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NOTE

Influence of molecular weight on the photoinduced reorientation of photo-cross-linkable liquid crystalline polymeric films

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INTRODUCTION

Photoalignment is emerging as a promising alternative to mechanical rubbing and stretching for orienting molecular structures because it is free from dust and static electricity and is easily patterned.[1–6] Photoalignment is based on the axis-selective photoreaction of photosensitive polymeric films with linearly polarized (LP) light. It is utilized as an alignment layer for low-molecular-weight liquid crystals (LCs) in LC displays and to fabricate molecularly oriented functional films.[1–6]

Several types of photoreactive materials have been used for photoalignment, including polymers composed of azobenzene,[7,8] cinnamate ester,[3–6,9] cinnamic acid[10] and phenyl benzoate.[11] Exposing these films to LP light induces a small optical anisotropy due to the axis-selective photoreaction of the photosensitive moieties. If the photoreaction does not induce molecular reorientation, the photoinduced in-plane order parameter (S) is very small (< 0.1).[12] In contrast, a large optical anisotropy ($S > 0.5$) occurs when molecular reorientation is induced by the photoreaction[7] or if thermal amplification occurs.[6,10,11]

We previously reported that photoreactive liquid crystalline polymers exhibit thermally enhanced photoinduced molecular reorientation of their poly(meth)acrylate photo-cross-linkable side groups.[5,6] For these liquid crystalline polymers, a small photoinduced optical anisotropy based on axis-selective photo-cross-linking is amplified either parallel or perpendicular to the polarization (E) of the LP light due to the intrinsic reorientation of the LC phases of the material.[5] Photo-cross-linkable liquid crystalline polymers composed of cinnamate ester derivative side groups (PMCB6M, Figure 1) can achieve thermally enhanced photoinduced in-plane molecular reorientation parallel to E. These liquid crystalline polymers may be applicable for birefringent films,[6,13] photoalignment layers for functional materials,[14,15] and polarization holographic optical devices.[16]

During thermal amplification of PMCB6M films, the axis-selective photo-cross-linked mesogenic side groups undergo in-plane self-organization, acting as anchors that reorient the non-photoreacted groups such that they are parallel. This process is dictated by the thermal mobility of the mesogenic groups. The intrinsic self-organization in the parallel and perpendicular directions controls the reorientation of the axis-selectively photoreacted PMCB6M film. Previously, we achieved thermally enhanced in-plane molecular reorientation ($S > 0.7$) of PMCB6M films with a number-average molecular weight (M_n) of approximately 3×10^4 (polydispersity index; DPI ~ 3) when the degree of the photoreaction (DP) was approximately 8–15%.[6] Because this thermally enhanced self-organization depends on the anisotropic stiffness and the intrinsic reorientation ordering ability of the material, both the cross-linking density and the initial molecular weight of the material can affect the mobility of the mesogenic side groups and the main polymer chains at elevated temperatures. However, the influence of molecular weight on thermally enhanced molecular reorientation has yet to be explored.

In this study, we investigated the influence of molecular PMCB6M weight on thermally enhanced photoinduced molecular reorientation. Reversible addition fragmentation chain transfer and free radical polymerization were used to synthesize PMCB6Ms of varying molecular weights. Exposure to LP ultraviolet light followed by annealing resulted in photoinduced reorientation as evaluated by polarized ultraviolet–visible spectroscopy. Changes in the solubility of the PMCB6M films resulting from axis-selective photo-cross-linking depend on the initial molecular weight of the polymer, which also has an important role in the thermally enhanced self-organization behavior.

EXPERIMENTAL PROCEDURE

The methacrylate monomer (MCB6M) was synthesized according to a previous study.[6] PMCB6Ms with low number-average molecular weights
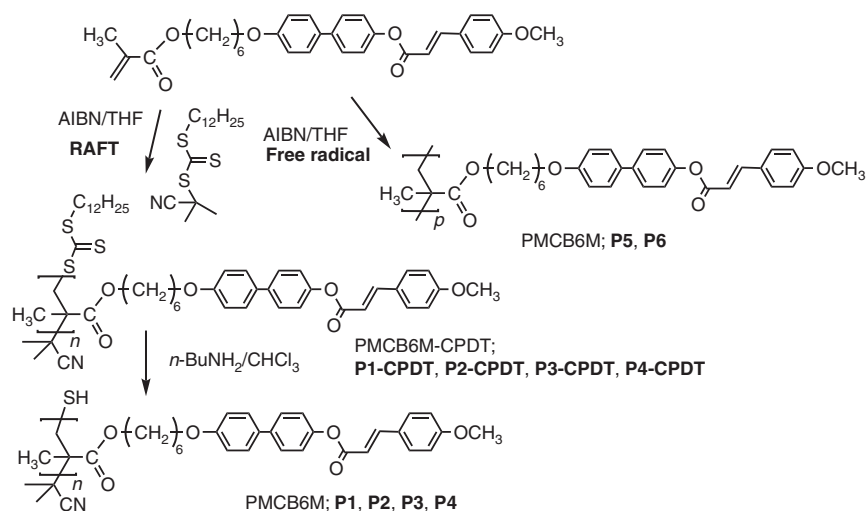
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Figure 1 Synthetic route of PMCB6Ms, **P1–P6**.

