ORIGINAL ARTICLE

Fabrication of UV-inactive photoaligned films by photoinduced orientation of H-bonded composites of non-photoreactive polymer and cinnamate derivative

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We explored the fabrication of ultraviolet (UV)-inactive photoaligned film by photoinduced orientation of H-bonded composites of non-photoreactive polymethacrylate consisting of hexylene spacer groups terminated with a benzoic acid (BA) moiety in its side chain (pM6BA) and low-molecular 4-methoxycinnamic acid (4MCA). The pM6BA/4MCA composite films exhibit liquid crystal characteristics owing to the presence of H-bonds between BA and 4MCA as well as between the BA groups. Exposure to linearly polarized UV light gives rise to axis-selective photoreaction of the 4MCAs, while thermal treatment induces the molecular reorientation of the BA side groups accompanied by the sublimation of unreacted 4MCA. As a result, the reoriented film is durable with respect to UV light irradiation, which may be useful for display applications.

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INTRODUCTION

Photoalignment based on axis-selective photoreaction of photo-sensitive polymeric films has received much attention recently owing to its potential use in many types of optical and photonic applications.^{1–7} In particular, photoalignment of a uniform liquid crystal (LC) alignment has already replaced the traditional mechanical rubbing method in LC display (LCD) industry, because the rubbing method suffers from electrical charging and resulting dust. Many types of photoalignment materials such as azobenzene, coumarin, chalcone and cinnamate-containing polymers, as well as photodegradable polyimides have been investigated for use in LCDs. Strong interactions between the photoalignment layer and LC monomers are expected to be present when these LC photoalignment materials exhibit photo-induced molecular reorientation. Several types of photoreactive materials, including azobenzene derivatives,^{8–15} *N*-benzylideneaniline (NBA) derivatives,^{16–23} cinnamate and cinnamic acid (CA) derivatives^{2–4,24–29} containing polymers, have been shown to exhibit photoinduced molecular orientation where an exposure to linearly polarized UV (LPUV) light generates an axis-selective photoreaction of these photoalignable groups combined with molecular reorientation.²⁴

In previous investigations, we have systematically studied photo-crosslinkable LC polymers containing cinnamate derivative side groups.^{30–38} It was discovered that irradiation of the photo-crosslinkable LC polymer films with LPUV light generates photo-induced optical anisotropy, and a subsequent thermal treatment induces molecular reorientation owing to LC characteristics of the material. Additionally, we have shown that a polymethacrylate with a hexylene spacer group terminated with a CA moiety in its side chain

(pM6CA; Figure 1) exhibited large photoinduced molecular reorientation with high photoreactivity toward LPUV light.^{37,38} Furthermore, uniform alignment control of low molecular LCs on the resultant photoaligned film was achieved by adjusting the exposure doses.

It is well known that aromatic carboxylic acid derivatives, such as benzoic acid (BA) and CA, exhibit an LC phase owing to hydrogen (H)-bonded dimers.³⁹ Additionally, H-bond formation between two different carboxylic acid compounds alters the LC properties of the materials. Copolymethacrylates with CA and BA side groups and composite films of polymethacrylates with BA and CA side groups show cooperative molecular orientation of both side groups.^{37,38,40} These findings indicate that the axis-selective photoreaction of CA side groups initiates thermally amplified cooperative molecular reorientation in all the H-bonded LC side groups of CA-CA, BA-BA and BA-CA. However, optical and mechanical properties of the resultant reoriented film may change upon exposure to UV light owing to the remaining photosensitive CA moieties. Additionally, Seki and colleagues have reported the use of detachable azobenzene molecules for fabricating optically transparent surface relief gratings.⁴¹ Monomeric azobenzene with imidazole moiety forms H-bonds with BA side groups in acrylate polymer and can be extracted selectively by organic solvent (tetrahydrofuran or ethanol) from the film while retaining the periodic structures.

