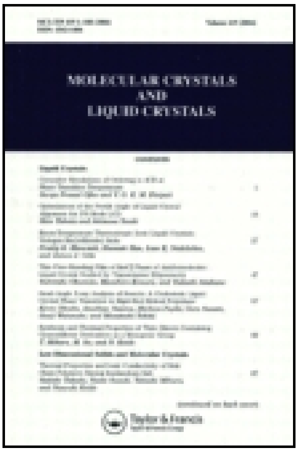

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Photoinduced Cooperative Orientation and Pattern Formation in Copolymer Films with 4-Methoyazobenzene and Benzoic Acid Side Groups

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Version of record first published: 02 Aug 2012.

To cite this article: Hiroshi Shoji , Kouki Tsubaki , Mizuho Kondo & Nobuhiro Kawatsuki (2012): Photoinduced Cooperative Orientation and Pattern Formation in Copolymer Films with 4-Methoyazobenzene and Benzoic Acid Side Groups, Molecular Crystals and Liquid Crystals, 563:1, 131-138

To link to this article: http://dx.doi.org/10.1080/15421406.2012.689146

*Mol. Cryst. Liq. Cryst.*, Vol. 563: pp. 131–138, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.689146

# Photoinduced Cooperative Orientation and Pattern Formation in Copolymer Films with 4-Methoyazobenzene and Benzoic Acid Side Groups

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*Photoinduced cooperative molecular reorientation in liquid crystalline (LC) methacrylate copolymers with hexamethylene spacer groups terminated with 4-methoxyazobenzene and benzoic acid in the side chain, and the influence of the copolymerization ratio on the thermally enhanced photoinduced molecular reorientation behavior were investigated. All copolymers exhibited a LC phase, and sufficient thermally enhanced photoinduced in-plane molecular reorientation was achieved by irradiating with linearly polarized (LP) UV light and subsequent annealing when the azobenzene composition was greater than 5 mol%. Adjusting the exposure energy and the polarization of the LPUV light attained a patterned oriented structure, which can be useful as alignment layer for functional materials. Finally, a patterned birefringent film was fabricated using photocurable liquid crystals on the patterned copolymer film.*

**Keywords** Azobenzene; patterned retarder; photoinduced orientation; polymer liquid crystal

## Introduction

Photoinduced reorientation in azobenzene-containing polymeric films has been intensively studied due to its applicability to optical and holographic memories, and birefringent optical devices [1–3]. Additionally, axis-selective photoisomerization of azobenzene molecules with linearly polarized (LP) light acts as "command surface," which controls the alignment direction of low-molecular-weight liquid crystal (LC) molecules [4,5]. Many azobenzene-containing materials have been investigated as the photoalignment materials for LCs and functional materials [6,7]. Furthermore, the irradiation an azobenzene-containing LC polymeric film with LP light generates molecular reorientation perpendicular to the polarization (**E**) of LP light due to an axis-selective trans-cis-trans photoisomerization [5,8,9]. Thermal enhancement of the photoinduced optical anisotropy in azobenzene-containing LC polymeric film was also reported [10–12]. However, applicability of the azobenzene-containing

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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, Hyogo, 671-2280, Japan. Tel: +81-79-267-4886. Fax: +81-79-267-4885. E-mail: kawatuki@eng.u-hyogo.ac.jp materials to display devises is limited because azobenzene molecules are colored in the visible region.

Cooperative photoinduced molecular reorientation is observed in photosensitive LC polymeric films when the non-photoreactive mesogenic side groups are introduced in the photosensitive LC copolymer [13–17]. The photoinduced reorientation of the azobenzene groups cooperatively reorient with non-photosensitive mesogenic side groups [13–15]. The efficiency of the cooperative reorientation depended on exposure doses, type of the non-photosensitive mesogenic side groups, and copolymerization ratio of the copolymer [13–17]. The copolymerization of azobenzene-containing polymers with non-photoreactive mesogenic side groups that do not show photo-absorption in the visible region is effective to reduce the colored characteristics of the material.

A poly(meth)acrylate with benzoic acid (BA) side groups reveals LC characteristics due to H-bonded dimmer of BA moieties and is transparent in the visible region [18]. Several photosensitive polymers containing BA side groups exhibited cooperative photoinduced molecular reorientation [19,20]. Additionally, introduction of the transparent comonomer into the copolymer and ease of the synthetic procedure of the comonomer with BA side groups are useful not only to improve the transparency of the material but also to reduce the material's cost.

