Surface effects on photopolymerization induced anisotropic phase separation in liquid crystal and polymer composites

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The surface effects on the anisotropic phase separation in photopolymerization induced phase separation of liquid crystal and polymer composites have been studied. It was found that the surface interaction between the substrate and the prepolymer and/or liquid crystal plays a crucial role in anisotropic phase separation. A theoretical model is suggested to describe the surface effects by adapting a phenomenological free energy approach. The formation of polymer layer in the presence of surface effects can be understood as competition between entropic flow and surface directed flow of polymer and liquid crystal. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734376]

In the past 20 years, techniques to prepare dispersions of microscopic liquid crystal droplets in a polymer matrix have been developed.[1–3] The well-known and simple method of the formation of these polymer dispersed liquid crystals (PDLCs) is by strong irradiation of ultraviolet (UV) light on the photocurable polymer and liquid crystal (LC) mixture. PDLC structures are a result of isotropic and relatively fast phase separation. Recently, an anisotropic phase separation method using photopolymerization induced phase separation (PIPS) was developed to fabricate phase-separated composite organic films (PSCOFs) of LC and polymer.[4–6] The rate of phase separation is controlled and deliberately kept low to allow the system to undergo a complete phase separation in two regions of nearly pure LC and solid polymer. This PSCOF method can, in general, be used to prepare multilayer structures either parallel or perpendicular to the substrates. In the simplest case, it yields adjacent uniform and parallel layers of the LC and polymer.

In order to explain the mechanism responsible for the formation of PSCOF, Qian *et al.*[7] developed a theoretical model that is based on the one-dimensional kinetic approach. Droplet formation is inhibited because of the UV intensity gradient due to absorption by LC molecules and relatively slow rate of phase separation due to weak UV intensity compared to the time for approaching thermal equilibrium. The polymerization rate can be controlled by UV intensity. If the polymerization rate is faster than the time for thermal equilibrium, then LC droplets are formed in polymer network, namely, PDLC. In the model, however, the authors did not consider the surface effects on anisotropic phase separation.

Recently, it was reported that the morphology after phase separation is greatly affected by the surface interaction between the LC/prepolymer and surface layer.[8] By optical microscopic studying of phase separation for various monomers, it was found that the resultant structures depend not only on bulk properties of the LC/monomer but also on the surface interaction with the surface layer. However, there has

been no systematic study on the surface effects on PIPS. In this letter, the experimental results using various couples of surface layers and monomers will be described and a theoretical model of the photopolymerization induced anisotropic phase separation in the presence of surface effects is proposed. Through numerical simulation, the surface effects on the morphology after phase separation will be explained qualitatively.

The materials used in this study were nematic LCs (NLCs) LC17 and photocurable prepolymers NOA72, NOA73 (Norland Optical Adhesives), and SK9 (Summers Laboratories). Two glass substrates coated by transparent indium tin oxide(ITO) were used for electrodes. The alignment layers used in this study were nylon 6 (Sigma Aldrich) and RN1286 (Chisso Co.). The alignment layers are spin coated on one substrate and rubbed to obtain homogeneous LC alignment. The other substrate remains without alignment layers. Glass bead spacers of 5 μm diameter were used to fix the cell spacing. The mixing ratio was fixed for the LC:prepolymer as 70:30 wt %. Cells thus prepared are filled by capillary action with the mixtures at a temperature corresponding to the isotropic phase of the LC, i.e., 100 °C. Phase separation was induced by exposure to UV light of 0.78 mW/cm^2 from a high pressure mercury lamp reflected from an UV mirror. During the exposure, the cell was kept at the temperature of 100 °C, so the LC is in isotropic phase. Figure 1(a) schematically shows the main features of the PSCOF structure between the two substrates.[7] In order to obtain a scanning electron microscopy (SEM) image of the polymer structure after UV irradiation, the samples were treated in a hexane solution for 24 h after cutting, in order to remove the LC molecules in the cell.

The microscopic and SEM images for the samples fabricated, using various prepolymers with nylon 6 and RN1286 alignment layers, are shown in Fig. 1(b). The samples with NOA72 on a nylon 6 alignment layer show a uniform alignment texture, as shown in the figure. From the result, it was confirmed that the LC molecules are homogeneously aligned in the sample. The cross sectional SEM image shows that the polymer layer of 1.3 μm is well formed on the upper substrate with bare ITO. The thickness of the polymer layer