($M_n < 1.8 \times 10^4$, **P1–P4**) were synthesized by reversible addition fragmentation chain transfer polymerization.[17] Higher number-average molecular weight polymers ($M_n \sim 5.9 \times 10^4$, **P5** and **P6**) were prepared by free radical polymerization using 2,2′-azobisisobutyronitrile (AIBN). After reversible addition fragmentation chain transfer polymerization, the dodecyltrithiocarbonate end groups were decomposed using *n*-buthylamine (Figure 1).[17,18]

A typical reversible addition fragmentation chain transfer polymerization procedure for the synthesis of **P2** is carried out as follows. First, 3.7 g (7.2 mmol) of MCB6M, 252 mg (0.73 mmol) of 2-cyano-2-propyldodecyl-trithiocarbonate (CPDT), and 46 mg (0.28 mmol) of AIBN are dissolved in 30 ml of tetrahydrofuran (THF), and the solution is degassed. After heating at 55 °C for 1 day, the solution is poured into diethyl ether. The slightly yellow polymer is then purified three times by reprecipitation from chloroform to diethyl ether. (**P2-CPDT**, yield 2.6 g, 64 wt%). Next, 0.6 g of **P2-CPDT** and 0.86 g (12 mmol) of *n*-butylamine are dissolved in 8 ml of chloroform and stirred at r.t. for 1 h. The solution is then poured into diethyl ether and the colorless polymer is purified two times by reprecipitation from chloroform to diethyl ether (**P2**, yield 509 mg, 85 wt%). Finally, decomposition of the CPDT end group can be confirmed by ^{1}H-NMR.

The other polymers (**P1**, **P3** and **P4**) were synthesized using similar methods, except the CPDT/MCB6M ratios were adjusted. Free radical polymerization was performed using AIBN as an initiator in the tetrahydrofuran. The AIBN concentrations were adjusted to control the molecular weight. Table 1 summarizes the molecular weight, thermal properties and spectroscopic properties of the PMCB6Ms synthesized in this study.

Thin polymeric films (0.1–0.2 μm thick) were prepared by spin-coating a solution of methylene chloride and the polymers (1 w/w%) onto quartz substrates. The photoreactions were performed at r.t. using a high-pressure Hg lamp equipped with Glan–Taylor prisms and a cutoff filter of less than 300 nm at 365 nm light intensity of 50 mW cm^{-2}. After irradiation, the films were annealed at higher temperatures for 10 min. The DP was estimated by observing the decrease in absorbance at 315 nm. Photoinduced optical dichroism ($\Delta A = A_{\parallel} - A_{\perp}$) was used to measure the photoinduced optical anisotropy. The in-plane order was evaluated using the in-plane order parameter, $S = (A_{\parallel} - A_{\perp})/(A_{larger} + 2A_{smaller})$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbance values parallel and perpendicular to **E** of the LP light, respectively, and A_{larger} and $A_{smaller}$ are the larger and smaller absorbance values of $A_{\parallel}$ and $A_{\perp}$, respectively. To evaluate the photoinduced insolubility of the thin films, the spin-coated films were exposed to ultraviolet light for various exposure times. The films were then treated in chloroform for 1 min, rinsed in diethyl ether for 1 min, and dried. The final film thickness was measured by interferometry (VertScan2.0, Ryoka Systems Inc., Tokyo, Japan).

Table 1 Molecular weight, and thermal and spectroscopic properties of the synthesized polymers

	Molecular weight (g mol)[a]			λ_{max} (nm)	
Polymer	M_n ($\times 10^{-4}$)	PDI[c]	Thermal property[b] (°C)	Solution[d]	Film[e]
P1	0.31	1.55	C 97 N 266 I	313	285
P2	0.46	1.43	C 102 N 277 I	313	289
P3	1.02	1.17	C 106 N 298 I	313	290
P4	1.82	1.22	C 116 N > 300 I	313	294
P5	3.90	2.08	C 115 N > 300 I	313	294
P6	5.90	2.01	C 116 N > 300 I	313	294

Abbreviations: DSC, differential scanning calorimetry; GPC, gel permeation chromatography; PDI, polydispersity index; POM, polarizing optical microscopy; THF, tetrahydrofuran.
[a]Determined by GPC, polystyrene standards in chloroform standards.
[b]Measured with DSC and POM observation.
[c]Polydispersity index.
[d]In THF.
[e]On quartz substrate.

