

LETTER

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Effect of surface treatment on molecular alignment behavior by scanning wave photopolymerization

Masaki Ishizu^{1,2} , Miho Aizawa^{1,2}, Norihisa Akamatsu^{1,2}, Kyohei Hisano^{1,3}, Shigenori Fujikawa^{1,4}, Christopher J Barrett^{1,5}, and Atsushi Shishido^{1,2*}

¹Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan

²Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan

³Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

⁴International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Nishi, Fukuoka 819-0395, Japan

⁵Department of Chemistry, McGill University, Montreal, Quebec H3A 0B8, Canada

*E-mail: ashishid@res.titech.ac.jp

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Alignment of anisotropic molecules can provide high-performance display materials, and can be achieved by using a photoresponsive alignment layer. By contrast, scanning wave photopolymerization (SWaP) based on molecular diffusion offers direct alignment of liquid crystal (LC) polymers without the need for polarized light or photoreactive dyes. By demonstrating this alignment method on a variety of templates to compare surface conditions with and without alignment layers, we present a process to align LCs regardless of surface treatment, even in the opposite direction of surface rubbing, indicating that SWaP enables robust and facile molecular alignment. © 2019 The Japan Society of Applied Physics

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Alignment control of anisotropic molecules has been widely developed for enhancing performance of optical materials and providing new display functionalities. To date, alignment control of anisotropic materials such as liquid crystals (LCs) has led to the development of materials with dramatic improvement in mechanical, electrical and optical properties.^{1–4} Conventionally, a surface rubbing effect on a substrate, over which LCs can be uniformly aligned, has been widely used since it is easy, versatile, and practical.^{5–7} However, this method has some drawbacks, such as low manufacturing yield due to static electricity generation and contamination of dust, and an inability for fabricating two-dimensional alignment patterns or high-resolution features.

As an alternative method to rubbing, photoresponsive surface alignment of LCs have been developed to utilize axis-selective photochemical reactions of dye molecules on irradiation with linearly polarized light. Using light without direct contact, provides the advantage of inducing a uniform molecular alignment over large areas. Furthermore, fine control of the polarization pattern of the light allows one to inscribe arbitrary and complex two-dimensional alignment patterns of LCs.⁸ Over the last several decades, these photoalignment layers, termed “command surfaces”, have been increasingly used for achieving the precise and highly-controlled patterning necessary for various high-performance devices such as state-of-the-art LC displays.^{9–12} Moreover, soft actuators with LC alignment patterns have also been produced by command surfaces, to pattern the degree of LC alignment, which can then change their shape under external stimuli such as heat or photoirradiation.¹³ Furthermore, photoalignment with spatially periodic polarization patterns allows one to generate polarization holograms that can be applicable for memory storage, diffractive waveplates, and so on.¹⁴ These previous molecular alignment applications have been achieved generally by using the axis-selective photochemical reactions of azobenzene,^{15,16} or cinnamate^{12,17} derivatives.¹⁸ However, such photoalignment always requires photoreactive dyes to be added, which limits colour

and transparency, molecular design, and the choice of substrate used. Furthermore, a multi-step process containing preparation of an alignment layer, photoirradiation, and then injection of LCs is unavoidably complex in principle.¹⁸

Most recently, we have developed a single-step, dye-free photo-alignment process, termed “scanning wave photopolymerization (SWaP)”, which generates a mass flow of molecules during photopolymerization and enables one to directly control alignment in a wide range of LCs in polymer films.^{19–21} Photopolymerization in selected localized regions generates a gradient of chemical potential between irradiated and unirradiated regions, resulting in a mass flow from molecular diffusion,^{22–24} allowing one to align LCs in arbitrary high-resolution patterns. Thus, arbitrary scanning of incident light patterns enables one to achieve a wide variety of precise alignment patterns over large areas simply in a single step.²⁰ In contrast to conventional photoalignment, this method can be processed with unpolarized light, and without any need for alignment layers or dyes. This means that SWaP has far fewer limitations on molecular structures applicable, and thus, is a platform to align a wider variety of optical materials.

