Birefringent Control of Photo-Oriented Polymeric Films by *in situ* Exchange of Functional Moieties

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Thermally stimulated photoinduced molecular reorientation with high dichroism ($D > 0.6$) is explored in liquid crystalline (LC) copolymerthacrylate films comprising of 4-methoxy-*N*-benzylideneaniline (MNBA) and benzoic acid (BA) side groups. Thermal hydrolysis of MNBA side groups induces free phenyl aldehyde (PA) side groups in the oriented film. Birefringence of the oriented films is adjusted by introducing 2,7-diaminofluorene (FL) to form new imine bonds with free PA side groups. Meanwhile, *in situ* exchange from MNBA to FL-based imine also controls the birefringence of the oriented film. The initial birefringence of the oriented copolymer film increases up to 0.22 after introducing oriented FL moieties.

Keywords: Photoalignment, Molecular orientation, Birefringence, Liquid crystalline polymer

1. Introduction

Photoalignment of photosensitive polymeric films is applicable to fabricating optical and display devices [1–8]. Basically, axis-selective photo-reaction of the photosensitive moieties generates optical anisotropy and/or molecular reorientation, which attains the birefringence of the film [4–8]. Direct fabrication of a molecularly oriented structure of the polymeric films is achieved using photoalignable liquid crystalline (LC) polymers by means of linearly polarized (LP) light exposure, and in some cases, thermally stimulated self-organization [6–9].

Photoalignable LC polymers containing cinnamate or azobenzene-containing materials have been explored to realize thermally stimulated photoinduced molecular reorientation based on axis-selective photo-cross-linking or *trans-cis-trans* photoisomerization [6–13]. We have been carried out a systematic study on thermally stimulated photo-induced molecular reorientation of LC (co)polymers with 4-methoxy-*N*-benzylideneaniline (MNBA) side groups [14–16], which under-

go axis-selective *trans-cis-trans* photoisomerization likewise the photoinduced reorientation of azobenzene-containing polymeric films.

Because an aromatic imine (C=N) bond is easily formed from aromatic aldehyde and amine derivatives [17,18], position-selective formation of MNBA side groups in a polymethacrylate film with phenyl aldehyde (PA) side groups by coating of 4-methoxyphenyl amine (AN) molecules leads to a photoinduced birefringent pattern [15]. Additionally, thermal hydrolysis of the reoriented MNBA side groups in an LC copolymerthacrylate with benzoic acid (BA) and MNBA side groups after the cooperative molecular reorientation converts a photoinactive oriented film with free PA side groups [16,19]. In this case, re-coating the aromatic amine derivatives other than AN molecules by means of sublimation and/or inkjet printing controls the optical and thermal property of the oriented film [16]. To improve the birefringence of the reoriented film *via* this technique, it is acceptable to increase the composition of free PA side groups in the reoriented copolymer film and introduction of

aromatic amine derivatives with high inherent birefringence.

This paper describes the thermally stimulated photoinduced molecular reorientation of LC copolymethacrylate films comprising of MNBA and BA side groups (Fig. 1). The influence of the copolymer composition on the photoinduced reorientation and thermal hydrolysis of the oriented film is investigated. Birefringence control using 2,7-diaminofluorene (FL) on the hydrolyzed oriented copolymer film and simultaneous amine-exchange technique is explored to reveal an increased birefringence from 0.14 to 0.22.

Fig. 1. Chemical structure of LC copolymethacrylates **P1–P5** used in this study.

2. Experimental

2.1. Materials

All starting materials were used as received from TCI. FL was recrystallized from ethanol prior to use. Copolymers with BA and BA side groups (Fig. 1, **P1 – P5**) were synthesized by a free radical polymerization from the corresponding methacrylate monomers using AIBN as an initiator in tetrahydrofuran (THF) [20]. Table 1 summarizes composition, molecular weight, thermal property and spectroscopic data of copolymers.

Table 1. Composition, molecular weight, and thermal property of copolymers.