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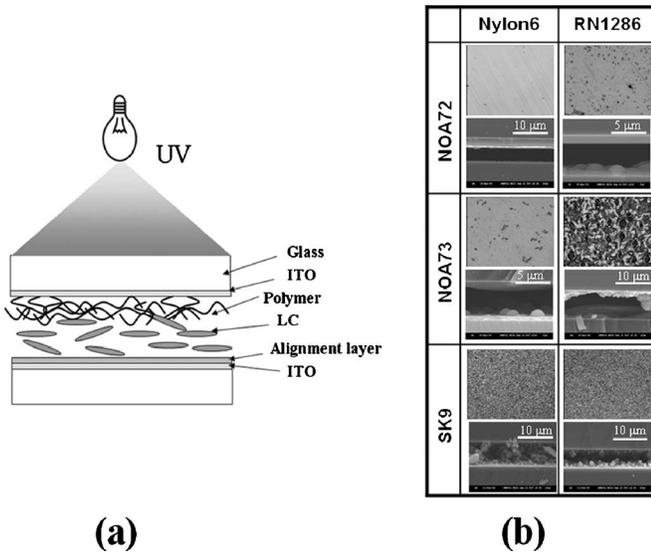
FIG. 1. (a) Schematic of phase-separated composite film (PSCOF). (b) Optical microscopic and SEM images of PSCOF for LC+various polymers of NOA72, NOA73, and SK-9 on nylon 6 and RN1286 alignment materials.

FIG. 2. Measured contact angle data vs time for various polymers on (a) nylon 6 and (b) RN1286 alignment layers. Below reference lines, a LC alignment shows a defect structure due to solidified polymers on the alignment layer.

matches well with the calculated thickness, using the mixing ratio. It can also be seen that there is a sharp boundary between the LC and the polymer layers. For the case of NOA73 on nylon 6, defects exist in the alignment textures, which indicates a loss of alignment due to the morphology of the formed polymer. By observing the cross sectional SEM image, it was found that a relatively large amount of polymers is formed on the bottom substrate. Moreover, the surface morphology of polymers on both substrate is neither flat nor uniform. The nonuniform optical microscopic texture may be due to these irregular formations of polymer layers. The alignment texture of the sample with SK9 on nylon 6 shows a fully unaligned texture. The SEM image shows that the droplet shapes of the polymer structures are dispersed in whole areas of the sample due to fast polymerization even under weak UV irradiation, which is totally different from the results with NOA 72 and 73.

The alignment textures and polymer structures on RN1286 are a little bit different from those on nylon 6. The microscopic texture and SEM image with NOA72 on RN1286 are similar to those with NOA73 on nylon 6. The sample with NOA73 on RN1286, however, shows that fully unaligned textures and more irregular polymer structures exist on top of the substrate, as shown in the figure. Moreover, a relatively large quantity of polymers is piled up on the bottom substrate with the alignment layer. In the case of SK9, the results are almost the same as that on nylon 6.

In order to explore the surface interaction, the contact angles of the prepolymers on the alignment layers were measured. Figure 2 shows the contact angles of various prepolymers on the nylon 6 and RN1286 alignment layers as a function of time after dropping. In the data, the fluctuation in the contact angles with time is within the range of experimental error. The contact angles of NOA72, NOA73, and SK9 on nylon 6 are saturated at about 37°, 28°, and 10°, respectively. The contact angles are changed to 30°, 22°, and 13° on RN1286, respectively. We note that the LCs used were fully wetted on both alignment layers and dewetted on the ITO substrate. Due to the difference of surface wetting properties, there exists a competitive interaction of the LC and prepoly-

mers with the surface alignment layers to form network structures with UV exposure. However, the LC molecules near the alignment layer respond to its anchoring potential and align parallel to the rubbing direction. Oriented LC molecules determine the microscopic structure of the polymer-LC interface, which becomes compatible with their alignment. Therefore, the presence of the alignment layer promotes the surface-induced anisotropic phase separation in the direction of the sample thickness.
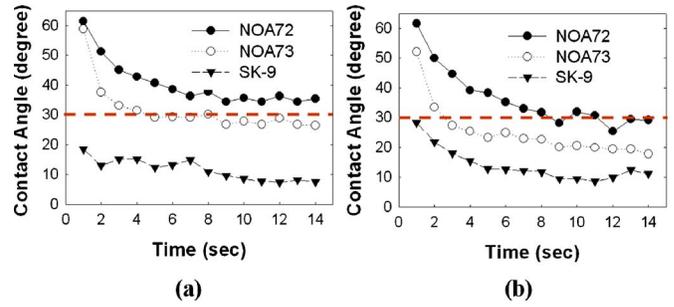
The theoretical model of photopolymerization by induced anisotropic phase separation was developed previously in a simple one-dimensional kinetic theory.[7] In that model, surface interaction effects were not considered. In order to obtain the diffusion current in the presence of surface effects, we start from the total free energy consideration including surface interaction term. The free energy G can be written as

$$G = \int (g + V_L\psi_L + V_M\psi_M + V_P\psi_P)dv, \qquad (1)$$

where $g = \psi_L \ln \psi_L + \psi_M \ln \psi_M + \chi(\psi_L\psi_M + \psi_M\psi_P)$ is the isotropic mixing free energy and ψ_L, ψ_M, and ψ_P are the concentrations of LC molecules, prepolymer, and immobile polymer network, respectively. V_i means the potential energy from the surface for each species of molecule. χ is the molecule-molecule interaction parameter in Flory-Huggins theory. The current equation is given by