For further development, key to the establishment of SWaP as a versatile molecular alignment platform, is to demonstrate SWaP in a wide variety of templates and material systems with different interfaces. However, the effect of surface boundary conditions on the alignment results of SWaP has not yet been investigated. Therefore, there is a pressing need for investigating the effect of surface anchoring on LC alignment, induced by SWaP, to be explored and optimized. Specifically, we sought to investigate how molecular alignment could be achieved by SWaP under the experimental conditions with a variety of alignment layers. In this study, we investigated the compatibility of various currently-employed alignment layers, on LC alignment induced by SWaP patterning techniques. To compare the effect of substrates, surfaces of glass were covered with and without an alignment layer, and we examined how molecular alignment control by SWaP was restricted from surface

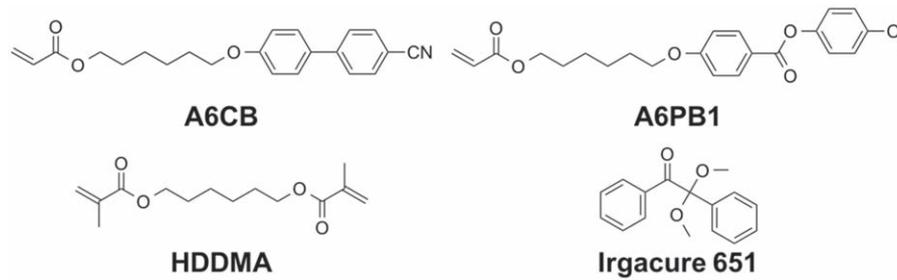


Fig. 1. Chemical structures used in this study.

anchoring. It was revealed that when monomers are above their clearing temperature before photopolymerization, SWaP has the ability to overcome surface anchoring, and successfully aligned adjacent LCs independent of an alignment layer.

We prepared two samples. One was composed of 4'-[6-(acryloyloxy)hexyloxy]-4-cyanobiphenyl (**A6CB**) as an anisotropic monomer and hexanediol dimethacrylate (**HDDMA**; Wako Chemical) mixed together at the molar ratio of 97:3, and additionally Irgacure 651 photoinitiator (Tokyo Chemical Industry Co.) was doped in at a concentration of 1.0 mol%, following the preparation procedures of similar compounds described previously.²⁰ Even without **HDDMA**, similar molecular alignment can be obtained by SWaP. But the addition of 3-mol% **HDDMA** in **A6CB**, enhanced the degree of molecular alignment due to an increased polymerization rate and as a result, an increased chemical potential gradient.²⁰ The other sample was 4'-methoxyphenyl 4-[6-(acryloyloxy)hexyloxy] benzoate (**A6PB1**) as a nematic LC monomer mixed with 1.0 mol% of Irgacure 651. The chemical structures of these compounds are shown in Fig. 1. These mixtures were dissolved and stirred in THF at room temperature, and subsequently dried completely under vacuum to obtain photopolymerizable samples. Figures S1.1–S1.4 are available online at stacks.iop.org/APEX/12/041004/mmedia in the online supplementary data, and displays phase transition behaviors of monomers and polymers used. **A6CB** does not show an LC phase, which means that **A6CB** is an isotropic monomer, and the resultant polymer of **A6CB** exhibited a nematic LC phase below 119 °C. **A6PB1** exhibited a nematic LC phase between 36 °C–47 °C, and the polymer showed a smectic LC phase below 92 °C and a nematic phase between 92 °C–119 °C.