Copolymer	x^a	y^a	z^a	Molecular weight ^{b)}		Thermal property ^{c)}	$\lambda_{\max}^d$
				M_n	M_w/M_n		
P1	21	75	4	26000	2.5	G 70 N 139 I	262
P2	38	59	3	81000	1.6	G 45 N 139 I	266
P3	44	51	5	110000	1.6	G 31 N 126 I	268
P4	56	40	4	19000	2.3	G 47 N 121 I	269
P5	60	37	3	27000	2.5	G 69 N 120 I	276

a) Determined by $^1\text{H-NMR}$. b) Measured by GPC, polystyrene standards. c) Measured by DSC. G: amorphous glass, N: nematic, I: isotropic. d) Absorption maxima of a film on quartz substrate.

2.2. Film preparation and photoirradiation

Copolymer films (thickness; approximately 200 nm) were prepared by spin-coating a THF solution onto quartz substrates.

Photoreactions were carried out using a high-pressure Hg lamp equipped with a glass plate placed at Brewster's angle and a 365-nm bandpass filter (Asahi Spectra REX-250), yielding a light intensity of 30 mW/cm^2 at 365 nm. After photoirradiation, the films were annealed at elevated temperatures to thermally stimulate molecular reorientation under a dry N_2 atmosphere.

2.3. Characterization

$^1\text{H-NMR}$ spectra using a Bruker DRX-500 FT-NMR and FT-IR spectra (JASCO FTIR-6600) confirmed the copolymers. The molecular weight of the copolymer was measured by GPC (JASCO PU-2080 and RI-2031 GPC system with a Shodex column using THF as the eluent) calibrated using polystyrene standards. The thermal properties were examined using a POM (Olympus BX51) equipped with a Linkam TH600PM heating and cooling stage as well as differential scanning calorimetry (DSC; Seiko-I SSC5200H). As a measure of the photoinduced optical anisotropy, the photoinduced in-plane dichroism (D) was evaluated from the polarization absorption spectra with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms. D is estimated as

$$D = (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel}) \quad (1),$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**) of LP 365 nm light, respectively. Birefringence of the oriented films was measured by the Senarmont method at 633 nm.

3. Results and discussion

3.1. Synthesis and thermally stimulated photoinduced reorientation of copolymer films

All copolymers were synthesized by a free radical copolymerization from corresponding methacrylate monomers [20]. Upon the reprecipitation process under the humid condition ($\text{RH}=30\text{--}50\%$), partial hydrolysis of MNBA side groups occurs, resulting in that the copolymers partially include PA side groups ($<5 \text{ mol}\%$, Table 1). The synthesized copolymers show a nematic LC characteristics, where the isotropic transition temperature (T_i) increases as the content of BA side groups increases. Figure 2a shows absorption spectra of copolymer films, showing that the absorption maximum ($\lambda_{\max}$) slightly shifts to longer wavelength as decreasing the BA content due to the absorption of MNBA moiety at longer wavelength.

When the copolymer films are exposed to LP 365 nm light, negative photoinduced reorientation

occurs due to the axis-selective photoisomerization of MNBA side groups ($\Delta A = A_{\parallel} - A_{\perp} < 0$), and the subsequent annealing at the LC temperature range of the film under dry N_2 atmosphere amplifies the cooperative molecular reorientation of both mesogenic side groups [16,20]. Figures 2b – f show the change in the polarized absorption spectra of **P1** – **P5** films before and after exposure to LP 365 nm light for 2 – 15 J/cm², and subsequent annealing at LC temperature range of the material for 10 min. For all films, the photoinduced negative optical anisotropy is significantly amplified after the annealing, where $D_{\lambda_{\max}}$ (D_{335}) is 0.74 – 0.77 (0.68 – 0.75) (Table 2). At present, the amplified D values are larger than those previously reported because the hydrolysis of MNBA groups is restricted since the annealing process is carried out under dry N_2 condition [16,20]. Additionally, Δn of the reoriented film slightly increases when the BA composition decreases while the generated D values are similar to each other. This is due to larger inherent birefringence of MNBA side groups than that of BA.

