy. Figure 2 shows absorption spectra of copolymer films on quartz substrate. It reveals two independent absorption maxima around 270 nm and 330 nm, which are ascribable to absorption of BA and MBA, and MBA side groups, respectively. Additionally, the absorption intensities are according to the copolymer composition.

Axis-selective Photoreaction of Copolymer Films

Irradiating a polymethacrylate with MBA side groups (homopolymer **P0**) with LPUV light reveals photoinduced molecular orientation perpendicular to **E** based on the axis-selective trans-cis-trans photoisomerization likewise the azobenzene-containing polymeric films [12,13]. Figures 3a-f plot changes in absorbances parallel and perpendicular to **E** of LPUV light at λ_{max} of LCP films as functions of exposure energy. For all LCPs, absorbance in perpendicular direction once increases, while that in parallel direction decreases. This indicates the cooperative photoinduced in-plane molecular orientation perpendicular to **E** of LPUV light. However, the generated negative maximum δA and S values decreases when

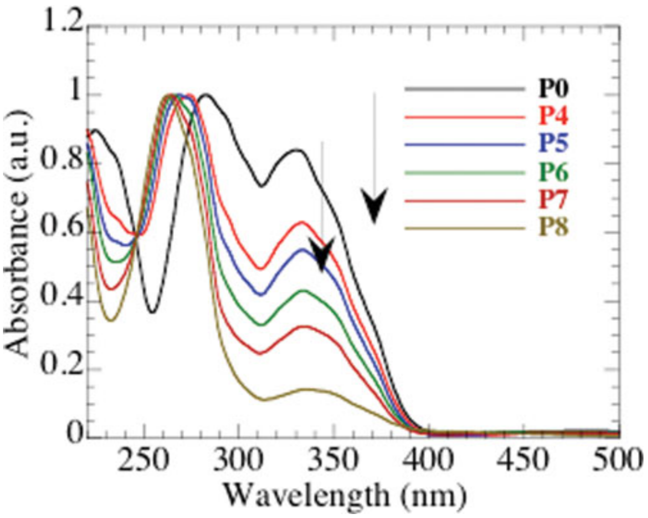

Figure 2. UV absorption spectra of LCP films on quartz substrate.

the BA composition increases (Table 2). Cooperative motion of BA side groups is difficult when the composition of BA-containing comonomer increases.

Additionally, photoinduced δA decreases after showing the maximum value when the LPUV light irradiation proceeds. This is due to the side-photoreactions of NBA side groups that disturb the orientation structure [13].

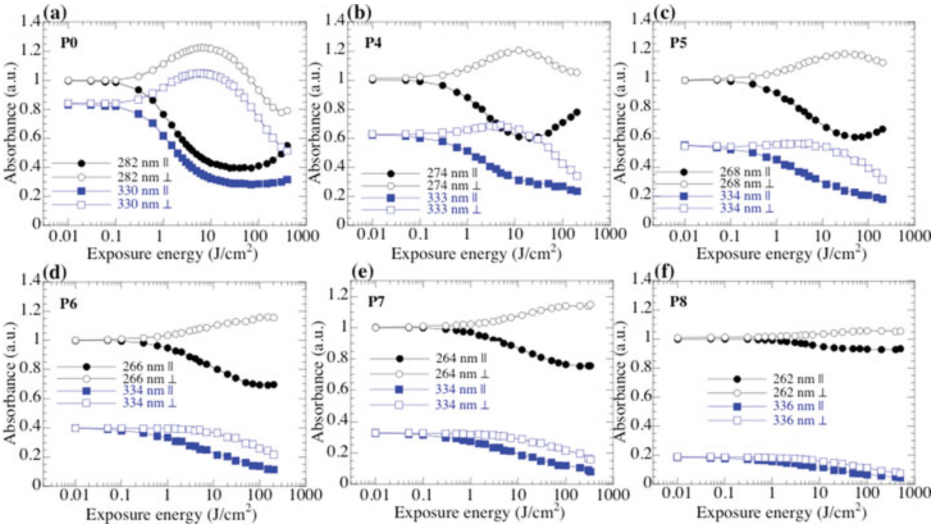

Figure 3. Change in absorbances of $A_{\parallel}$ and $A_{\perp}$ at λ_{max} of LCP films as functions of exposure energy. (a) **P0**, (b) **P4**, (c) **P5**, (d) **P6**, (e) **P7**, (f) **P8**.

Table 2. Maximum photoinduced δA and S values of LCP films

LCP	exposure energy[a)]	$\lvert\delta A\rvert$ at $\lambda_{\max 1}$	S, after exposure at $\lambda_{\max 1}$	S, after exposure at $\lambda_{\max 2}$
P0	10	0.79	0.38	0.42
P4	12	0.60	0.25	0.27
P5	50	0.57	0.24	0.24
P6	150	0.47	0.18	0.26
P7	200	0.39	0.15	0.22
P8	200	0.13	0.04	0.17

a) Jcm^{-2} at 365 nm.

Thermally Stimulated Amplification of the Orientation Structure of Copolymer Films

The photoinduced optical anisotropy of LCP films is thermally amplified when the exposed films are annealed at the elevated temperature. Figure 4a shows polarized UV absorption spectra of a **P7** film before and after LPUV light exposure for 4 Jcm^{-2} and subsequent annealing at 120 °C. After exposure, the photoinduced anisotropy is small ($S_{264\mathrm{nm}} = 0.01$), while annealing procedure amplified the S value to 0.59. Great amplification is achieved although the photoinduced orientation ability of the **P7** film is inferior. This amplification is due to the small difference in the self-organization ability between perpendicular and parallel directions of **E** of LPUV light. Additionally, the amplified S value depends on the exposure energy as shown in Fig. 4b. Sufficient amplification is obtained when the exposure energy is approximately 5 Jcm^{-2}, and the amplification decreases at the higher exposure region because the large amount of side photoreactions reduces LC characteristics of the material.