For photopolymerization, glass cells were prepared with various surface conditions. Glass cells (20 mm × 20 mm; cell gap 3 μm) were prepared by adhering two glass substrates with glue including silica spacers (Fig. 2). All glass substrates were cleaned ultrasonically with 1 wt% neutral detergent in water, distilled water, and then 2-propanol in advance. In some cases, a polyimide layer was coated on cleaned glass substrates in the following steps. Firstly, glass substrates were treated with an ultraviolet (UV)-ozone cleaner, then a polyimide solution (JSR AL1254) was spin-coated on the substrates and dried at 120 °C for 2 h. Rubbing the polyimide layer at 800 rpm with a roller (E.H.C RM-50) resulted in an alignment layer. We thus obtained three cleaned glass cells: (a) without any surface treatment, and cells covered with (b) rubbed and (c) unrubbed polyimide layers. The cell gap of each cell was measured with a UV-vis spectrophotometer

(JASCO Corporation V-650ST) and the Fabry–Perot measurement method.²⁵

A 1D molecularly aligned polymer film was fabricated by a SWaP sample of **A6CB** as shown in Fig. 2. The prepared sample was injected into a glass cell at 150 °C, which is at the isotropic temperatures for both of a monomer and a polymer, and then allowed to cool down to the photopolymerization temperature of 100 °C. The cell was irradiated with 365 nm UV light from a high-pressure mercury lamp (USHIO USH-500SC) normal to the surface, equipped with glass filters (AGC Techno Glass IRA-25S and UV-36A) and neutral density filters. An **A6CB** mixture was irradiated at an intensity of 1.2 mW cm⁻² through a slit mask (width 250 μm) at a scanning rate of 20 μm s⁻¹. Then, the mask was removed to irradiate throughout the cell for 5 min to complete photopolymerization and fix any molecular alignment generated. After photopolymerization, the glass cell was rapidly cooled down to room temperature by immersing it in liquid nitrogen. The resultant polymer film was observed with a polarized optical microscope (Olympus BX53) equipped with a Berek compensator (Olympus U-CBE), and the birefringence (Δn) and optic axis of the film were evaluated. The order parameter (S), the degree of in-plane alignment of mesogenic units such as cyanobiphenyl moieties, was calculated from absorbance from UV-vis spectroscopy (JASCO V-650ST) by the following Eq. (1):²⁶

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}) \quad (1)$$

where, A_{\parallel} and A_{\perp} represent the absorbances with incident polarized light that was parallel or perpendicular to the light scanning direction, respectively.

Figure 3(a) depicts the polarized optical micrographs (POMs) of films obtained by (i), (ii) photoirradiation throughout the cell and (iii)–(v) SWaP of an **A6CB** mixture in two types of glass cells coated with an unrubbed polyimide layer, or a rubbed polyimide layer (alignment layer). Control experiments where cells covered with an unrubbed polyimide layer or a rubbed polyimide layer were irradiated with UV light without a SWaP process showed an opaque appearance due to polydomain structures that is typical for nematic LC polymers. This means that **A6CB** molecules were not aligned uniformly with or without anchoring surfaces [Fig. 3(a)-(i), (ii)]. On the other hand, SWaP of **A6CB** in a cell covered with an unrubbed polyimide layer resulted in a transparent, colourless film. POM observation revealed that the film had uniform optical anisotropy with an optic axis lying along the light scanning direction [Fig. 3(a)-(iii)]. Moreover, UV-vis spectroscopy revealed that cyanobiphenyl moieties were aligned along the light scanning direction, and the order

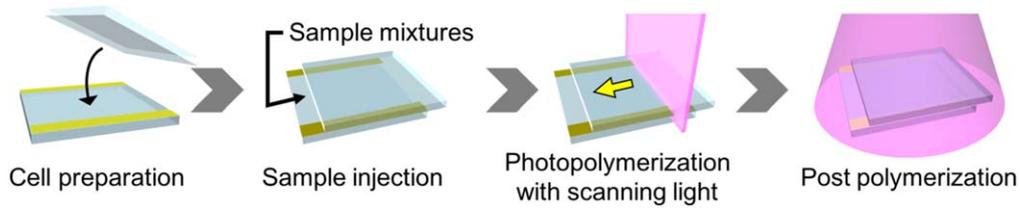


Fig. 2. (Color online) Schematic illustrations of cell preparation and photopolymerization process.