Here we present new photoalignable materials consisting of a non-photoreactive polymethacrylate with its side chain hexylene spacer groups terminated with a BA moiety and low-molecular CA derivatives (pM6BA and 4MCA, respectively; Figure 1). Because

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4MCA forms H-bonds with the BA side groups in pM6BA, the process consisting of axis-selective photoreaction of the composite film and subsequent annealing of a pM6BA/4MCA composite film generates thermally amplified molecular reorientation. This is accompanied by the elimination of monomeric non-photoreacted 4MCA molecules and photodimerized molecules (Figure 2). Therefore, the resultant reoriented film is robust with respect to UV light irradiation. Here we explore the influence of the composite ratio and exposure energy on the photoinduced reorientation behavior of the composite film. Moreover, we demonstrate an application of the reoriented films for low-molecular LC alignment.

EXPERIMENTAL PROCEDURE

Materials

pM6BA is prepared following the method described in the literature,^{37,38} and all other materials were purchased from TCI (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). The number-average molecular weight and polydispersity of pM6BA were 25 000 and 1.92, respectively.

Figure 1 Chemical structures of pM6BA, pM6CA and 4MCA.

Figure 2 Schematic diagram of thermally enhanced molecular reorientation in pM6BA/4MCA composite film. A full color version of this figure is available at the *Polymer Journal* online.

Figure 3 DSC 2nd heating curves (10 K min^{-1}) of pM6BA/4MCA (0–100 wt%). A full color version of this figure is available at the *Polymer Journal* online.

Preparation of composite powder and thin films

The composite powders of pM6BA/4MCA (95/5–50/50 wt/wt) were prepared by dissolving pM6BA and 4MCA in tetrahydrofuran, followed by gradual evaporation of tetrahydrofuran. Thin pM6BA/4MCA composite films (thickness 100 nm) were prepared by spin-coating from a 4 wt% *N*-methyl-2-pyrrolidone/butyl cellosolve (60/40 wt/wt) mixed solution onto quartz or glass substrates. The samples were subsequently annealed at 70 °C for 90 s.

Measurement of thermal properties of the composite powder

Thermal properties of pM6BA, pM6BA/4MCA (5–50 wt%) composite and 4MCA were evaluated using a polarized optical microscope (POM; Nikon ECLIPS E600 POL, Nikon Corporation, Tokyo, Japan) equipped with a Linkam 10084 and AxioCam MRC and differential scanning calorimetry (METTLER TOLEDO DSC 1, Mettler-Toledo Inc, Tokyo, Japan) analysis with heating and cooling rates of 10 °C min^{-1} .

Photoreaction and molecular reorientation of composite thin films

The photoreaction of thin films was carried out using an LPUV light source (Cerma Precision MUL-S60POL (Cerma Precision Inc., Tokyo, Japan) equipped with an ultrahigh pressure mercury lamp (HG-1000 MPK, Cerma Precision Inc.) with a band pass filter (300–330 nm)). After irradiation, the exposed films were annealed at 170 °C for 10 min to generate the thermally stimulated molecular reorientation. To conventionally evaluate the reorientation structure in the bulk, the polarized absorption UV-Vis spectra were measured using a UV-Vis spectrometer (SHIMADZU UV-3600, Shimadzu corporation, Kyoto, Japan) equipped with Glan–Taylor polarizing prisms. The photoinduced optical anisotropy of thin films was measured using polarization UV-Vis spectroscopy. The photoinduced optical dichroism ($\Delta A < 0$; $\Delta A = A_{\parallel} - A_{\perp}$) after LPUV light irradiation and the in-plane order parameters ($S = (A_{\perp} - A_{\parallel}) / (A_{\perp} + 2A_{\parallel})$) after annealing were calculated from measured absorbance parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the polarization electric field (E) of the LPUV light.

Figure 4 Change in UV absorption spectrum of a pM6BA/4MCA (30 wt%) film upon irradiation with 313-nm light. A full color version of this figure is available at the *Polymer Journal* online.

