Alignment layer-free molecular ordering induced by masked photopolymerization with non-polarized light

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Abstract

Soft materials, such as polymers, colloids, and liquid crystals (LCs), with highly and macroscopically ordered alignments, are playing important roles in electronics, photonics, and medical devices because of the manifestations of their functional properties.1–3 Precise control of molecular alignment in polymer films generally has been processed with the assistance of an alignment layer, over which building blocks, such as LCs, can be aligned and in which their alignments are fixed by subsequent photopolymerization.4–6 Standard procedures for generating an alignment layer include a rubbing process that offers both an advantage and a complication: simple, facile fabrication of macroscopic unidirectional (1D) alignment and difficulty in forming two-dimensional (2D) patterns.4,6 Recently, 2D patterns of alignment have been required for exploring fundamental research and for enhancing the functionality of polymer films, especially in photonic applications such as diffraction gratings, polarization converters, and vortex retarders.

A photoreactive alignment layer has been proposed as an alternative procedure for controlling molecular alignment in 2D; in this procedure, molecules are aligned through irradiation with linearly polarized light that causes photochemical reactions of photocrosslinkable, photoisomerisable, or photodegradable compounds.7–13 Ichimura et al. first demonstrated control of the alignment of a photoreactive alignment layer, referred to as a “command surface”, which includes azobenzene molecules.13 Irradiation with linearly polarized light on the surface can control the nematic LCs over the surface and switch them reversibly from homeotropic (out-of-plane) to homogeneous (in-plane) alignments. During the past decades, these photorealignment methods demonstrated impressive success in controlling the alignment of molecules; these methods have been launched in LC displays.7,8,13–19 These methods, however, require complicated procedures for fabricating molecular alignment layers and subsequently aligning the LCs. In addition, a molecular alignment layer is activated only by irradiating specific photoreactive compounds with linearly polarized light. Here we report a simple method demonstrating that masked photopolymerization of a photochemically inert monomer and crosslinker causes molecular alignment from 1D to 2D patterns. The method requires no alignment layer; the photopolymerization is carried out with non-polarized light. Masked photopolymerization brings about molecular transport towards irradiated or unirradiated regions, depending on the chemical potential, which triggers 1D or 2D alignment. So far, the photopolymerization-induced diffusion of LCs has achieved remarkable maturity in the fabrication of optical films having spatially controlled LC alignment. Elaborate integration of molecules is achieved by restricting the transport of polymers under specific photopolymerization conditions, such as low temperatures or high concentrations of polymer and crosslinker combined with the molecular alignment layer.20–24 Until now, however, no one has reported the direct induction of molecular alignment through diffusion with no alignment layer. Based on the previous articles, we designed a new system where polymer concentration and viscosity are kept relatively low during polymerization. This enhances the molecular mobility that enables direct rotation and alignment of molecules by the diffusion.

We prepared a sample mixture, composed of 6-(4-cyano-4′-biphenyloxy)hexyl acrylate (A6CB, 97 mol %), hexanediol dimethacrylate (HDDMA; Wako Chemical, 3 mol %), and a photoinitiator (Ciba Specialty Chemicals Irgacure 651). A6CB was synthesized according to a procedure similar to the previous report.13 In the present system, we conducted photopolymerization of an isotropic monomer, which has relatively lower viscosity, following the procedure depicted in Fig. 1(a). The sample mixture was melted at 150 °C and injected into a 3-μm-thick handmade glass cell, constructed of two glass substrates with no surface treatment. Subsequently, the cell was cooled down to the photopolymerization temperature of 60 °C, which is above the glass transition temperature of a homopolymer of A6CB.25 The cell was vertically irradiated with 365 nm ultraviolet (UV) light (USHIO USH-500SC) through glass filters (AGC Techno Glass IRA-25S, UV-36A, ND50) and a photomask, following the so-called masked process. During the photopolymerization using a 250 μm slit photomask, as shown in Fig. 1(b),...
polymerization occurred only in the irradiated region. Thus, molecules diffuse unidirectionally between irradiated and unirradiated regions, owing to the difference in chemical potential between them.\(^{20–24}\) We observed the polymerization process by embedding a handmade polarized optical microscope (POM) within the photopolymerization setup. The in situ observation revealed that uniform and unidirectional (1D) optical anisotropy was generated only in an irradiated region 20 s after the initiation of UV irradiation, as shown in Fig. 1(c). Additionally, as the exposure time increased, the optically anisotropic region became larger along the vector normal to the boundary of the irradiated region. Given the finding that photopolymerization-induced diffusion occurs at the boundary of an irradiated region,\(^{20–24}\) the polymer concentration should be highest at the center and lowest at that boundary. These results imply that the spatial distribution of the polymer concentration is very important both for the appearance of optical anisotropy and for the generation of molecular diffusion.

