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Facile Fabrication, Photoinduced Orientation, and Birefringent Pattern Control of Photoalignable Films Comprised of *N*-Benzylideneaniline Side Groups

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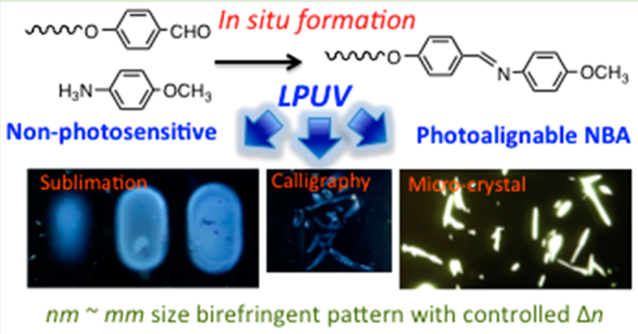
Supporting Information

ABSTRACT: Facile fabrication of a photoalignable film from a nonphotoreactive polymethacrylate with 4-oxybenzaldehyde side groups (**1**) and a monomeric 4-methoxyaniline (**2**) composite is investigated. A **1**/**2** composite film fabrication and the annealing process form photoalignable *N*-benzylideneaniline (NBA) side groups, while the linearly polarized (LP) 365 nm light exposure to the resultant film induces sufficient molecular reorientation of NBA side groups. Furthermore, patterned coating of **2** on a **1** film and subsequent LP light exposure generate a patterned molecular orientation combined with controlled birefringence.



Because the photoinduced reorientation has potential for optical and display applications, various types of photoresponsive materials have been studied to fabricate optically anisotropic films.[1−5] In general, photoinduced optical anisotropy is created when a photoresponsive polymeric film is exposed to linearly polarized (LP) light, based on an axis-selective photoreaction.[6] Many kinds of azobenzene-containing polymers have been investigated as candidates for photoinduced molecular reorientation perpendicular to the polarization of LP light, due to axis-selective trans−cis−trans photoisomerization.[1,7−9] Recently, we reported new photoalignable materials consisting of a polymethacrylate with *N*-benzylideneaniline (NBA) derivative side groups, where the photoinduced molecular reorientation perpendicular to the polarization of LP ultraviolet (UV) light is achieved similar to azobenzene derivatives.[10,11] In the case of the photoalignable materials investigated so far, photomasks and/or laser beam drawing techniques are required to fabricate a patterned photoinduced orientation structure.[12]

In the meantime, it is well-known that monomeric and polymeric liquid crystals (LCs) can align homogeneously on thin photoalignment films.[13−18] Many types of photoresponsive materials have been investigated for the LC photoalignment layers, where the LC materials self-organize on the anisotropic photoreacted film's surface. Additionally, using patterned LP light exposure to the photoalignment layer creates patterned LC alignment.[19−22] In contrast, Seki et al. have investigated a new approach to control the orientation of LC polymeric films from the free (air) surface side.[23] They demonstrated a photoalignment patterning of a nonphotoresponsive LC polymer film induced by the surface coated with a thin azobenzene-containing polymeric layer. These photoalignment techniques orient LC materials using the under- or top-coated photoresponsive polymeric film.

Because the NBA moieties are easily synthesized by the condensation of benzaldehyde and phenylamine derivatives,[24] it should be possible to form NBA moieties after film formation from a composite of benzaldehyde derivatives—containing polymer and monomeric phenylamine derivatives. It is worth noting that the photoreactivity of the film is provided *after* the film formation. Additionally, drawing the pattern of the phenylamine derivatives on the benzaldehyde derivative polymeric films, and subsequent LP UV light exposure, introduces a birefringence in the required area; thereby, the photoalignable NBA groups are generated after the preparation of a polymer film.