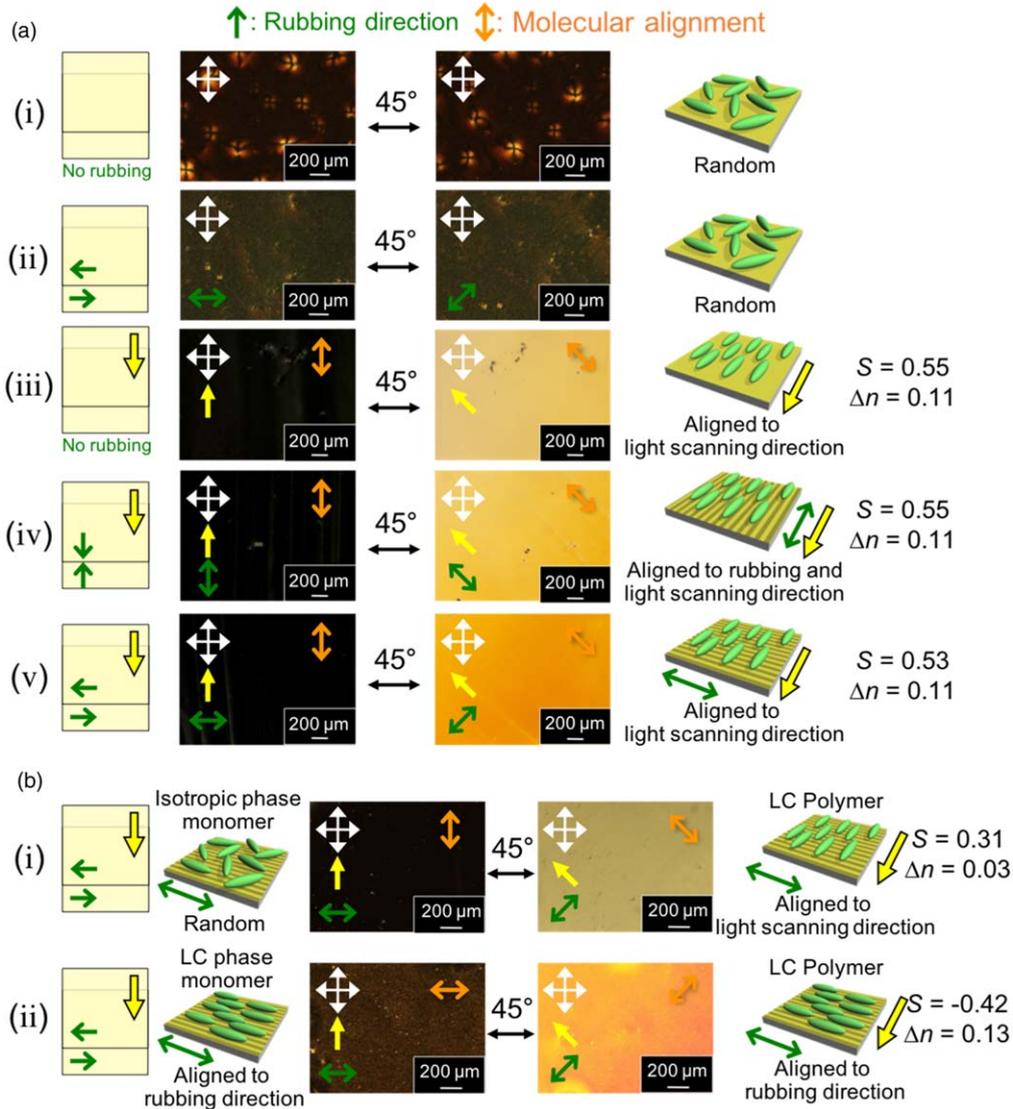


Fig. 3. (Color online) (a) Polarized optical micrographs, order parameters (S) and birefringence values (Δn) of the films obtained by photopolymerization with **A6CB**. Yellow arrows indicate the light scanning direction. Films were obtained by photopolymerization (i) without light scanning with unrubbed polyimide layers, (ii) without light scanning with rubbed polyimide layers, (iii) by SWaP with unrubbed polyimide layers, (iv) by SWaP with polyimide layers rubbed parallel to light scanning direction and (v) by SWaP with polyimide layers rubbed perpendicular to light scanning direction. (b) Polarized optical micrographs, order parameters (S) and birefringence values (Δn) of the films obtained by SWaP with **A6PB1** with polyimide layers rubbed perpendicular to light scanning direction. Samples were photopolymerized in (i) their isotropic phase at 70 °C, and in (ii) their LC phase at 40 °C.

parameter was found to be 0.55. These results indicate that uniform molecular alignment can be achieved by SWaP, whereas photopolymerization with UV irradiation throughout the cell never caused unidirectional molecular alignment.