Figure 5 (a) Change in polarized UV-Vis absorption spectra of pM6BA/4MCA (30 wt%) composite film before and after irradiation with LP 313-nm light with exposure energy of 150 mJ cm^{-2} and subsequent annealing at 170°C for 10 min. (b) Dichroism (ΔA) of pM6BA/4MCA (30 wt%) composite films at 319 nm after LP 313-nm light irradiation, and photoinduced in-plane order parameter (S) values at 262 nm after LP 313-nm light irradiation and subsequent annealing at 170°C for 10 min as functions of exposure energy. A full color version of this figure is available at the *Polymer Journal* online.

Nematic LC cell fabrication

To evaluate the LC alignment characteristics of the reoriented pM6BA/4MCA composite film, a parallel LC cell was fabricated using two photoreacted substrates. The cell ($6\text{-}\mu\text{m}$ thick) was filled with a nematic LC mixture (MLC-2041; Merck Ltd., Tokyo, Japan; $T_i = 80^\circ\text{C}$) using the vacuum pressure impregnation method.

RESULTS AND DISCUSSION

Thermal properties of the composites

Thermal properties of pM6BA/4MCA composites were evaluated by POM and differential scanning calorimetric observations (Figure 3). POM observation reveals no phase separation and nematic LC phase for all compositions, suggesting the formation of H-bonds between the BA side groups and 4MCA (Supplementary Figure S1). Figure 3 shows that nematic to isotropic transition temperature (T_i) of pM6BA/4MCA is lower than those of pM6BA and 4MCA, while T_i of pM6BA (4MCA) is 178°C (186°C). The H-bonds between the BA side groups and 4MCA decrease the LC temperature range of the materials by lowering the cross-linking density via the H-bonds of BA-BA side groups.

Photoreaction and photoinduced orientation of composite films

Figure 4 shows changes in the UV absorption spectra of pM6BA/4MCA (30 wt%) upon exposure to UV light. The intensity of the

Figure 6 Changes in polarized UV-Vis absorption spectra of reoriented (a) pM6BA/4MCA (30 wt%) and (b) pM6CA films before and after irradiation with unpolarized UV 313-nm light with exposure energy of 1 J cm^{-2} . Red (green) lines; before (after) irradiation. A full color version of this figure is available at the *Polymer Journal* online.

Figure 7 POM photographs of parallel LC cells under crossed-polarizers. MLC-2041 (Merck Japan, $T_i = 80^\circ\text{C}$) was used. The cells were prepared by using reoriented (a) pM6BA/4MCA (10 wt%) and (b) pM6BA/4MCA (30 wt %) films after LP 313-nm light irradiation (exposure energies of 8 and 150 mJ cm^{-2} , respectively), after annealing at 170°C for 10 min. A full color version of this figure is available at the *Polymer Journal* online.

absorption band at 315 nm decreases with increasing exposure energy even though pM6BA films rarely exhibit photoreactivity (Supplementary Figure S2). This spectrum change is similar to that of the pM6CA film; the same photoreactivity is observed for 4MCA composition of 5, 10 and 50 wt% (Supplementary Figure S3).

The axis-selective photoreaction occurs when LPUV light is used, and it was found that the subsequent annealing procedure amplified the photoinduced optical anisotropy, similar to that of the pM6CA film. Figure 5a shows the changes in polarization absorption spectra of the pM6BA/4MCA (30 wt%) composite film before and after exposure to LPUV light with exposure energy of 150 mJ cm^{-2} and also after the subsequent annealing at 170°C . A small negative anisotropy ($\Delta A < 0$) is observed at 319 nm after the exposure owing to the axis-selective photoreaction of 4MCA. Additionally, anisotropy is rarely induced at 262 nm because BA side groups do not photoreact. In contrast, the annealing procedure increases (decreases) the absorbance at 262 nm of the component perpendicular (parallel) to the LPUV light E direction, indicating the occurrence of thermally amplified molecular reorientation. The decreased intensity of the absorption band at 319 nm (4MCA) after the annealing can be clearly observed. This means that the thermal side groups self-organization process is accompanied by sublimation of unreacted 4MCA.

