Hydrogen-Bonded Photoreactive Polymer Liquid Crystal Containing Pyridyl-Terminated *N*-Benzylideneaniline

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Three kinds of polymeric composites consisting of a monomeric pyridine-terminated photoreactive compound and polymethacrylate with photo-inactive benzoic acid side chains were prepared and their photoinduced reorientation behavior was investigated using linearly polarized (LP) UV light and thermally induced self-organization. Due to the different structures of the photoreactive dopants, the reorientation direction and performance were different among the samples. The dopant containing methoxybiphenyl and pyridine connected by an imine bond exhibited no mesomorphism and underwent a slight axis-selective photoreaction in the composite, while the dopant with phenylpyridine and methoxybenzene showed a nematic phase and exhibited axis-selective photoreaction but no thermo-induced amplification of anisotropy in the composite. On the other hand, the dopant consisting of pyridine and methoxybenzene showed a nematic phase with a low glass transition temperature by combination with the host polymer. The composite exhibited thermo-induced molecular reorientation behavior by LPUV exposure below room temperature and subsequent annealing at 120 °C.

Keywords: Hydrogen bonding, Liquid crystal, *N*-Benzylideneaniline

1. Introduction

Photoalignment based on the axis-selective photoreaction of photosensitive polymeric films has received much attention due to its potential in versatile optical applications [1-5]. Photoalignment can overcome drawbacks in conventional mechanical rubbed or stretched aligned films such as generation of scratches and electrical charges of the film surface. In particular, photoreactive liquid crystalline polymers (PLCPs) with photoresponsive mesogenic side groups, which exhibit thermally stimulated photoinduced molecular reorientations, have been intensively investigated because they can generate large optical anisotropy and selectivity in the anisotropy direction. Recently, we focused on PLCPs with *N*-benzylideneaniline (NBA) side groups. Several types of NBA derivatives are transparent in the visible region and exhibit photoreactivity toward *trans-cis* photoisomerization. Additionally, NBA

exhibits *trans-cis-trans* reorientation upon exposure to linearly polarized UV light [6,7]. In conventional photoalignable PLCPs, exposing the resultant oriented film to UV light alters its optical and mechanical properties because the photosensitive mesogenic side groups remain. To resolve this issue, we explored the photoinduced molecular reorientation of composite films consisting of a photo-inactive polymethacrylate with a benzoic acid (BA) side group (**P6BAM**) and monomeric photoreactive carboxylic acid derivatives, where the H-bonded acid photoreacts axis-selectively with BA side groups, and the acid monomers sublime during thermal amplification, providing photodurability to the resultant oriented films [8,9].

We have also reported functional materials using hydrogen-bonded polymeric composite films such as photomobile materials [10], mechanochromic compounds [11] and polarized

photoemissive substrates [12,13] using pyridine-terminated monomeric compounds and acidic polymers including BA or cinnamic acid polymethacrylate. By using a pyridine-terminated monomeric functional material, the acidic host polymer easily forms a composite because the dopant suppresses self-dimerization and subsequent precipitation, compared to the previous acidic dopant. Several researchers reported the photoinduced reorientation behavior of polymeric pyridine-acid (or halogen) composite films [14-18] but no report was found using NBA moieties.

In this work, we prepared hydrogen-bonded composite films consisting of **P6BAM** and pyridine-terminated photoresponsive compounds, and explored their photoalignment behavior. We used three types of monomeric dopants connected by imine bonds: methoxybiphenyl and pyridine (NPy1), phenylpyridine and methoxybenzene (NPy2), and pyridine and methoxybenzene (NPy3).

2. Experimental section

2.1. Materials

All starting materials were purchased from Tokyo Kasei Chemicals and used as received. The methacrylate monomer possessing a hexamethylene spacer group was synthesized according to the literature [19,20]. Polymethacrylate BA was synthesized by solution radical polymerization using AIBN as an initiator.

The polymer and dopant were dissolved in THF with a feed ratio of the dye equivalent to the carboxylic acid side chains. The solvent was removed completely by heating under reduced pressure, yielding a uniform composite powder.