Fig. 2. (a) Absorption spectra of copolymer films on quartz substrate. (b – f) Changes in the polarized absorption spectra of copolymer films before and after exposure to LP 365 nm light and subsequent annealing for 10 min. Copolymer, exposure energy and annealing temperature are shown in each figure.

3.2. Thermal hydrolysis of MNBA side groups of the reoriented films

Table 2. Dichroism (D), birefringence (Δn), and degree of hydrolysis (DH) of the reoriented copolymer films and FL-introduced film.

Co-polymer	Photoinduced $D^{a)}$			Hydrolysis ^{c)}		Introduction of FL			
	$D_{\lambda_{\max}}$	D_{335}	$\Delta n^{b)}$	DH ^{d)}	$D_{\lambda_{\max}}$	FL% ^{e)}	$D_{\lambda_{\max}}$	D_{375}	$\Delta n^{b)}$
P1	0.77	0.68	0.14	85	0.69	69	0.72	0.74	0.18
P2	0.75	0.74	0.15	63	0.69	70	0.68	0.73	0.19
P3	0.74	0.74	0.15	58	0.63	60	0.67	0.70	0.20
P4	0.74	0.75	0.15	-	-	85	0.60	0.69	0.22
P5	0.75	0.75	0.16	-	-	90	0.60	0.64	0.22

a) D values of oriented films in Fig. 2. b) At 633 nm. c) Thermal hydrolysis. d) Degree of hydrolysis (%). e) FL introduction to calculated free PA side groups.

We have previously reported that the oriented MNBA moieties are hydrolyzed to form free PA side groups with maintaining the oriented structure of the film, when the reoriented film is annealed under humid condition [16]. Figures 3a – c show change in the polarized absorption spectra of oriented **P1** – **P3** films before and after annealing under air (RH = 35%) at 125 °C for 80 min for **P1**, at 100 °C for 180 min for **P2**, and at 90 °C for 540 min for **P3**, respectively. After the annealing, absorption band of MNBA decreases [degree of hydrolysis (DH) = 85% (**P1**), 63% (**P2**), and 58% (**P3**)], while the orientational order almost unchanged ($D_{\lambda_{\max}}$ = 0.69, 0.69, and 0.63) (Tab. 2). In contrast, orientational structure of the **P4** film is collapsed when the film is annealed for 30 min at 100 °C (DH = 65%), but 10 min-annealing (DH = 26%) keeps the orientational structure (D_{269} = 0.70, Fig. 3d). For **P4**, LC characteristics of the oriented film diminishes when the DH increases due to higher content of MNBA side groups, resulting in the random orientation of

Fig. 3. (a) Changes in the polarized absorption spectra of oriented copolymer films before and after post-annealing at elevated temperature under humid air (RH = 35%). (a) **P1**, (b) **P2**, (c) **P3** and (d) **P4**. Post-annealing condition is shown in each figure.

the film at elevated temperature.

When the hydrolysis of MNBA side groups proceeds, transition temperature to the isotropic state (T_i) of the film decreases. Additionally, LC characteristics of the hydrolyzed film will disappear when the composition of PA side groups is larger than 50%, which is expected by evaluating the thermal property of copolymethacrylate with BA and PA side groups (Fig. 4). Therefore, the hydrolyzed oriented **P4** film could hold the LC state at 100 °C when DH is 26%, but further hydrolysis no longer shows LC characteristics of the film at 100 °C, resulting in the random orientation. Namely, thermal hydrolysis to form free PA moieties should be carried out with maintaining the LC characteristics to hold the orientational structure of the film.

Fig. 4. Glass transition temperature (T_g), and isotropic transition temperature (T_i) of copolymethacrylate with BA and PA side groups and T_i of LC copolymers (**P1** – **P5**) as a function of BA composition.

