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ORIGINAL ARTICLE

Unpolarized light-induced alignment of azobenzene by scanning wave photopolymerization

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Abstract

Controlling the alignment of various functional molecules is important for the development of many next-generation, high-performance optical devices. However, there are some limitations in inducing molecular alignment using the current methods. We report herein the alignment control of azobenzene in a polymer film by a simple, new alignment-patterning technique based on a scanning wave photopolymerization (SWaP) concept. In this technique, molecular alignment was induced by the spatiotemporal control of the non-polarized light. A photoisomerizable azobenzene molecule, Disperse Red 1 (DR1), was doped into the photopolymerizable mixture, and it was successfully aligned along the direction of the neighboring mesogens; the alignment was induced by SWaP with unpolarized light. The alignment behavior showed that the degree of photoisomerization of the doped azobenzene moieties was proportional to the light intensity, and the unidirectional alignment of DR1 was achieved through optimization of the photopolymerization conditions. This finding indicates that SWaP could be employed as a novel and simple fabrication process for preparing a wide variety of highly functional optical devices requiring alignment control.

Introduction

Molecular alignment has received much attention because the orienting molecules can provide increased functionality and enhanced device performance. Therefore, molecular alignment methods play an important role in the development and the production of electronic, photonic, and mechanical devices [1–3]. In recent years, techniques to control the large-area alignment of liquid crystals (LCs) have been developed to fabricate functional materials and devices [4–6]. Standard procedures for aligning LCs include mechanical techniques such as stretching or rubbing treatments and optical methods such as photoalignment using axis-selective photoresponsive materials [7–10]. Mechanical alignment methods are simpler and more practical processes, particularly for large-area treatments, but alignment patterning with these techniques is impossible. Furthermore, the contact nature of mechanical methods can result in problems involving contamination by dust, static electricity buildup, and poor uniformity, as well as a lower molecular order limit in the case of rubbing treatments. In response to these difficulties, non-contact photoalignment methods have been explored, as they can induce strong, uniform, and spatially selective molecular alignment. Furthermore, optical methods possess great potential for fine control of complex alignment patterns by controlling the polarization state of the incident light, and they allow high resolution.

The first demonstration of photoalignment of LCs was provided by Ichimura et al. in 1988 [11]. In this system, the driving force for switching the alignment of nematic LCs between homeotropic and planar modes was the trans-cis photoisomerization of an azobenzene monolayer, which was termed a “command surface” [12]. Motivated by this pioneering study, the photoalignment of various azobenzenes has been widely studied based on either the photoinduction of anisotropy in the alignment of thin layers of the substrate or the incorporation of photoresponsive units into the bulk of the liquid-crystal material [13, 14].

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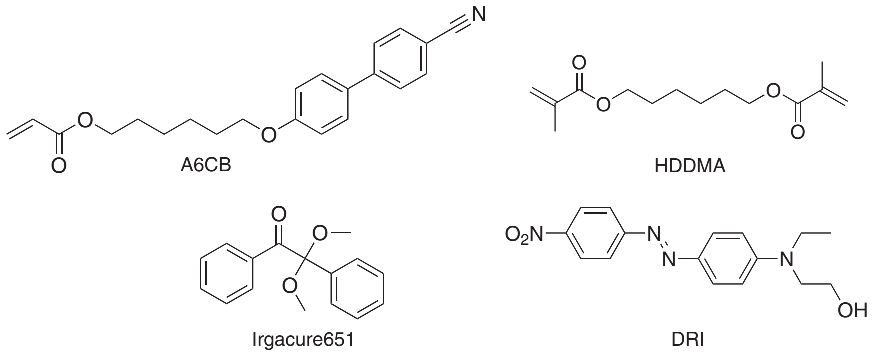

Fig. 1 Chemical structures of the compounds used in this study

Most recently, Seki et al. reported a new strategy to control the alignment of liquid crystals using free-surface molecular command systems [15, 16]. In addition to azo-based chromophores, other approaches toward photochemical alignment have included the development of new photoresponsive materials. In 1992, the photoalignment of liquid crystals on polyvinyl cinnamate films with linearly polarized light was reported [17, 18], and the photo-crosslinkable LC polymers containing cinnamate were developed [19–21]. Moreover, photoinduced molecular alignment techniques have been utilized for optical and photomechanical applications [2, 22, 23]. For example, holographic gratings containing photoresponsive materials [24–26] have been inscribed, and several types of actuators responding to optical, thermal, or chemical stimuli with complex alignment patterns have been demonstrated [27–29]. However, even with these advantages, there still remains some challenges with these techniques, such as requiring polarized light to control the alignment of photoresponsive molecules, and the alignment processes become complicated when the induction of complex alignment patterns is necessary. In addition, the size of the alignment pattern is limited to the size of the focused spot of the incident light in the photoalignment process.