2.2. Photoreaction

Thin polymeric composite films were prepared by spin-coating a THF solution of the polymer onto quartz or CaF₂ substrates. The film thickness must be approximately 200 nm in order to evaluate the reorientation behavior using spectroscopic methods. Photoreactions were performed using a high pressure Hg lamp equipped with a glass plate placed at Brewster's angle and a band-pass filter at 365 nm (Asahi Spectra REX-250).

2.3. Characterization

¹H-NMR spectra were collected using a Bruker DRX-500 spectrometer. NMR and FT-IR spectra (JASCO FTIR-6600) confirmed the structures of the monomers and polymers. The molecular weight

of the polymers was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, THF) calibrated using PMMA standards. The thermal properties were examined using a polarization optical microscope (POM; Olympus BX51) equipped with heating and cooling stages, in addition to differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at heating and cooling rates of 10 °C min⁻¹. Polarization absorption spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms. The absorbance was normalized to the initial absorption value at 260 nm, assigned to the absorption spectrum peak of pristine **P6BAM** and the FT-IR spectrum was normalized at 1720 cm⁻¹ assigned to the carbonyl of the polymer backbone. The in-plane dichroic ratio, DR, which was evaluated using the polarization absorption spectra, is expressed as Eq. 1,

$$DR = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + A_{\parallel}} \quad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization direction of the linearly polarized actinic beam, respectively. Annealing the exposed film at an elevated temperature for 10 min induced thermally enhanced molecular reorientation.

3. Results and discussion

Chemical structures of the host polymer and dopants are shown in Fig. 1 and the thermal properties of the composites used in this study are summarized in Table 1. The **NPy1** composite shows no mesophase while the **NPy2** composite shows a nematic phase between 117 °C and 227 °C.

Fig. 1. Chemical structures and nomenclature of host polymer (a) and dopants (b) used in this study. Number average molecular weight (M_n) and polydispersive index (PDI) of the polymer are shown in (a).

Additionally, the **NPy3** composite exhibits a nematic phase with low glass transition temperature. The mesomorphic property of the composite is unstable in comparison to previous work that used a carboxylic acid-terminated NBA photoaligner [8]. Figure 2(a) shows the changes in polarized absorption spectra of the **NPy1** composite before and after irradiation with LPUV light and subsequent annealing. The absorbance parallel to the polarization direction of LPUV beam decreased while the absorbance perpendicular to the polarization direction of LPUV beam increased after UV irradiation. However, the anisotropy was completely erased when the photoirradiated film was annealed at 170 °C for 10 min. Additionally, the absorbance at 360 nm originating from the NBA dopant was reduced after annealing and the absorption peak showed a

Table 1. Mesomorphic properties of the composites.

Sample	dopant	Thermal Property (°C) ^a
P6BAM	-	G 130 N 195 I
C-NPy1	NPy1	G 95 I
C-NPy2	NPy2	G 117 N 227 I
C-NPy3	NPy3	G -5 N 138 I

^a G: Glassy; N: nematic; I: isotropic

Fig. 2. Change in absorption (a) and FT-IR spectra (b) of **C-NPy1** film. The initial spectrum and those after photoirradiation and thermal annealing are colored in black, blue and red, respectively. Dashed and solid lines indicate $A_{\parallel}$ and $A_{\perp}$ for each stage, respectively.

red shift from 260 nm to 280 nm. Figure 2(b) shows changes in the IR spectra of the end groups. The pre-annealed film shows broad absorption peaks at 1900 cm^{-1} and 2500 cm^{-1} while no absorption was observed in the annealed film complex at these positions. These bands corresponded to OH H-bonded with the N-atom of the pyridine ring, supporting the existence of intermolecular interactions between the dye and the host polymer. These bands and the absorbance at 1730 cm^{-1} assigned to the C=N stretching band of NBA were reduced after the annealing process. These changes in the UV-vis and IR spectra suggest the NBA dye was vaporized or decomposed during the annealing process. **C-NPy2** also shows axis-selective photoreaction and the generated photoinduced anisotropy was larger than that of **C-NPy1** but the change in the absorption spectrum after annealing was similar to the annealed **C-NPy1** composite film (Fig. 3(a)). In addition, FT-IR spectroscopy showed the loss of hydrogen bonding and the peak from the imine bond, indicating reduction of the monomeric moiety was induced in the annealing process (Fig. 3(b)), Anisotropy was lost when the composite film was annealed at lower temperature suggesting that the pyridine-terminated composite exhibited lower thermal stability compared to carboxylic acid-