In this paper, methacrylate copolymers with 4-methoxyazobenzene (4 MAz) and BA in the side chain were synthesized and their thermally enhanced photoinduced cooperative reorientation behavior was investigated by the use of LPUV light and subsequent annealing. The influence of the copolymerization ratio, exposure energy, and annealing temperature on the reorientation behavior was explored. Patterned reoriented structure of the copolymer film was fabricated by adjusting the polarization of the LPUV light with a photomask. Finally, a patterned birefringent film was demonstrated using a photocurable LC monomer on the patterned reoriented copolymer film.

## Experimental

### *Materials and Copolymer Synthesis*

All starting materials were used as received from Tokyo Kasei Chemicals. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored below 0°C. Methacrylate monomers with 4-MAz (4 MAzM) and BA (BAM) side groups were synthesized according to the literatures [10,11,19]. Photocurable LC monomer (M1 in Fig. 1) was synthesized by similar procedure according to the literature [22]. Photoinitiator (Irgacure 907, BASF) was used for photocuring of M1 film.

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 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. Polarization UV-vis spectra were measured using a spectrometer equipped with Glan-Taylor polarizing prisms. The in-plane

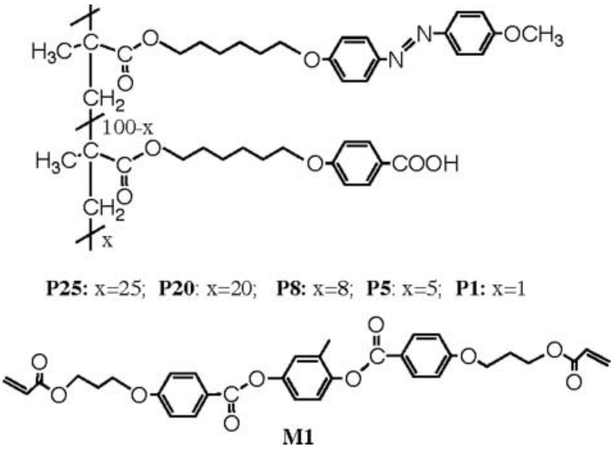

**Figure 1.** Chemical structure of copolymers in this study.

order parameter, *S*, is expressed in the form of equation 1;

$$S = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + 2A_{\parallel}} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively. *S* was calculated by polarized UV-vis spectroscopy using wavelengths at 262 nm (BA group) and at 360 nm (4 MAz group). The retardation of the film was evaluated using a polarimeter at 517 nm.

### *Photoirradiation*

Thin films were prepared by spin-coating a THF solution of copolymers (1 wt/wt-%) onto a quartz substrate. The film thickness was approximately 0.2 $\mu$m. 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$^2$

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

| | | Molecular weight[b)] | | |
|---|---|---|---|---|
| Polymer | x[a)] | $M_n X10^{-4}$ | $M_w/M_n$ | Thermal property[c)] (°C) (ΔH, J/g) |
| **P25** | 25 | 1.9 | 5.4 | G 60 N 150 (8.5) I |
| **P20** | 20 | 1.2 | 3.1 | G 67 N159 (19) I |
| **P8** | 8 | 0.85 | 2.8 | G 70 N 165 (23) I |
| **P5** | 5 | 1.2 | 4.0 | G 66 N 175 (27) I |
| **P1** | 1 | 0.9 | 4.4 | G 78 N 175 (28) I |

a) Determined by $^1$H-NMR. b) After esterification of BA moieties. Determined by GPC. Polystyrene standards, chloroform eluent. c) Determined by DSC. 2nd heating. G: glassy, N: nematic, I: isotropic.

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 were soluble in THF but insoluble in methylene chloride and chloroform. All the copolymers revealed a LC phase, which was confirmed by POM observation, and materials did not show phase separation. The introduction BA group is useful because the absorption band of BA is separated from that of 4 MAz moiety and the synthetic procedure is easy. Figures 2a and b show absorption spectra of copolymers in a THF solution and films on quartz substrate. Both figures revealed two independent absorption maxima around 260 nm and 360 nm, which were ascribable to absorption of BA and 4 MAz side groups, respectively. Additionally, the absorption properties of films are similar to that of solution regardless of the copolymer composition, indicating that the mesogenic side groups do not form molecular aggregation in the film state.

### *Thermally Enhanced Molecular Reorientation of Copolymer Films*

Irradiating a polymethacrylate with 4 MAz side groups with LPUV light generates axis-selective trans-cis photoisomerization and subsequent annealing enhances the photoinduced optical anisotropy [10,11]. Similarly, copolymers in this study revealed axis-selective trans-cis photoisomerization when irradiating with LPUV light and thermal enhancement of the generated optical anisotropy occurred when the exposed films was annealed at elevated temperature. Figures 3a and b plot the thermally enhanced *S* values at 262 nm and 360 nm of copolymer films as a function of exposure energy. The annealing temperatures were 135°C for **P25**, 145°C for **P20**, 155°C for **P8,** 165°C for **P5**, 170°C for **P1**.