Recently, we reported a novel alignment-patterning technique based on the new concept of scanning wave photopolymerization (SWaP), which achieves a spatial light-triggered mass flow to generate molecular order [30, 31]. In this method, the molecular alignment was determined by the spatiotemporal control of the guided light, which triggers a mass flow in the film as the polymerization reaction propagates. The driving force behind the alignment was the mass flow induced by molecular diffusion in the light intensity gradient, which can be of much higher resolution than the wavelength of the light employed [32–34]. Therefore, this new technique is able to generate molecular alignment over large areas and complex alignment patterns with high resolution without requiring an alignment layer, irradiation with polarized light, or photoresponsive molecules. We discovered that the doped molecules that are not photoresponsive themselves could be aligned parallel to the light-scanning direction; thus, if the alignment control of other functional materials could be achieved, SWaP represents a new pathway for fabricating highly functional patterned films. In the present report, we demonstrate the alignment control of azobenzene via SWaP, which is one of the most common and versatile photoresponsive molecules. This study revealed that the doped azobenzene groups are aligned parallel to the mesogenic moieties, and subsequent photoisomerization of azobenzene can then generate the molecular alignment in the desired orientations. A unidirectionally aligned polymer film was obtained under the optimized photopolymerization conditions.

Experimental procedures

Materials

The chemical structures of the materials used in this study are shown in Fig. 1. The photopolymerizable monomer, A6CB (4′-[6-(acryloyloxy)hexyloxy]-4-cyanobiphenyl) was synthesized using a procedure similar to that of a previous report [26]. The crosslinker, HDDMA (1,6-bis(methacryloyloxy)hexane), was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. The product was washed with a 5 wt% aqueous sodium hydroxide solution, dried over anhydrous magnesium sulfate, and then purified by filtration. The azobenzene molecule, Disperse Red 1 (DR1), was obtained from Sigma-Aldrich Inc., MO, USA, and it was used without further purification. Irgacure 651, used as the photoinitiator without further purification, was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan.

Preparation of glass cells

The cleaning of the glass substrates was carried out as follows: first, 25 mm × 25 mm glass substrates were ultrasonically cleaned with 1.0 wt% neutral detergent (Cica clean LX-II, Kanto Chemical Co. Inc., Tokyo, Japan), distilled water, and 2-propanol. Second, the cleaned substrates

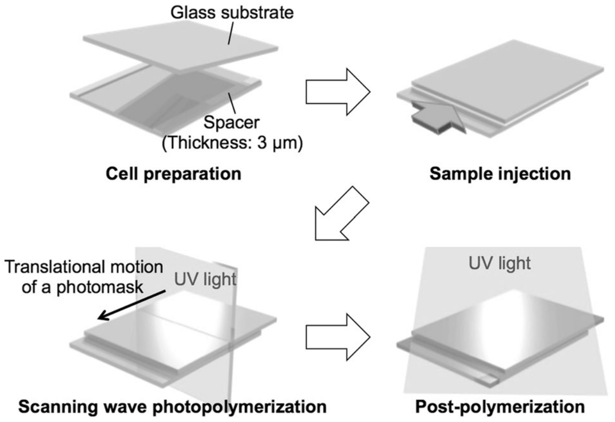

Fig. 2 Schematic illustrations of the procedure for fabricating an azobenzene-doped film

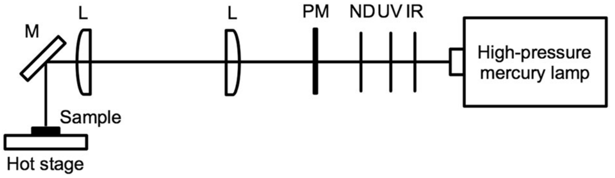

Fig. 3 Side view of the optical setup used for photopolymerization reactions. IR IR-cut filter, UV UV-bandpass filter, ND neutral-density filter, PM photomask, L plane convex lens, and M Mirror

were treated with an ultraviolet (UV)-ozone cleaner (NL-UV42, Takeda Rika Kogyo Co. Ltd., Tokyo, Japan) for 10 min. Next, the glass cells were handmade by using glue to bind the two glass substrates separated with 2–5 μm thick silica spacers (dry borosilicate glass microspheres, Thermo Scientific, CA, USA) (Fig. 2a). The thickness of a cell was determined by UV-vis spectroscopy, based on the Fabry-Perot method with a UV-vis absorption spectrometer (V-650ST, JASCO Corporation, Tokyo, Japan) [35].