3.3. Introduction of FL molecules into the oriented films

When the oriented film includes free PA side groups, introducing the different phenyl amine derivatives to form a new imine ($C=N$) bonds changes the optical and thermal properties of the film [16]. For **P1**, **P2** and **P3**, *in situ* condensation of FL molecules with free PA side groups in the hydrolyzed oriented film is achieved. Figure 5a (b) shows change in the polarized absorption spectra of a hydrolyzed oriented **P1** (**P2**) film [DH = 85% (63%)] before and after introducing FL molecules, where the film is coated using a methanol solution of FL molecules and annealed at 120 °C (100 °C) followed by rinsing with methanol and diethyl ether. New absorption at 375 nm ($D_{375}=0.74$, $D_{266}=0.72$ for **P1**, $D_{375}=0.73$, $D_{266}=0.68$ for **P2**) appears, which is assigned FL molecules with $C=N$ formation. Similar introducing of oriented FL molecules to form $C=N$ bonds is observed for a **P3** film (Fig. 5c).

In contrast, simultaneous exchange of AN to FL is attained for the oriented **P4** and **P5** films since the

Fig. 5. Changes in the polarized absorption spectra of hydrolyzed oriented copolymer films before and after coating FL molecules followed by annealing at elevated temperature under N_2 atmosphere. (a) **P1**, (b) **P2**, and (c) **P3**. Annealing condition is shown in each figure.

hydrolyzed oriented **P4** and **P5** films cannot be obtained. Because AN is sublimed at 100–110 °C upon the thermal hydrolysis and FL molecules do not sublime at this temperature, condensation between free PA side groups and FL molecules will simultaneously occur. Figure 6a shows change in the polarized absorption spectra of an oriented **P4** film before FL-coating and after annealing the FL-coated film at 110 °C for 60 min under N_2 atmosphere. In this case, FL molecules are coated from ethylene glycol solution and the excess FL molecules are eliminated by rinsing using diethyl ether and methanol after the annealing. Similar to the introduction of FL molecules into hydrolyzed **P1** – **P3** films, absorption band at 375 nm ($D_{375}=0.69$, $D_{269}=0.60$) appears, indicating the simultaneous hydrolysis of MNBA and formation of a new $C=N$ bond of FL molecules. Similar spectral change is observed for a **P5** film (Fig. 6b).

Fig. 6. Changes in the polarized absorption spectra of oriented copolymer films before and after *in situ* exchanging from MNBA to FL-based Schiff-base. (a) **P4**, and (b) **P5**. Annealing condition is shown in each figure.

The introduction of FL molecules into the oriented film leads improvement of birefringence and thermal stability of the film due to the cross-linked structure. Table 2 summarizes changes in D values and birefringence of **P1** – **P5** films before and after introducing FL molecules. The introduction of FL moieties is 70 – 95% as compared to the hydrolyzed PA groups, and D_{375} is 0.60 – 0.72, while the birefringence increases up to 0.22 as increasing the FL moieties in the oriented film. Additionally, thermal stability increases approximately up to 170 °C for all the films, at which the collapse of the hydrogen bonds of dimerized BA side groups occur (Fig. 7). However, the orientation structure is partially stable above this temperature when the composition of BA side groups decreases due to the higher density of crosslinking.

Fig. 7. Thermal stability test (birefringence) of FL-introduced oriented copolymer films in Figs. 5 and 6 when the film is annealed at elevated temperature.

4. Conclusion

Thermally stimulated photoinduced molecular reorientation of LC copolymethacrylate with MNBA and BA side groups is investigated. Cooperative molecular orientation with high dichroism ($D > 0.6$) is achieved for all copolymer films. Thermal hydrolysis of MNBA side groups attains the oriented copolymer film with free PA side groups when the MNBA composition is below 44 %, while the orientational structure is collapsed for the copolymer with higher MNBA composition. Introduction of FL molecules to form a new imine bonds in the oriented hydrolyzed film improves the birefringence and thermal stability of the film. The *in situ* exchange of the imine side groups from MNBA to FL-introduced side groups for the

copolymer with higher MNBA composition attains the birefringence of the oriented film up to 0.22.

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