Next, we investigated the effect of an alignment layer by conducting SWaP of **A6CB** in a glass cell coated with an alignment layer of a rubbed polyimide. SWaP where light was scanned along or across the rubbing direction resulted in films with unidirectional molecular alignment parallel to the

light scanning direction, independent of the rubbing direction [Figs. 3(a)-(iv) and 3(a)-(v)]. The order parameters of these films were found to be ~ 0.5 . This means that the degree of the alignment of cyanobiphenyl moieties was not significantly different among these films. Birefringence of these films was also evaluated, and both films had birefringence of 0.11. The values of order parameter and birefringence indicate that surface anchoring from the substrates has no effect on the generation of molecular alignment by SWaP.

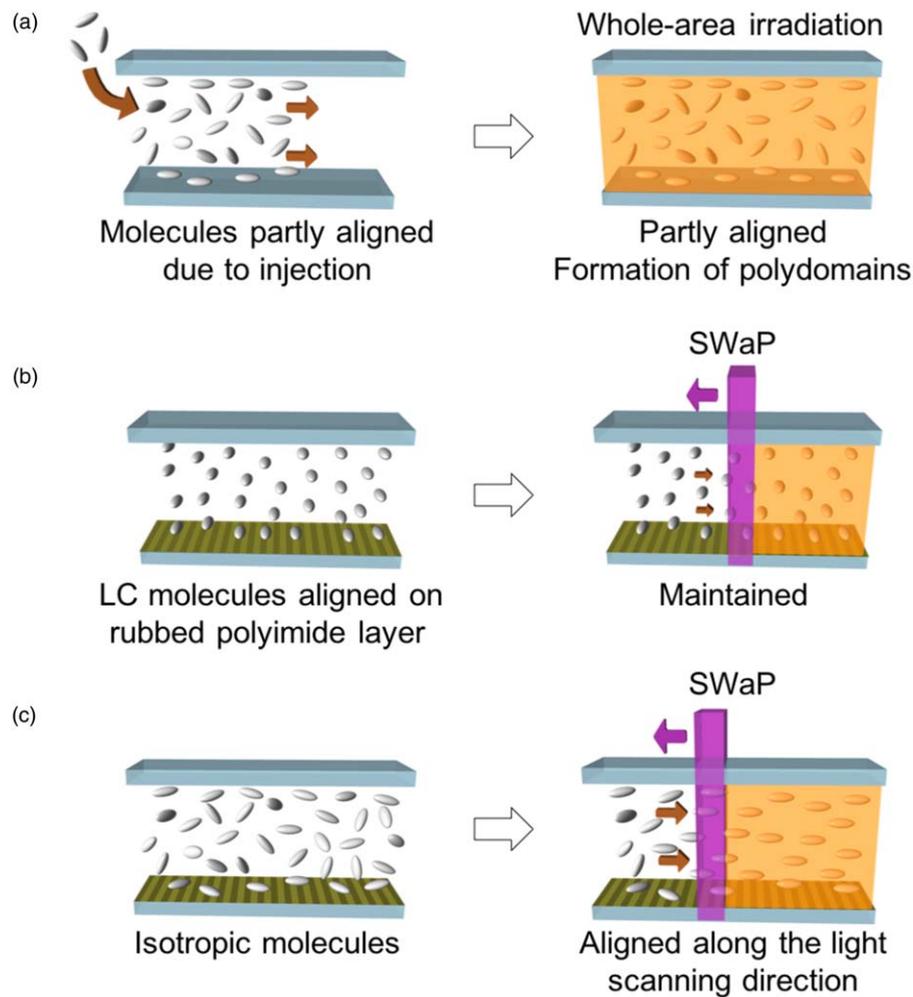


Fig. 4. (Color online) Schematics showing the mechanism of SWaP and the effect of surface treatment. (a) Photopolymerization without SWaP, (b) SWaP with monomers in a LC phase in a rubbed cell and (c) SWaP with monomers in an isotropic phase.