Photopolymerization process

A6CB, an anisotropic monomer, and HDDMA, a cross-linker, were mixed at a molar ratio of 97:3 in a dark brown vial, and the photoinitiator, Irgacure 651, was added to the mixture at a concentration of 1.0 mol%. Subsequently, DR1, the azobenzene dye, was doped into the mixture at a concentration of 0.5 mol%. The mixture was dissolved in tetrahydrofuran (THF), and the solution was stirred at 25 °C for 30 min. After stirring, the solvent was completely removed under vacuum. The DR1-doped mixture was inserted into the glass cells by capillary action at 150 °C on a hot stage, and then the cells were cooled to the photopolymerization temperature, 120 °C (Fig. 2b). Photopolymerization was carried out though a slit mask with 365 nm UV light from a high-pressure mercury lamp (USH-500SC, Ushio Inc., Tokyo, Japan) equipped with glass filters (IRA-25S, UV-36A, AGC Techno Glass, Co., Ltd., Shizuoka, Japan). The UV light intensity was controlled with neutral-density filters (ND-50, ND-70, AGC Techno Glass, Co., Ltd., Shizuoka, Japan) (Fig. 2c). A 250-μm wide slit mask was one dimensionally scanned at a rate of 20 μm/s. The optical setup used in the photopolymerization process is shown in Fig. 3. Subsequently, the whole-cell was irradiated with UV light to complete photopolymerization and fix the molecular alignment (Fig. 2d). Finally, the resulting polymer film was obtained by rapid cooling the film in liquid nitrogen to below its glass transition temperature.

Evaluation of the molecular alignment

The molecular alignment was evaluated using a polarized optical microscope (BX50, Olympus, Tokyo, Japan) and a UV-vis absorption spectrometer equipped with a polarizer. Absorbances parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the light-scanning direction were obtained from the polarized UV-vis absorption spectra. The degree of in-plane alignment of the mesogens and azobenzene molecules, given by the order parameter (S), was calculated by the following equation [36]: $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$.

Results and discussion

Absorption spectra of A6CB and DR1

Figure 4 shows the UV-vis absorption spectra of A6CB and DR1. The absorption peak due to the cyanobiphenyl moieties was observed at ~330 nm in the spectrum of A6CB. On the other hand, DR1 exhibited an absorption maximum at ~500 nm. The absorption bands of the cyanobiphenyl moieties and azobenzene molecule were resolved, which means that the alignment behavior of each moiety could be clearly determined from the UV-vis absorption spectra.

Characterization of the alignment of doped azobenzene

To examine the effect of the doped azobenzene molecules on the alignment behavior in the film, scanning wave photopolymerization was conducted under the same conditions as were discussed previously. Figure 5a shows the photographs and polarized optical micrographs of the films photopolymerized at a light intensity of 1.2 mW/cm^2 in the developed process. The obtained film showed a uniform red color and optical transparency. The polarized optical

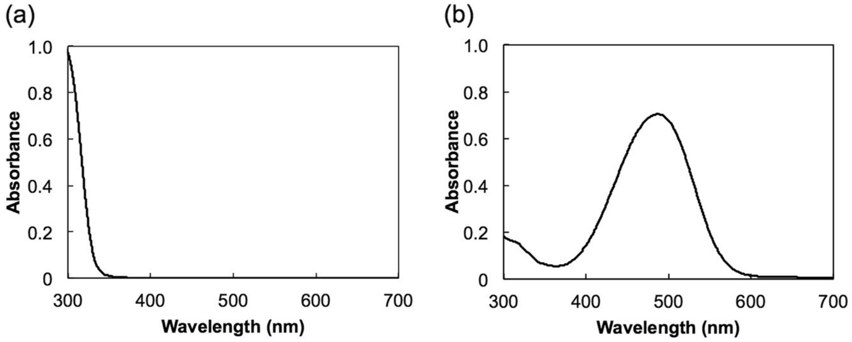

Fig. 4 Absorption spectra of A6CB (**a**) and DR1 (**b**) in THF at concentrations of 1.0×10^{-5} and 3.0×10^{-5} mol/l, respectively