On the basis of this concept, we propose here facile fabrication of photoalignable polymeric films using two nonphotoreactive materials. A composite of a polymethacrylate with 4-oxybenzaldehyde side groups (**1**) and a monomeric 4-methoxyaniline (**2**) (Figure 1) is employed to produce photoalignable NBA side groups. We investigate their photoinduced molecular orientation behavior and birefringent pattern formation. Additionally, coating the adjusted amount of **2** on the **1** film's free surface and subsequently irradiating with LP 365 nm light achieve the controlled birefringence pattern with controlled birefringence. Furthermore, micro-

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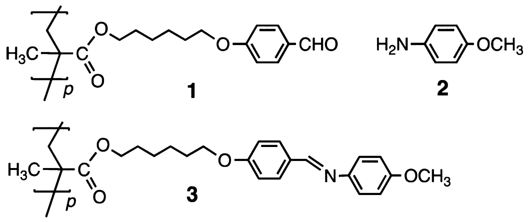

Figure 1. Chemical structures of the materials used in this study.

meter-sized oriented structure is demonstrated by the use of a minute crystal of **2** placed on a **1** film.

A polymethacrylate with benzaldehyde side groups (**1**) (Tg = 0 °C, Mn = 40 000, M_w/M_n = 2.2) was obtained from the corresponding methacrylate monomer.[11] Polymerization was carried out by free radical polymerization in THF. Monomeric phenylamine **2** (mp = 59 °C) was purchased from TCI Japan. For comparison, a polymethacrylate with NBA side groups **3** (Mn = 49 000, M_w/M_n = 2.4), which reveals an LC phase between 45 and 127 °C, was used.[10,11] Thin films of **1**, **1** and **2** mixture (**1**/**2**), and **3** were prepared from methylene chloride solutions. Each film had approximately 200 nm thickness. Detailed photoreactions and evaluation methods are described in the Supporting Information.

Figure 2 shows UV absorption spectra of the films of **1**, **2** in poly(methyl methacrylate) (PMMA), and **1**/**2** (1/3 mol/mol) on quartz substrates, before and after annealing at 100 °C. There is no absorption band longer than 310 nm for a **1** film, whereas **2** in the PMMA film has an absorption maximum at 310 nm. The **1**/**2** composite film shows a new absorption band at 285 nm and new broad absorptions longer than 330 nm, suggesting the condensation of benzaldehyde side groups and **2** molecules to form NBA moieties upon spin-coating. These bands shift to 282 and around 330−360 nm after the annealing, consistent with the absorption bands of an annealed **3** film (Figure S1a, Supporting Information). The broad absorption at longer wavelength (>400 nm) is due to scattering of the film. Additionally, the absorption spectrum of the **1**/**2** mixture in a solution at room temperature shows independent absorption bands of **1** and **2** with slight new absorption bands (Figure S1b, Supporting Information), indicating an insufficient condensation in a solution.

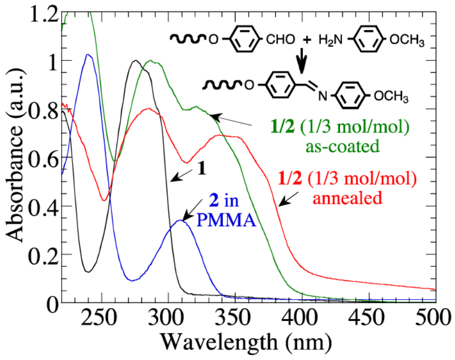

Figure 2. UV absorption spectra of **1**, **2** in PMMA, and **1**/**2** mixture (1/3 mol/mol) films before and after annealing at 100 °C.

FT-IR spectroscopy confirms the formation of NBA groups (Figure S1c, Supporting Information), where absorption at 1620 cm^{-1} (C=N stretching) is detected and the aldehyde C=O stretching at 1690 cm^{-1} greatly decreases after spin-coating, and the annealing process almost diminishes the absorption bands at 1690, and 3356, and 3439 cm^{-1} (NH_2). These observations indicate that most of the NBA side groups is formed upon the film formation, and the annealing process accelerates the condensation and sublimation of excess **2**. By comparison with the FT-IR spectrum of **3**, over 95% of aldehyde converts to NBA side groups. Furthermore, polarized optical microscope (POM) observation shows a transition from the scattered structure to an isotropic state at 131 °C (Figure S1d, Supporting Information). This indicates that the annealed **1**/**2** (1/3 mol/mol) film exhibits nematic LC characteristics similar to **3**, and the scattering of the annealed film is due to multidomain formation of NBA side groups.