Fig. 3. Change in absorption (a) and FT-IR spectra (b) of **C-NPy2** film. The initial spectrum and those after photoirradiation and thermal annealing are colored in black, blue and red, respectively. Dashed and solid lines indicate $A_{\parallel}$ and $A_{\perp}$ for each stage, respectively.

terminated composites.

In contrast, **C-NPy3** exhibited thermo-induced amplification after annealing. Figure 4(a) shows the changes in the absorption spectra of the **NPy3** composite film after exposure to LPUV light for 20 J cm⁻² at -5 °C and subsequent annealing at 120 °C. After exposure to LP 365-nm light, a decrease in $A_{||}$ and an increase in $A_{\perp}$ were observed, indicating photoinduced orientation of the BA and NBA moieties. Annealing significantly amplified the optical anisotropy ($DR = 0.49$ at 262 nm) and the absorbance at 365 nm disappeared. Furthermore, Absorption bands from hydrogen bonding and the imine moiety in the FT-IR spectra decreased after annealing similar to the other composite films (Fig. 4(b)). Contrary to photoirradiation at -5 °C, little anisotropy was generated after subsequent annealing when the film was photoirradiated at room temperature. This is because the high thermal movement of the mesogenic composite canceled out the axis-selective photoreaction at room temperature. The photoresponsiveness of **C-NPy1** is completely different from that of **C-NPy3** despite the similar chemical structures of **NPy1** and **NPy3** around the imine bond. In addition, **NPy1** and **NPy2** are geometrical isomers while **NPy2** and **NPy3** have the same methoxyaniline

molecular terminal, however only the **NPy3** composite exhibits thermo-induced molecular reorientation. This indicates that the molecular terminal structure plays an important role in the axis-selective photoreaction and liquid crystallinity.

Figure 5 shows the effect of the annealing temperature. The composite shows maximum anisotropy at 120 °C. The temperature for thermal amplification was reduced in comparison to the previous carboxylic acid terminate composite. The reduction in the annealing temperature enables formation of the photoalignment film on the flexible substrate. Although the optimized temperature is in the liquid crystalline temperature range of the host polymer and the composite, this seems to bear no relation to the thermal properties of the composite. It can be presumed that several thermo-induced processes such as vaporization or decomposition of dopant change the thermal properties of the composite during annealing. The temperature of maximum molecular reorientation is ascribed to the change in liquid crystallinity from the composite to the pristine **P6BAM** host polymer and detailed analysis of these thermodynamic processes is now under investigation.

Fig. 4. Change in absorption (a) and FT-IR spectra (b) of **C-NPy3** film. The initial spectrum and those after photoirradiation and thermal annealing are colored in black, blue and red, respectively. Dashed and solid lines indicate $A_{||}$ and $A_{\perp}$ for each stage, respectively.

Fig. 5. Maximum dichroic ratio of **NPy3** composite annealed at various temperatures.

4. Conclusion

Three kinds of polymeric composites consisting of monomeric pyridine-terminated photoreactive compounds and polymethacrylate with photo-inactive benzoic acid side chains were prepared and their photoinduced reorientation behavior was investigated using linearly polarized UV light and thermally induced self-organization. **NPy1** exhibited no mesomorphism and a slight axis-selective photoreaction in the composite, while the dopant **NPy2** showed a nematic phase

and exhibited axis-selective photoreaction but no thermo-induced amplification of anisotropy in the composite. On the other hand, **NPY3** showed a nematic phase with low glass transition temperature by combination with the host polymer. The composite exhibited thermo-induced molecular reorientation behavior by LPUV exposure at room temperature and annealing at 120 °C. Further optimization of the **NPY3** composite is now under investigation.

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