RESULTS AND DISCUSSION

All of the polymers have a nematic LC phase and similar thermal properties ($T_m \sim 115$ °C, $T_i > 300$ °C) when M_n is greater than 1.8×10^4 (**P4–P6**). T_m and T_i degrease as M_n decreases (**P1–P3**). As shown in Figure 2a, the spectroscopic properties in solution are the same among the polymers (absorption maxima; $\lambda_{max} = 313$ nm). The λ_{max} of the film state shifts to a shorter wavelength and becomes broader due to partial H-aggregation of the mesogenic side groups (Figure 2b). Additionally, the spectroscopic properties of the film state are similar when M_n is greater than 1.8×10^4 ($\lambda_{max} = 294$ nm). The λ_{max} shifts to an even shorter wavelength ($\lambda_{max} = 285$–290 nm) as the molecular weight decreases (Table 1). H-aggregation of the mesogenic side groups in the film state is favorable for low molecular weight polymers.

Figure 3a and its inset show the DP and photoinduced ΔA values at 314 nm, resulting from axis-selective photoreaction of the side groups, as a function of LP ultraviolet light exposure energy. In all cases, the same photoreactivity and maximum absolute value of ΔA ($|\Delta A|$) are obtained when the exposure energy is 3.5 J cm^{-2} (DP $\sim 40\%$). Because the photoreaction of the cinnamate derivatives includes [2+2] photodimerization and *trans–cis* photoisomerization, photo-cross-linking should change the solubility of the material.
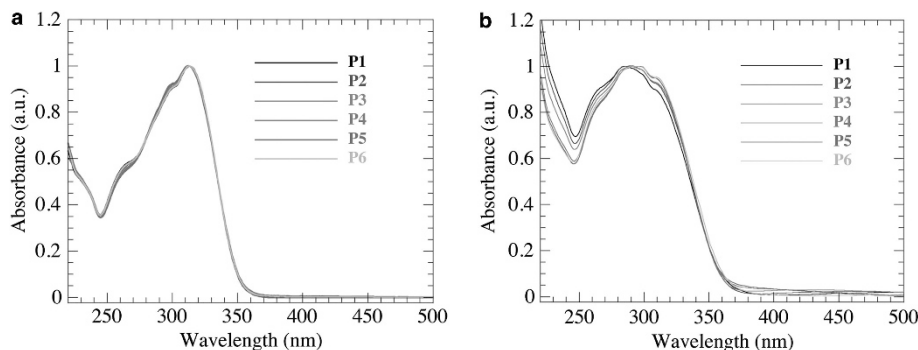
Figure 2 Ultraviolet–visible absorption spectra of (**a**) solutions in tetrahydrofuran and (**b**) films on quartz substrates. A full color version of this figure is available at *Polymer Journal* online.
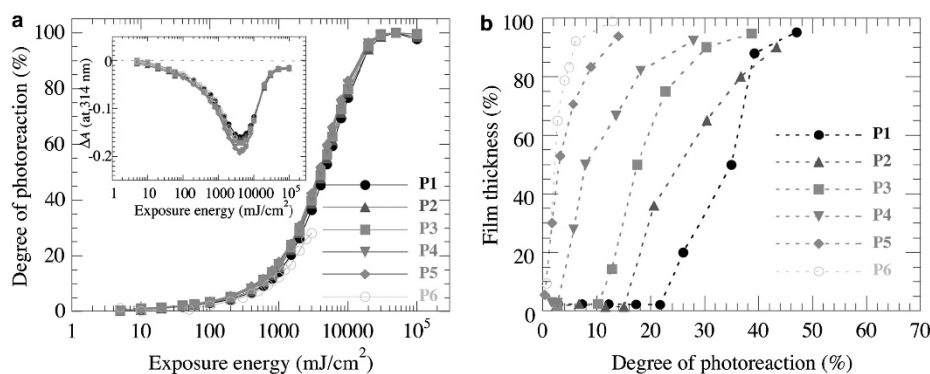

Figure 3 (**a**) Degree of the photoreaction as a function of exposure energy. Inset plots photoinduced ΔA values as functions of exposure energy. (**b**) Insolubilization of PMCB6M films upon irradiation with linearly polarized ultraviolet light. A full color version of this figure is available at *Polymer Journal* online.

To evaluate the influence of molecular weight on solubility, we compared the time required for gelation of each of the film (Figure 3a). Figure 3b plots the normalized film thickness as a function of the DP after the irradiated films were immersed into chloroform. As the molecular weight decreases, the DP required for insolubility increases, indicating that both photo-cross-linking density and initial molecular weight are related to film solubility. Additionally, the higher solubility of the low molecular weight films is partially due to their preference for H-aggregation.