Figure 3a shows the polarization absorption spectra of a **1**/**2** (1/3 mol/mol) film before and after exposure to LP 365 nm light for 10 J/cm^2. After the irradiation, absorbance perpendicular (parallel) to the direction to polarization (**E**) of LP 365 nm light [$A_\perp$ ($A_\parallel$), where $A_\parallel$ and $A_\perp$ are the absorbances parallel and perpendicular to polarization (**E**) of LP 365 nm light, respectively] becomes larger (smaller) than the initial absorbance, indicating photoinduced in-plane molecular reorientation perpendicular to the **E** of LP light. The generated in-plane order parameter, S [= $(A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$], is 0.40 (0.49) at 282 (330) nm. These values are similar to the photoinduced orientation of a **3** film (Figure S2a, Supporting Information). It should be noted that the scattering of the film at longer wavelengths (>400 nm) diminishes after the photoirradiation, due to the significant molecular reorientation of NBA side groups, which dissociated the multidomain structure. Additionally, the S values decrease when the exposure energy exceeds 30 J/cm^2 due to the disorder of in-plane orientation structure and the partial photodegradation of

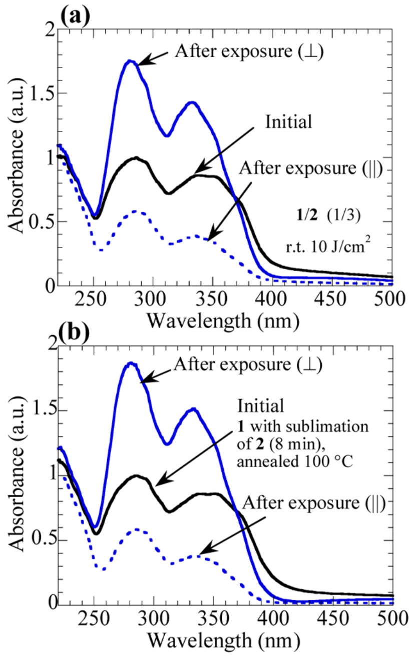

Figure 3. (a) Changes in the polarized UV absorption spectra of an annealed **1**/**2** mixture (1/3 mol/mol) film at 100 °C and after subsequent irradiation with LP 365 nm light for 10 J/cm^2. (b) Changes in polarized UV absorption spectra of a **1** film with sublimation of **2** for 8 min followed by annealing at 100 °C and after subsequent irradiating with LP 365 nm light for 16 J/cm^2.

the NBA side groups (Figure S2b, Supporting Information). This is similar to the photoinduced reorientation behavior of a **3** film.[11]

Next, sublimation coating of **2** molecules onto a thin **1** film easily achieves a photoalignable film. The sublimation apparatus is shown in Figure S3a (Supporting Information). First, **2** molecules are heated to 100 °C to sublimate and deposit on a 200 nm thick **1** film, and the resultant film is subsequently annealed to form NBA. The FT-IR spectrum indicates NBA formation (Figure S3b, Supporting Information), where the aldehyde vibration at 1690 cm^{-1} diminishes and the C=N vibration at 1620 cm^{-1} appears, after the sublimation of **2** (for 8 min) and an annealing. The similar photoinduced reorientation behavior to the **1**/**2** (1/3 mol/mol) film is observed as shown in Figure 3b and Figure S4 (Supporting Information), which plot the polarization absorption spectra of a **1** film with sublimation of **2** for 8 min before and after exposure to LP 365 nm light for 16 J/cm^2 [S = 0.42 (0.51) at 282 (330) nm] and generated S values as a function of exposure energy, respectively.

Additionally, the sublimation time controls the amount of NBA formation in the film. Figure 4a plots UV absorption spectra of annealed **1**/**2** films, when the sublimation time of **2** is varied. It shows that the sublimation time adjusts the absorbance at 330 nm, suggesting the way to control the amount of NBA formation. These films show different photoinduced orientation performance (Figure 4b), indicating that sublimation time and exposure energy control the photoinduced Δn. The generated photoinduced Δn value increases when the sublimation time increases due to an increase in the formation of NBA side groups in the film. Namely, penetration of **2** molecules to form NBA varies with sublimation time, resulting in a difference in the photoinduced birefringence of the film.