Sufficient cooperative thermal amplification of the molecular reorientation was observed in **P25**, **P20**, **P8**, and **P5** films when the exposure energy was less than 200 mJcm$^{-2}$. The enhanced *S* values are greater than 0.5 for both side groups. After exposure, azobenzene moieties exhibited negative optical anisotropy due to axis-selective photoisomerization

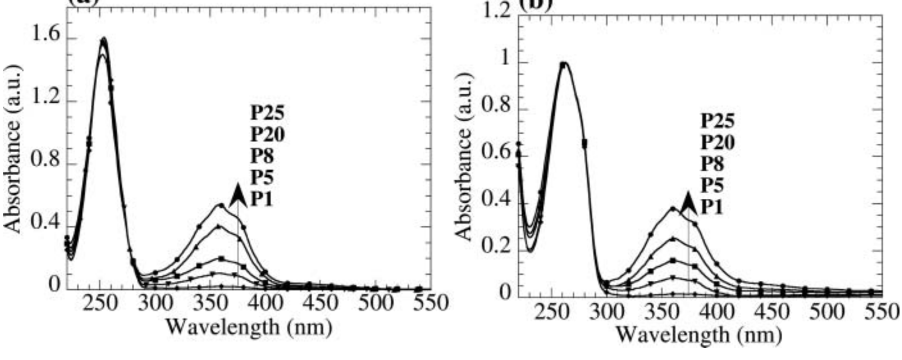

**Figure 2.** UV-vis absorption spectra of copolymers. (a) THF solution, (b) Films on quartz substrates.

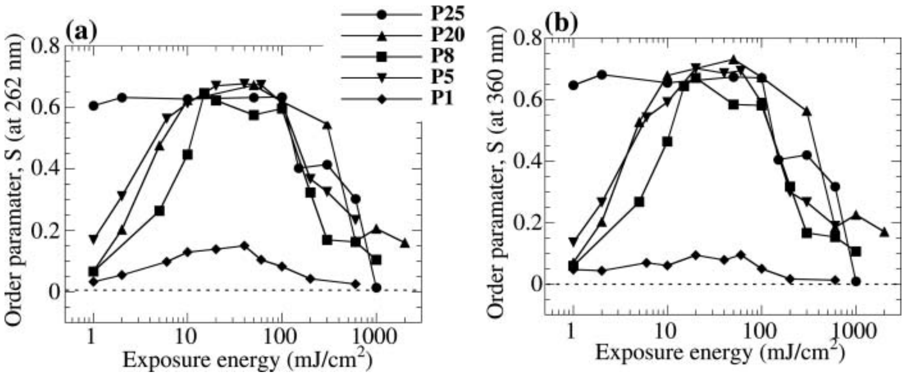

**Figure 3.** Thermally enhanced *S* values at (a) 262 nm and (b) 360 nm of the photoreacted copolymer films as a function of exposure energy. Annealing temperatures: 135°C for **P25**, 145°C for **P20**, 155°C for **P8,** 165°C for **P5**, 170°C for **P1**.

[10,11]. This small photoinduced optical anisotropy is greatly enhanced by annealing the film in the LC temperature range of the material [11]. The thermally induced reorientation of 4 MAz groups cooperatively reoriented BA groups. However, thermally enhanced *S* values were less than 0.1 for **P1** films. The content of 4 MAz groups was too low to generate cooperative reorientation even though 4 MAz groups generated photoinduced optical anisotropy.

The influence of the annealing temperature on the thermal amplification of the photoinduced negative optical anisotropy of the copolymer films was investigated in detail. Figures 4a and b plot *S* values of copolymer films annealed at various temperatures when the exposure energies were 50 mJcm$^{-2}$ for **P25** and **P20**, 20 mJcm$^{-2}$ for **P8**, and 40 mJcm$^{-2}$ for **P5** and **P1**. They show that effective reorientational order was obtained when the annealing temperature was in the LC temperature of the copolymer. Especially, annealing close to the isotropic transition temperature yielded sufficient cooperative reorientation of