Annealing the irradiated films within the LC temperature range suggested for non-exposed films enhances their photoinduced optical anisotropy parallel to **E**. Figure 4 plots the thermally enhanced S values as a function of the DP 10 min of annealing. **P3–P6** films exhibit a thermal enhancement with a maximum S (S_{max}) of > 0.7 for **P4**, **P5**, and **P6** and ~ 0.6 for **P3**. For these films, the required DP is less than 18%. The DP required for effective molecular reorientation decreases as M_n increases. In contrast, for **P1** and **P2** films, the S_{max} is less than 0.3. For these films, the DP required to reach the S_{max} exceeds 20%. For **P1** and **P2**, the S_{max} values decrease and the required DP increases as M_n decreases. Although **P3** requires a higher DP than **P4–P6** to reach S_{max}, it can still self-organize ($S \sim 0.6$) because the film maintains its intrinsic reorientation properties in the LC mesophase.

For **P4–P6**, the small amounts of axis-selective photo-cross-linked mesogenic side groups anchor the polymers to thermally reorient the non-photoreacted mesogenic side groups. At elevated temperatures, a small number of photoproducts can generate large differences in the mobility of the mesogenic side groups parallel and perpendicular to **E**, regulating the anisotropic thermal mobility.
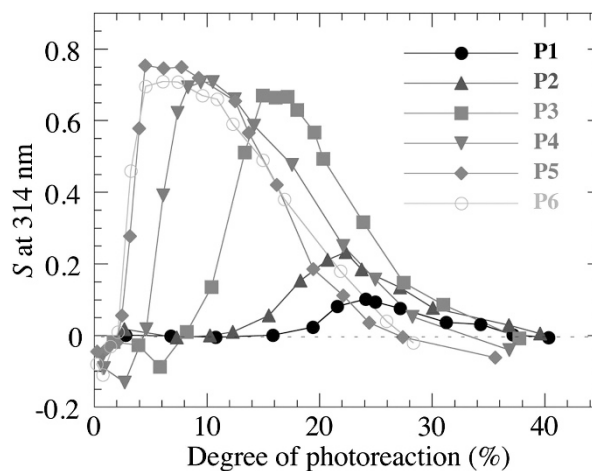

Figure 4 Thermally enhanced S value of **P1–P6** films as functions of the degree of photoreaction. A full color version of this figure is available at *Polymer Journal* online.

By contrast, **P1** and **P2** axis-selective photo-cross-linking does not have much influence on regulating thermally generated self-organization because only small thermal mobility differences are present between the photo-cross-linked and non-photoreacted mesogenic side groups. Therefore, **P1** and **P2** require a higher DP to reveal a difference in the mobility between the photo-cross-linked and non-photoreacted mesogenic side groups. This requirement results in a decrease in

the axis selectivity and the LC ordering during the photoreaction, producing inferior self-organization.

It should be noted that thermally enhanced molecular reorientation parallel to **E** occurs simultaneously with precipitation (Figures 3b and 4). This finding confirms that the anisotropic change in the stiffness of the material influences the thermally enhanced molecular reorientation, which is related to the insolubility of the film. For **P4**–**P6**, a large change in the solubility with only a small amount of photoreaction could produce molecular reorientation.

Thermally enhanced reorientation perpendicular to **E** is observed for **P3** and **P4** when the DP is approximately 5%. However, the *S* value is small ($S < 0.2$). In this case, small amounts of photoproducts parallel to **E** act as impurities that thermally induce reorientation perpendicular to **E**.[5,6] However, for **P1** and **P2**, thermal enhancement does not occur, and the annealing process induces a multi-domain structure at the initial stage of the photoreaction. Furthermore, for **P5** and **P6**, reorientation perpendicular to **E** is not observed because the reorientation parallel to **E** competes with the anchoring effect due to the high stiffness of the material. The initial molecular weight regulates the anisotropic stiffness of the film and controls the thermal enhancement of the molecular reorganization.

In summary, we investigated the influence of molecular weight on thermally enhanced photoinduced molecular reorientation of PMCB6M films. Photoreacted mesogenic side groups parallel to **E** act as photo-cross-linked anchors to immobilize and thermally reorient the non-photoreacted mesogenic groups. This anchoring ability greatly depends on the molecular weight of the PMCB6M, which is related to the degree of photoreaction required for the films to become insoluble. When a film becomes insoluble, thermally generated self-organization parallel to **E** occurs. Additionally, molecular reorientation perpendicular to **E** occurs during the initial stage of the photoreaction when the molecular weight is 1.0–1.8×10^4. Adjusting the molecular weight of the material and the degree of photoreaction is important for effective thermally enhanced photoinduced molecular reorientation in this axis-selective photo-cross-linking system.

ACKNOWLEDGEMENTS

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