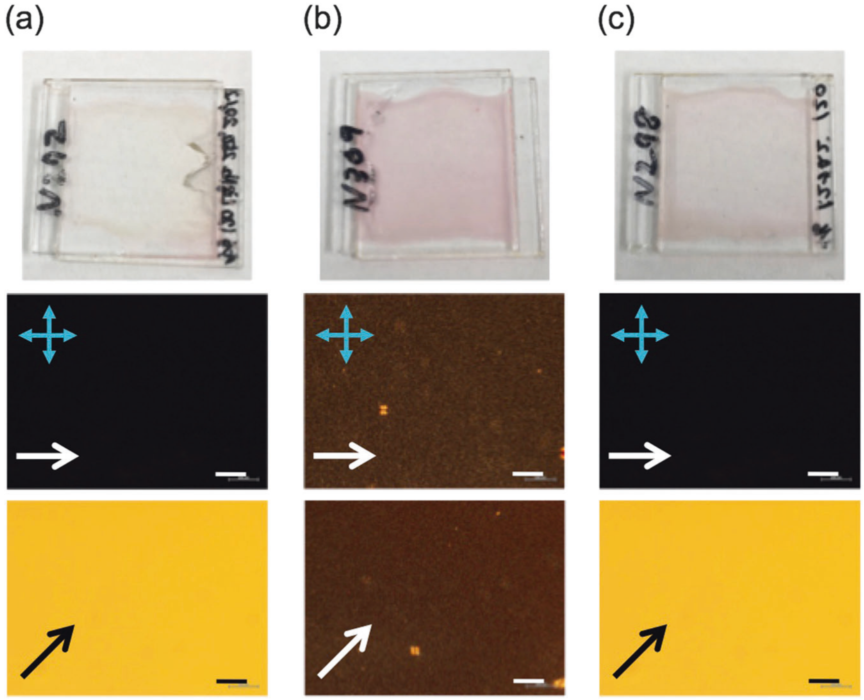

Fig. 5 Photographs and polarized optical micrographs of the DR1-doped films obtained by photopolymerization at light intensities of 1.2 mW/cm^2 (**a**), 0.2 mW/cm^2 (**b**), and 1.2 mW/cm^2 in the scanning wave photopolymerization process, and 0.2 mW/cm^2 in the post-polymerization process (**c**), respectively. White and black arrows show the direction of the motion of the UV light. Scale bar = 200 µm

microscopy analysis revealed that one-dimernsional optical anisotropy was induced in the film. In addition, the polarized UV-vis absorption spectra indicated that the absorbance was dependent on the polarization direction of the incident light (Figs. 6a and 7a). Positive anisotropy was observed at ~330 and 500 nm, which corresponds to the absorption bands of the cyanobiphenyl moieties and DR1, respectively. These results indicate that cyanobiphenyl and DR1 are aligned parallel to the light-scanning direction. To quantitatively examine the alignment of the cyanobiphenyl moieties and DR1, an in-plane order parameter (S) was calculated. The S values for the cyanobiphenyl moieties and DR1 were estimated at 340–348 nm and 490–530 nm, and were found to be 0.25 and 0.35, respectively. We previously obtained a higher S value (0.52) for the cyanobiphenyl moieties when the material was not doped with azobenzene [31]. This result suggests that the doped DR1 molecules affected SWaP and negatively impacted the alignment of the cyanobiphenyl moieties.

In SWaP, the molecular alignment is induced by light-triggered mass flow in the film as the polymerization reaction propagates. In this process, irradiation with UV light could cause photoisomerization of azobenzene, as well as photopolymerization of A6CB. Moreover, the out-of-plane photoreorientation of azobenzene can be induced by irradiation with unpolarized light because the propagation direction is perpendicular to the electric field vector of the incident light [37–40]. The molecular alignment induced by SWaP can be disrupted by photoisomerization, and the resultant out-of-plane orientation of DR1 during photopolymerization.

We investigated the effect of light intensity on SWaP, since this parameter can influence photoisomerization and orientation of DR1. First, photopolymerization with low-intensity light was conducted to suppress photoisomerization of DR1. As shown in Fig. 5b, the film photopolymerized with 0.2 mW/cm^2 light was darker and more opaque than the film photopolymerized at a light intensity

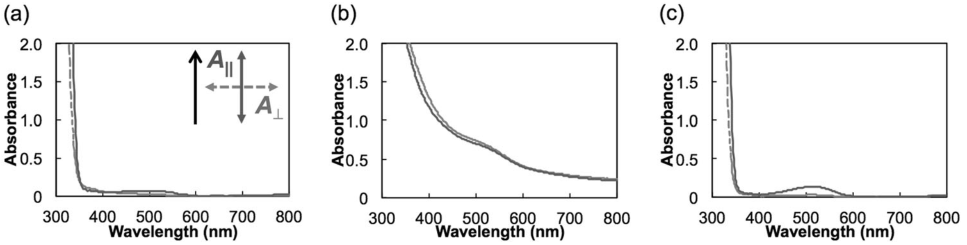

Fig. 6 Polarized UV-vis absorption spectra of the DR1-doped films obtained by photopolymerization at light intensities of 1.2 mW/cm^2 (**a**), 0.2 mW/cm^2 (**b**), and 1.2 mW/cm^2 in the scanning wave photopolymerization process and 0.2 mW/cm^2 in the post-polymerization process (**c**), respectively. The black arrow shows the direction of the motion of the UV light