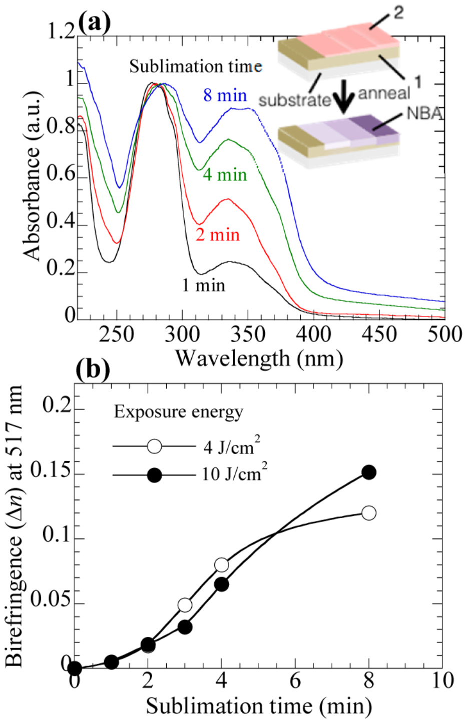

Figure 4. (a) UV absorption spectra of **1** films coated with **2** for different sublimation times and subsequent annealing at 100 °C. Inset is a schematic image of the formation of NBA side groups. (b) Photoinduced birefringence at 517 nm of **1** films coated with **2** followed by annealing at 100 °C and subsequent exposure to LP 365 nm light as a function of the sublimation time of **2**.

Adjusting sublimation time with a mask achieves the birefringent pattern with controlled reorientation. Figure 5a shows a birefringent pattern of a **1**/**2** film, when varying the sublimation times of **2**. After sublimation and annealing, the whole area was exposed to LP 365 nm light for 4 J/cm^2. The photoinduced birefringence is generated only in areas where **2** molecules are deposited and varies with sublimation time. Because the amount of **2** deposited on a **1** film is nonuniform when using a mask (size of the hole: ca. 2 × 4 mm^2, 0.5 mm thickness), the photoinduced birefringence is not uniform. The birefringence (Δn) of the center of each area is 0.05, 0.08, and 0.12 for sublimation times of 3, 4, and 8 min, respectively.

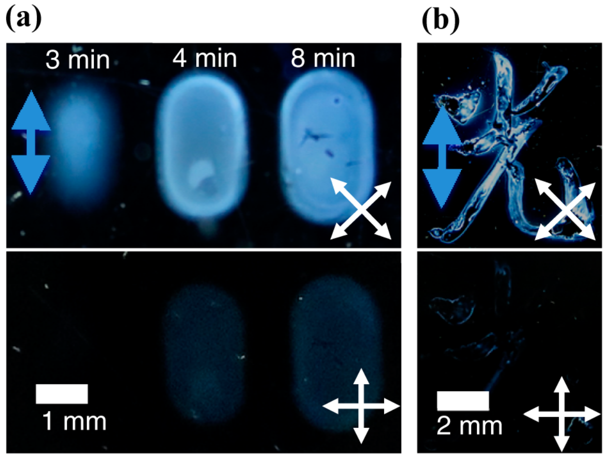

Figure 5. (a) Birefringent pattern of a **1** film coated with **2** with different sublimation times. Coated film is annealed at 100 °C and subsequently irradiated with LP 365 nm light for 4 J/cm^2. (b) Photoaligned Chinese character painted from a **2** solution onto a **1** film. Coated film is annealed at 100 °C and subsequently irradiated with LP 365 nm light for 10 J/cm^2. Blue arrows indicate the polarization of LP 365 nm light, while white arrows denote the polarizer and analyzer directions.

Furthermore, spin-coating a **2** solution in diethyl ether and subsequent annealing of the film yield a similar **1**/**2** film to that fabricated by the sublimation process (Figure S5a,b, Supporting Information) with a comparable photoinduced reorientation behavior (Figure S6a,b, Supporting Information). Using this technique, Figure 5b shows a photoaligned Chinese character, which was prepared by painting **2** in diethyl ether (10 wt %) on a **1** film, annealing at 100 °C, and subsequently exposing to LP 365 nm light for 10 J/cm^2. It shows clear birefringence that depends on the concentration of NBA formation in the film.