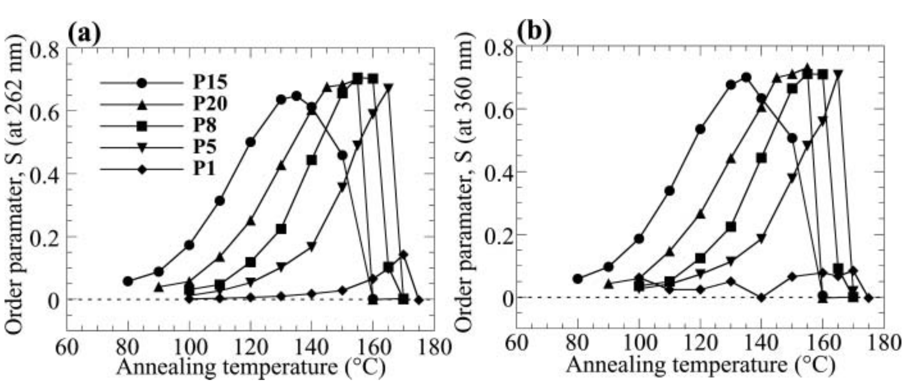

**Figure 4.** Thermally enhanced *S* values at (a) 262 nm and (b) 360 nm of the photoreacted copolymer films as a function of annealing temperature. Exposure energy: 50 mJcm$^{-2}$ for **P25** and **P20**, 20 mJcm$^{-2}$ for **P8**, and 40 mJcm$^{-2}$ for **P5** and **P1**.

the side groups. These results are similar to other photoreactive LC copolymer films that show cooperative photoinduced molecular reorientation [12].

### *Patterned Reoriented Film and Patterned Phase Retarder*

For a practical application to photoalignment layer for functional materials, pattern formation ability is important. Additionally, for the application to display devises, azobenzene content should be low to reduce the absorption in the visible region. Therefore, we used **P5** to fabricate patterned oriented film. Patterned oriented structure can be achieved by adjusting exposure energy and polarization direction of LPUV light with a photomask.

Figure 5a shows change in UV-vis polarization spectrum of a **P5** film before photoirradiation, after irradiation for 7 mJcm$^{-2}$ (thin lines), and after subsequent annealing at 165°C for 10 min (thick lines). After the annealing, cooperative orientation was observed with *S* values 0.58 at 262 nm, and 0.55 at 360 nm, respectively. Furthermore, a film with double exposure with adjusting the polarization and exposure energy (1st exposure was 7 mJcm$^{-2}$, and 2nd exposure with changing **E** of LPUV light by 90° was 60 mJcm$^{-2}$) showed similar cooperative reorientation as shown in Fig. 5b, showing that reorientation direction is parallel to the polarization of the first exposure. This is because the exposure energy of the second LPUV irradiation was much greater than that of first exposure. In this case, cooperative orientated *S* values were 0.59 at 262 nm, and 0.54 at 360 nm, respectively. This result means that the thermally enhanced reorientation direction can be controlled by the polarization direction of the second LPUV exposure with larger exposure energy. Additionally, absorbance at 400 nm of these films was less than 0.05 due to small content of 4 MAz moieties, which can be applicable to display applications.

Based on the above-mentioned concept, patterned reoriented **P5** film was fabricated by double exposure process using a photomask (Fig. 6a). Figure 6b shows a POM photograph of a patterned reoriented **P5** film with different orientation direction. This film should be useful for the patterned alignment layer to fabricate patterned birefringent film. Finally, we demonstrate a patterned retarder using patterned reoriented **P5** film and curable LC.

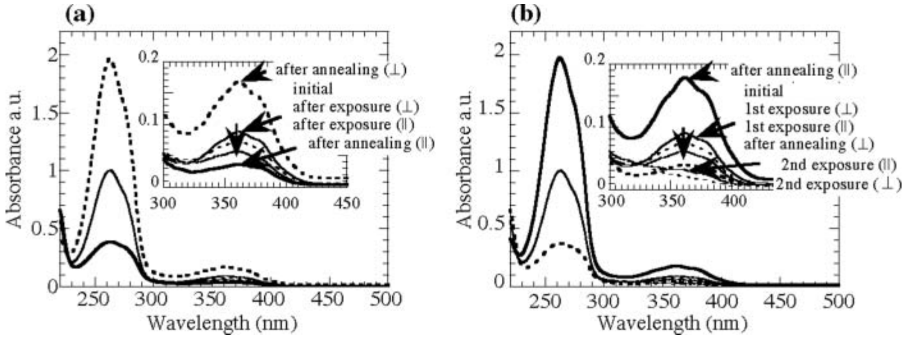

**Figure 5.** (a) Change in the polarization UV-vis polarization spectrum of a **P5** film before photoirradiating, after irradiating for 7 mJcm$^{-2}$ (thin lines), and after subsequent annealing at 165°C for 10 min (thick lines). (b) Change in the polarization UV-vis polarization spectrum of a **P5** film before photoirradiating, after irradiating for 7 mJcm$^{-2}$ followed by irradiating for 50 mJcm$^{-2}$ with change the polarization by 90° (thin lines), and after subsequent annealing at 165°C for 10 min (thick lines). Solid line represent $A_{\parallel}$, while dotted lines show $A_{\perp}$.