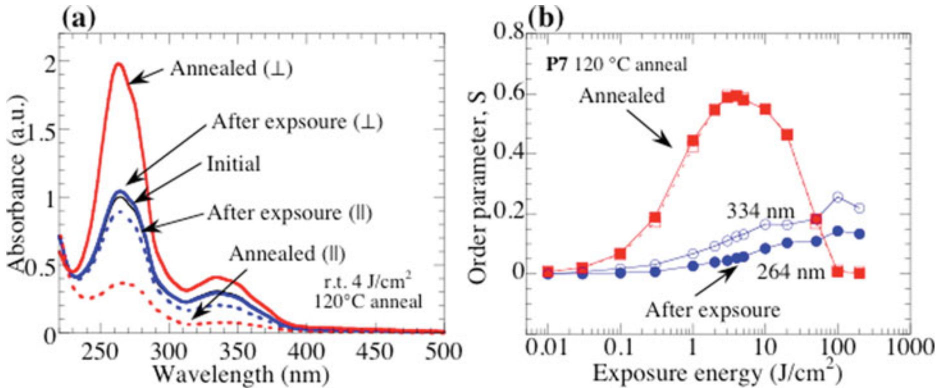

Figure 4. (a) Change in the polarization UV-vis polarization spectrum of a **P7** film before photoirradiating, after irradiating for 4 Jcm^{-2} (blue lines), and after subsequent annealing at 120 °C for 10 min (red lines). (b) Thermally enhanced S values at 264 nm and 364 nm of the photoreacted **P7** films as a function of exposure energy. Annealing temperatures: 120 °C.

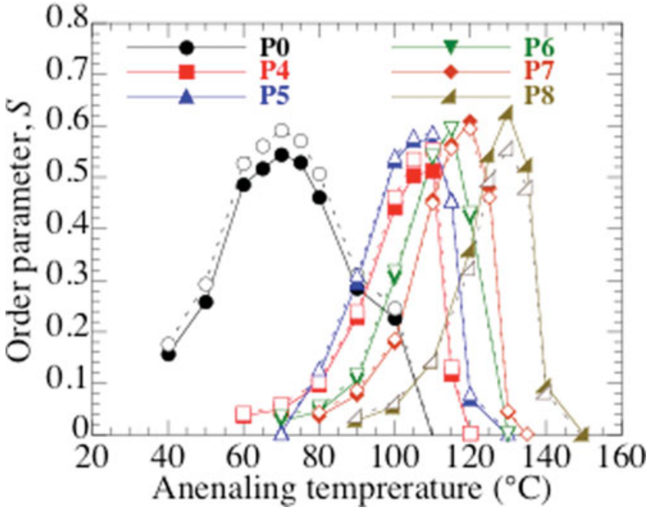

Figure 5. Thermally enhanced *S* values at 260 nm and 330 nm of LCP films as a function of annealing temperature. Exposure energy: 0.5 Jcm^{-2} for **P0**, 0.7 Jcm^{-2} for **P4**, 2 Jcm^{-2} for **P5** and **P6**, 4 Jcm^{-2} for **P7,** 10 Jcm^{-2} for **P8**. Closed (open) points; *S* at 260 (330 nm).

Other LCP films also show the thermal amplification of the photoinduced optical anisotropy. Figure 5 plots thermally amplified *S* values of LCP films as a function of annealing temperature when the exposure doses are 0.5 Jcm^{-2} for **P0**, 0.7 Jcm^{-2} for **P4**, 2 Jcm^{-2} for **P5** and **P6**, 4 Jcm^{-2} for **P7,** 10 Jcm^{-2} for **P8**, and Table 3 summarizes maximum thermally amplified *S* values. For all LCPs, maximum *S* values are approximately 0.6, suggesting that significant amplification of the photoinduced optical anisotropy occurs regardless of the copolymer composition. This means that the photoinduced small optical anisotropy can be amplified similar to other photoreactive LC copolymer films that show cooperative photoinduced molecular reorientation [3,4]. Additionally, it exhibits that annealing close to the isotropic transition temperature of the non-exposed LCP yields sufficient cooperative reorientation of the side groups.

Table 3. Maximum thermally amplified orientation condition of LCP films

LCP	exposure energy[a)]	annealing temperature	*S*, before annealing		*S*, After annealing	
			260 nm	330 nm	260 nm	330 nm
P0	1	120	0.17	0.18	0.56	0.61
P4	0.7	130	0.08	0.09	0.54	0.46
P5	2	120	0.09	0.13	0.59	0.59
P6	2	115	0.08	0.13	0.57	0.58
P7	4	110	0.05	0.12	0.58	0.60
P8	10	110	0.02	0.12	0.54	0.58

a) Jcm^{-2} at 365 nm.

Conclusions

Photosensitive polymethacrylates (LCPs) with NBA and BA side groups are synthesized and their photoinduced reorientation behavior is investigated. Cooperative molecular reorientation of both mesogenic side groups is observed, but the reorientation ability decreases when the BA-containing comonomer composition increases. However, for all LCPs, significant amplification ($S\sim0.6$) is achieved when the exposed films are annealed at the LC temperature range of the material. These LCPs are useful for LC alignment layer and birefringent film applications, where adjusting the copolymerization ratio can control the annealing temperature for the effective reorientation.

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