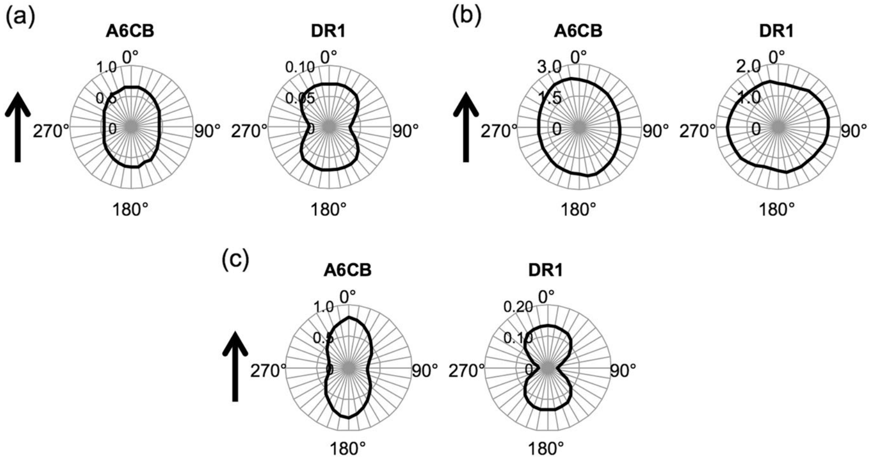

Fig. 7 Polar plots of the average absorbances ranging from 340 to 348 nm in A6CB and 490 to 530 nm in DR1 of the DR1-doped films obtained by photopolymerization at light intensities of 1.2 mW/cm^2 (**a**), 0.2 mW/cm^2 (**b**), and 1.2 mW/cm^2 in the scanning wave photopolymerization process and 0.2 mW/cm^2 in the post-polymerization process (**c**), respectively. The black arrow shows the direction of the motion of the UV light

of 1.2 mW/cm^2 (Fig. 5a). The polarized optical microscope measurements revealed that optical anisotropy was not induced, but instead, a poly-domain structure, typical for nematic LC polymers, was observed in the obtained polymer film (Fig. 5b). In polarized UV-vis absorption spectroscopy, the absorbance increased according to light scattering (Figs. 6b and 7b). Moreover, the absorption spectra obtained parallel and perpendicular to the light-scanning direction coalesced, which indicates that the cyanobiphenyl moieties and azobenzene were not aligned by SWaP. A light intensity of 0.2 mW/cm^2 might not be high enough to produce the mass flow required to induce molecular alignment. Therefore, we conducted the photopolymerization through a moving photomask with high-intensity light to obtain the efficient alignment of A6CB and carried out postpolymerization with low-intensity light to suppress the photoisomerization of DR1. Figure 5c shows that the film photopolymerized at a light intensity of 1.2 mW/cm^2 in the mask-moving process and 0.2 mW/cm^2 in the post-irradiation process. The obtained film was optically transparent and red, and the polarized optical micrographs showed that optical anisotropy was uniformly induced in the film. Furthermore, the polarized UV-vis absorption spectra revealed that both the cyanobiphenyl moieties and azobenzene were well-aligned in the film. The order-parameter values of the cyanobiphenyl moieties and DR1 were found to be 0.37 and 0.55, respectively (Figs. 6c and 7c). The results revealed that SWaP does not require linearly polarized light for the alignment of azobenzene moieties. In contrast, irradiation with polarized light is indispensable to induce the alignment of azobenzene in the current photoalignment processes, and the fabrication process does not allow the preparation of complex molecular alignment patterns. We suggest that SWaP can be used as an alternative fabrication method to induce the alignment of azobenzene moieties with unpolarized light and to obtain high-resolution alignment patterns.

Conclusion

In summary, the 1D alignment control of an azobenzene and a mesogenic moieties induced by SWaP with unpolarized light was demonstrated. It was revealed that both the cyanobiphenyl moieties and DR1 were aligned parallel to light-scanning direction. Because the doped azobenzene molecules responded to UV light, the alignment behavior was different than that of the non-doped system. However, the order parameter of DR1 was successfully increased to 0.55 by optimization of the photopolymerization conditions. This study proved that SWaP can be used as a platform for controlling the alignment of various kinds of materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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