Finally, setting **2** crystals on a 400 nm thick **1** film achieves a minute photoaligned pattern. Figure 6a shows a POM photograph of a **1** film with **2** crystals on the film's surface. Initially birefringence of **2** crystals is observed regardless of the polarizer direction, but it disappears when the film is annealed at 150 °C due to the formation of NBA side groups with molecularly random orientation (Figure 6b). At this stage, the NBA formed area is unclear because the film becomes amorphous, where the POM observation is dark at any crossed-polarizer's direction. After exposure to LP 365 nm light for 10 J/cm^2, a birefringent pattern at the NBA formed

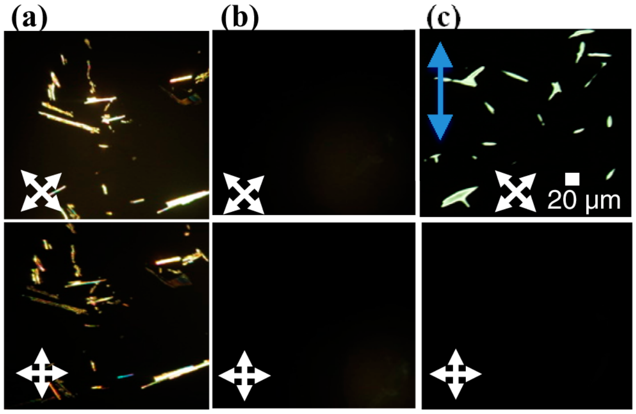

Figure 6. Birefringent pattern of a **1** film with **2** crystals. (a) Setting **2** crystals on a **1** film, (b) after annealing at 150 °C for 10 min, and (c) after subsequent exposure to LP 365 nm light for 10 J/cm^2. Blue arrows indicate the polarization of LP 365 nm light, while white arrows denote the polarizer and analyzer directions.

area appeared [Figure 6c (different area from Figure 6a)]. It seems that the size of the orientation area and the birefringence depend on the crystal size and its shape of **2**. The penetration of **2** molecules to form NBA groups in the film at the annealing process will affect the size, birefringence, and clearness of the birefringent area and its pattern.

At present, the amount of NBA formed and its penetration depth are not currently quantitatively analyzed, while it should be possible to realize a controlled molecular orientation structure via inkjet technology and the use of the micro-nanocrystals.

In summary, a facile preparation of a photoalignable polymeric film is demonstrated for the first time using polymethacrylate with phenylaldehyde side groups (**1**) and phenylamine derivative (**2**). The *in situ* formation of the NBA side groups by annealing a mixed film achieves photoalignability of the film. Additionally, coating **2** on the **1** film realizes the birefringent pattern and controlled birefringence due to the specified NBA formation. This technique provides adjustable photoinduced orientation ability from top-coating on the nonphotoreactive film. Further studies of the influence of the **1**/**2** mixing ratio on the photoinduced birefringence, clarification of the penetration depth of the formed NBA side groups in the film on the coating process of **2**, and inkjet printing of **2** molecules to form precise birefringent patterning are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedure, UV absorption spectra of a **3** film before and after annealing, UV absorption spectra of **1**, **2**, **1**/**2**, and **3** in methylene chloride solution, FT-IR spectra of a **1**/**2** (**1**/**3**) film, POM photograph of an annealed **1**/**2** (**1**/**3**) film, changes in polarized UV absorption spectra of an annealed **3** film exposed to LP 365 nm light, photoinduced *S* value of a **1**/**2** (**1**/**3**) film as a function of exposure energy, sublimation apparatus for 2 molecules, changes in FT-IR spectra of a **1** film with sublimation of **2**, photoinduced *S* value of a **1** film with sublimation of **2** (8 min) as a function of exposure energy, changes in FT-IR spectra of a **1** film coated with **2** solution, changes in polarized UV absorption spectra of a **1** film coated with **2** solution exposed to LP 365 nm light, and photoinduced *S* value of a **1** film coated with **2** solution as a function of exposure energy. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00357.

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Notes

The authors declare no competing financial interest.

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