Figure 5b shows the changes in photoinduced ΔA at 319 nm and in-plane order parameter (S) values at 262 nm for the pM6BA/4MCA (30 wt%) composite film before and after annealing at 170°C for different exposure doses. The axis-selective photoreaction of 4MCA groups occurs and the maximum ΔA (ΔA_{max}) is observed for the exposure energy of $600\text{--}1500 \text{ mJ cm}^{-2}$. The annealing procedure leads to the molecular reorientation of the BA side groups at 262 nm even though the photoreaction of BA is negligible (photoinduced S at 262 nm is zero). The amplified S at 262 nm is obtained when the exposure energy exceeds 8 mJ cm^{-2} , and the maximum S (S_{max}) of 0.36 is obtained when the exposure energy is 150 mJ cm^{-2} . Additionally, it was found that the exposure energy $> 600 \text{ mJ cm}^{-2}$ does not result in amplification because the large amount of photoreacting 4MCA inhibits the thermal motion of the BA side groups. These observations suggest that axis-selective photoreaction of a small amount of 4MCA groups amplifies the reorientation of BA side groups, accompanied by the sublimation of 4MCA.

The thermal amplification of the photoinduced optical anisotropy varies with pM6BA/4MCA composition (Supplementary Figure S4). Smaller exposure doses are required to obtain significant thermal amplification for increased 4MCA content. The obtained S_{max} values for 4MCA content of 5, 10, 30 and 50 wt% are 0.43 (30 J cm^{-2}), 0.51 (8 J cm^{-2}), 0.36 (150 mJ cm^{-2}) and 0.32 (60 mJ cm^{-2}), respectively. The total amount of photoreacted 4MCA groups in all the mesogenic side groups (BA-BA and BA-4MCA) in the film has an important role in the reorientation. This tendency is similar to the thermal amplification of the photoinduced optical anisotropy of copolymerethacrylates with CA and BA side groups.³⁸

Photostability of reoriented films

Because the thermal self-organization process is accompanied by sublimation of 4MCA molecules, the resultant reoriented film does not exhibit photoreactivity. Figure 6a displays the change in the polarization absorption spectra of reoriented pM6BA/4MCA (30 wt%) composite film (same as the film used to obtain the data presented in Figure 5a) before and after exposure to non-polarized UV light with an energy of 1 J cm^{-2} . The absorbance spectrum does not show any changes upon exposure, indicating that the thermal reorientation process provides photo-stability. On the other hand, for a reoriented

pM6CA film (fabricated by exposure to LPUV light with the energy of 6 mJ cm^{-2} and after subsequent annealing at 170°C), absorbances in both directions decrease significantly owing to the photoreaction of CA side groups (Figure 6b). The same photo-stability against UV light is observed for 5, 10 and 50 wt% 4MCA compositions (Supplementary Figure S5).

Nematic LC alignment

We previously reported that reoriented pM6CA films are useful as an LC alignment layer.^{37,38} Figure 7 presents POM photographs of parallel LC cells fabricated using reoriented pM6BA/4MCA composite films. LC alignment is clearly achieved regardless of the 4MCA composition with the composite film revealing significant molecular orientation structure. The strong interaction between the LC molecules and the photoalignment layer results in LC alignment. Further evaluation of anchoring energy and electric and static properties of the LC cells is underway.

CONCLUSION

In summary, photoinduced orientation of H-bonding composite films consisting of non-photoreactive pM6BA and 4MCA was investigated. Because of the formation of H-bonds between BA and 4MCA, all composite films with different pM6BA/4MCA compositions show LC characteristics without phase separation. Exposure to LPUV light gives rise to axis-selective photoreaction of the MCAs, and thermal treatment induces the molecular reorientation of the BA side groups. Because the remaining 4MCA is sublimed during the thermal self-organization process, the resultant reoriented film exhibits durability with respect to UV light irradiation. The reoriented films are useful as LC photoalignment layers and birefringent films for display device applications. Further studies of the use of different types of CA derivatives to control the photoreactivity and thermal properties of the films are in progress.

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