We then investigated the effect of liquid crystallinity of monomer with a **A6PB1** mixture that exhibits LC phase instead of an isotropic **A6CB** mixture. We conducted SWaP in the same process as described above except for the light intensity of 0.2 mW cm^{-2} , a slit mask with $500 \mu\text{m}$ width and at the light scanning rate of $10 \mu\text{m s}^{-1}$. **A6PB1** mixtures in the rubbed cell, which were kept at their LC temperature of 40°C , showed a unidirectional alignment parallel to the rubbing direction. Subsequent overall photoirradiation fixed the alignment, and resulted in a molecularly aligned polymer film in the same manner (for more details, see the supplementary data, Fig. S2). In contrast, photopolymerization by whole-area irradiation at its isotropic temperature of 70°C produced a randomly aligned polymer film even under surface anchoring conditions on a rubbed polyimide layer (supplementary data, Fig. S2). As shown in Fig. 3(b), SWaP of **A6PB1** in the rubbed cell resulted in polymer films with molecular alignment where the alignment direction was different depending on the temperature as well as the phase of monomers. When conducting SWaP at its isotropic temperature of 70°C , the molecular alignment direction of the resultant film was parallel to the light scanning direction, and was independent of the rubbing direction [Fig. 3(b)-(i)]. In the case of SWaP at its LC temperature of 40°C , molecules were aligned according to the rubbing direction.

This means that SWaP could not align molecules along the light scanning direction under a LC phase condition in the rubbed cell [Fig. 3(b)-(ii)].

From these results obtained by photopolymerization of **A6CB** and **A6PB1** mixtures, we considered the mechanism of molecular alignment and the effect of an alignment layer as summarized in Fig. 4. For the whole-area photoirradiation of a glass cell without any surface treatment, an opaque film with random molecular alignment was obtained [Fig. 4(a)]. In photopolymerization of monomers at an LC phase temperature in a cell coated with a rubbed alignment layer, the molecular alignment direction had been regulated by surface anchoring before polymerization. In this condition, the initial alignment was maintained and SWaP had no ability to reorient the molecular alignment direction due to its surface anchoring effect [Fig. 4(b)]. On the other hand, when a bare glass cell was used for monomers in an isotropic or an LC phase (see the supplementary data, Fig. S3), SWaP could generate molecular alignment along the light scanning direction since the initial alignment was random. Furthermore, the results of SWaP for **A6CB** and **A6PB1** mixtures at isotropic temperatures in a cell even with a rubbed alignment layer revealed that SWaP of isotropic monomers could generate unidirectional molecular alignment along the light scanning direction. This clearly indicates that an alignment layer as well as the surface

anchoring effect has almost no effect on the generation of molecular alignment achieved by SWaP [Fig. 4(c)].

In conclusion, we investigated the effect of surface alignment of substrates used on the generation of molecular photoalignment achieved by SWaP. SWaP could generate uniform molecular alignment along the light scanning direction when monomers were randomly oriented before photopolymerization. Of particular interest, is that SWaP therefore has the ability to achieve molecular alignment effectively for isotropic monomers regardless of the surface anchoring from substrates with an alignment layer that is vital to conventional alignment methods. Therefore, we believe that these results confirm that SWaP could function successfully as a versatile chemical platform for aligning functional anisotropic molecules over various substrates with any surface boundary conditions, and represents a facile and powerful pathway for fabricating functional flexible films.

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ORCID iDs Masaki Ishizu  <https://orcid.org/0000-0001-6633-0705>

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