To understand the detailed alignment behavior, we introduced a post-exposure process followed by masked photopolymerization for producing sufficient polymers immediately after molecular diffusion occurred. In the post-exposure process, we irradiated the entire area of the glass cell with UV light without a photomask, as shown in Fig. 1(a). As a result, we obtained a polymer film with optical anisotropy by performing masked photopolymerization for only 1 s, as Fig. 1(d) shows. Observation of the obtained film by POM (Olympus BX50) revealed that the optical anisotropy had expanded outside of the boundary. In contrast, when we carried out photopolymerization of the entire glass cell with no photomask, we never observed any uniform optical anisotropy in the glass cell. These results imply both that molecular diffusion owing to the masked process is a key to directing the uniform 1D alignment of molecules and that the spatial distribution of polymer concentration is required for the appearance of optical anisotropy in the polymer film.

Such optical anisotropy, induced only at the boundary, is explicable by assuming the alignment of cyanobiphenyl moieties in the resulting polymer films. The alignment is induced because of molecular diffusion during the masked process, as experimentally corroborated by the following three observations. Unless stated otherwise, we fabricated polymer films using the same procedures and photopolymerization conditions described in Fig. 1(a). Instead of a slit photomask, however, we used a commercially available photomask with a 500 µm line-space pattern, as shown in Fig. 2(a).

First, as shown in Fig. 2(b), POM observation of a film polymerized with the line-space photomask showed a uniform 1D optical anisotropy at every boundary between the irradiated and unirradiated regions. From the observation of the film with a Berek compensator (Olympus U-CBE), the optical axis of the anisotropy was found to be parallel to the vector direction normal to the lines of the photomask. However, the optical anisotropy was too small for the evaluation of its retardation \((d\Delta n)\) as well as its birefringence \((\Delta n)\). Because the magnitude of optical anisotropy was related to the duration of the masked process, we conducted the masked photopolymerization for 10 min, as shown in Fig. 2(c). As a result, the retardation and birefringence drastically increased to 458 nm and 0.15, respectively. This value of the birefringence should arise from the 1D alignment of cyanobiphenyl moieties, because a typical low-molecular-weight nematic LC having a cyanobiphenyl moiety exhibits birefringence of about 0.2. In fact, as Fig. 2(c) illustrates, the 1D alignment was evident in the polarized UV–visible (JASCO V-650ST) absorption spectra of the obtained polymer film. The absorbance in the absorption wavelength of the cyanobiphenyl moiety exhibited its highest and lowest values with polarized light parallel and perpendicular, respectively, to a vector direction normal to the lines of a photomask.

Second, we directly measured the surface profile of the polymer film with a surface profiler (Dektak 150, scan length: 900 µm) by opening the glass cell with a cutter. As shown in Fig. 2(d), the measurements revealed that the surface structure of the film was embossed. We found both that the apex of the surface structures was centered on the irradiated region and that the periodicity depended on the line-space pattern of the photomask. In addition, the height of the apex increased by \(\sim 500\%\) when the masked process time increased from 1 s to 10 min. These results suggest that the previous theoretical explanation, based on the Flory–Huggins theory, and the experimental results, related to the formation of embossed structures arising from photopolymerization-induced diffusion, are applicable to the present study, but show...
differences in the mobility of the polymer. In previous cases, to form highly embossed surfaces by accumulating molecules in an irradiated region, polymer diffusion toward an unirradiated region was greatly hindered by keeping the polymerization temperature below the glass transition temperature, by adjusting the crosslinker concentration to approximately 50%, or by employing photopolymer components. In contrast, we designed the present system to enhance mobility of both monomers and polymers. Concentration of the crosslinker was adjusted below 5 mol %, which is low. Photopolymerization was conducted at a high temperature above its glass transition temperature. Therefore, we inferred that the motion of polymers was a key factor leading to the emergence of uniform 1D alignment of cyanobiphenyl moieties.