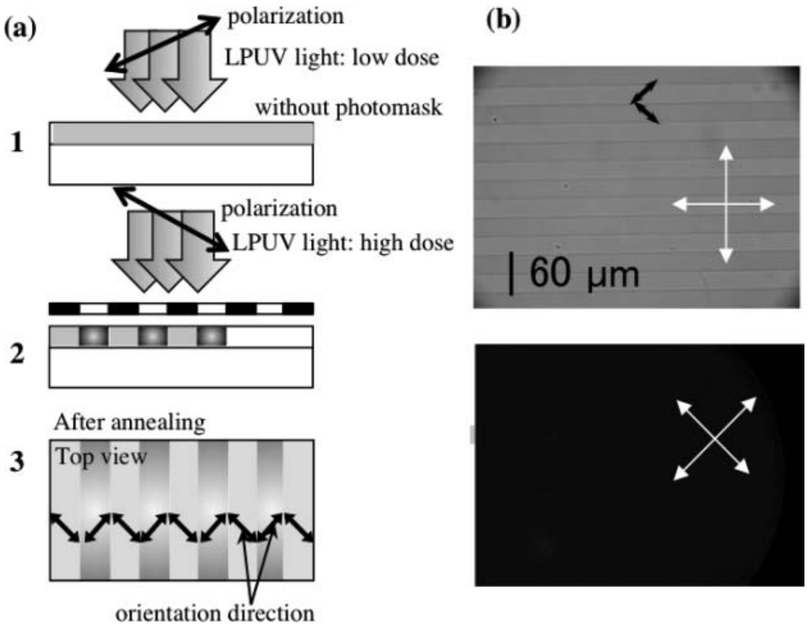

**Figure 6.** (a) Schematic illustration of the process to fabricate a patterned oriented film with one photomask. (b) Patterned reoriented **P5** film examined between crossed polarizers. Film was initially exposed to LPUV light for 7 mJcm$^{-2}$ without a photomask. It was subsequently exposed without a mask for 60 Jcm$^{-2}$ with a 90° rotation in the polarization and then annealed at 165°C. Black arrows indicate the molecular reoriented direction and white arrows are the polarizers direction.

Curable LC monomer M1 doped with 5 wt% of photoinitiator was coated on the **P5** film from a 2-methoxy-1-methylethyl acetate (PGMEA) solution and exposed to UV light for 300 mJcm$^{-2}$ for polymerization. Figure 7 displays POM observations of the fabricated patterned birefringent film. The birefringence of this film was 125 nm at 134 nm for each line. This film can be practically utilized as a patterned quarter-wave plate film in 3D display devices.

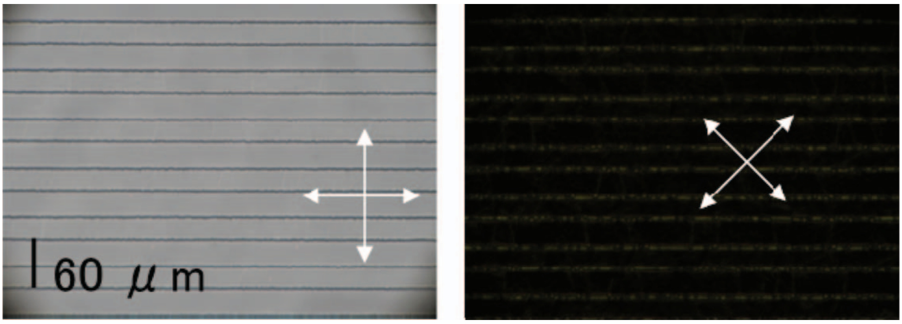

**Figure 7.** POM photographs of a patterned phase retarder using M1. M1 with 5 wt% of initiator was coated and exposed to UV light for 300 mJcm$^{-2}$.

## Conclusions

Photosensitive in LC methacrylate copolymers with 4 MAz and BA side groups were synthesized and thermally enhanced cooperative photoinduced reorientation behavior of these films were investigated. Sufficient cooperative orientation of both side groups was observed when the 4 MAz composition was greater than 5 mol%. By adjusting exposure energy and polarization of LPUV light using a photomask, patterned reoriented film was fabricated. Using a photocurable LC, a patterned phase retarder was fabricated, which is useful for a patterned quarter-wave plate for 3D displays.

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