Third, we demonstrated that the photopolymerization temperature, which is an important factor influencing the mobility of molecules, affected the alignment. As shown in Fig. 3, we conducted photopolymerizations at various temperatures from 60 to 150 °C, and evaluated the values of birefringence, the regions of molecular alignment, and the apex heights of embossed structures in the obtained films. As the photopolymerization temperature increased, the birefringence, the alignment region, and the apex height increased; however, when the temperature was above 100 °C, the birefringence slightly decreased and the embossed structure barely formed. This behavior may be due to the balance between the stability of molecular alignment and mobility of molecules. At higher temperatures, the viscosity of the system is reduced and the mobility of molecules is increased. The films polymerized at higher temperature below 130 °C have more ordered, larger alignments with highly embossed structures. After the temperature exceeds a certain point, manifestations of negative effects on the order and the height occur, owing to the increment of alignment relaxation and the polymer’s mobility, which increases the aligned region adversely. It should be noted that even photopolymerization at 150 °C above the
Fig. 4. Formation of radial molecular alignment by photopolymerization with a pinhole. (a) A micrograph of a pinhole with a 200 µm diameter. (b, c) A polarized optical micrograph and schematic of the obtained film with radial molecular alignment induced by the circular shape of the irradiated region. The scale bar is 100 µm.

isotropic temperature of polymers resulted in a uniform 1D alignment. In spite of the smallest apex height under isotropic conditions, the aligned region became the largest because the polymer diffused effectively towards an unirradiated region. Such behavior has never been reported in the aforementioned conventional alignment methods because they require the combination of alignment layers and the cooperative effects of LCs. Therefore, the results suggest that photopolymerization-induced alignment is achieved not by the cooperative effect of molecules or elongation of the film surface arising from embossing, but by the shear stress arising from molecular diffusion.

Based on the above-mentioned observations, it has been shown clearly that uniform 1D molecular alignment of mesogens is generated directly by the diffusion of molecules. First, photopolymerization through a photomask causes molecular diffusion at the boundary between the irradiated and unirradiated regions. The diffusion occurs along the vector direction normal to the boundary because of the difference of chemical potentials. Along the direction of diffusion that imposes shear stress, the anisotropic mesogens in the polymer are aligned. Subsequently, the post-process fixes the molecular alignment around the boundary.

The direction of alignment is controlled by the vector direction normal to the boundary and the resultant molecular diffusion direction. This means that 2D molecular alignment is also achieved by the spatial design of the photomask. We employed a 200-µm-diameter pinhole as a photomask, which was supposed to create radial molecular diffusion because of the circular boundary, as Fig. 4 shows. Interestingly, careful observation of the film by POM with a Berek compensator showed that radial molecular alignment with a +1 topological defect was formed merely by photopolymerization through a circular pinhole. This result indicates that the present method simply enables direct 1D and 2D molecular alignment only by UV irradiation through a designed photomask with no alignment layer, polarized light, or axis-selective photoactive compounds.

In conclusion, we have proposed a simple photopolymerization method in which we conducted photopolymerization through a photomask with non-polarized light and no alignment layer. The masked photopolymerization generates uniform 1D or 2D molecular alignment triggered by unidirectional molecular diffusion. The alignment direction is controlled by the vector direction normal to the boundary between the irradiated and unirradiated regions and the resultant molecular diffusion. Thus, the shape of 1D or 2D molecular alignment can be controlled simply by changing the shape of the photomask. To our knowledge, this is the first time that masked photopolymerization having no alignment layer directly caused molecular alignment. We believe that photopolymerization-induced molecular alignment can be a unique, alternative approach to precisely aligning molecules with various complex patterns. Further investigation will provide the novel techniques for fabricating specialty films with highly functional properties.

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