$$J_L = -\Lambda \nabla \left(\frac{\delta G}{\delta \psi_L} \right), \qquad (2)$$

where Λ is the mutual translational diffusion coefficient having the property of Onsager reciprocity.[9] For simplicity, we assume here that prepolymer and LC can be treated as monomers and cross-linked polymers are immobile.[10] Moreover, it is assumed that the diffusion constants of prepolymer and LC molecules are the same; therefore it is given by $\Lambda = D\psi_L\psi_M/(\psi_L+\psi_M)$, where D is the diffusion constant. As a result, by substituting Eq. (1) into Eq. (2), the current equation of the prepolymer with the surface interaction can be derived as

$$J_M = -J_L = \frac{D}{\psi_L+\psi_M}\left(-\psi_L\frac{\partial\psi_M}{\partial z} + \psi_M\frac{\partial\psi_L}{\partial z} - \chi\psi_L\psi_M\frac{\partial\psi_L}{\partial z} \right.$$
$$\left. + \psi_L\psi_M\frac{\partial V}{\partial z} \right), \qquad (3)$$

where $V(z) = V_L - V_M$ is the surface potential difference be-
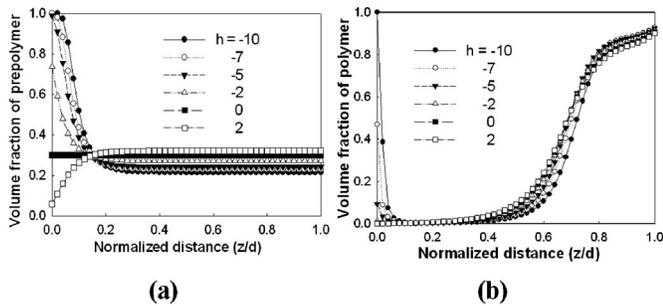
FIG. 3. Numerical simulation results of (a) volume fraction of prepolymer before UV exposure and (b) volume fraction of solidified polymer after UV exposure; the distance is normalized by the cell gap.

FIG. 4. Numerical simulation results for long range and large values of surface potentials. The simulation parameters are (i) $h=-20$, $\delta=5$, (ii) $h=50$, $\delta=2.5$, and (iii) $h=0$. The other simulation parameters are the same as those in Fig. 3.

tween the LC molecules and prepolymers with the surface.

In order to perform numerical simulations, it was assumed that the surface potential decays exponentially as a function of distance from the surface, i.e., $V=he^{-\delta z}$, where h is the potential at the surface and δ is the decaying parameter that is related to the effective range of the surface potential. With the current equation considering the surface effect, coupled equations describing the PIPS process[7] were used in numerical calculation. We fixed $\delta=25$ and bulk parameters such as relative polymerization and UV absorption length correspond to PSCOF structure.

The initial mixing ration of the LC:prepolymer was 70:30. It should be noted that the effective Flory-Huggins parameter χ is not clear for this simple one-dimensional system. Therefore the value was fixed in the reasonable range of the isotropic mixing state. Initially the numerical simulation was performed without the UV irradiation condition, in order to obtain equilibrium concentration profiles of the LC and the prepolymer, especially wetting properties of the LC and/or the prepolymer at the alignment surface, $z=0$. In the experiment, this corresponds to maintaining the temperature of 100 °C for 30 min before UV irradiation. The results are shown in Fig. 3(a). A complete wetting of prepolymers occurred below $h=-5$. The negative value of h means that the surface prefers more prepolymers to LC molecules. Using the above results as the initial concentration profile, numerical simulation was carried out again for UV irradiation; the result of which is shown in Fig. 3(b). The concentration profiles, including the surface, are different before and after UV exposure. Near $z=d$ (UV illumination side), polymers accumulated and formed a solidified polymer layer. However, near the alignment layer, a relatively small quantity of polymers accumulated, depending on the surface potential strength, and rapidly decreased as the distance from the surface increased.

As previously stated, polymerization starts in the high-intensity region near the UV source and those prepolymers in the low-intensity region diffuse to the high-intensity region, in order to maintain the relative concentration and join the polymerization reaction (entropic flow). Therefore, competition occurs between the entropic flow and the surface directed flow toward the alignment surface, while the concentration at the surface $z=0$ decreases.

In order to verify the competition between the entropic current and the surface directed current, numerical calculations for larger and longer ranges of surface potential func-

tions were carried out. Figure 4 shows the resultant polymeric concentration profiles for $h=-20$ and $\delta=5$, $h=50$ and $\delta=2.5$, and $h=0$. As shown in the figure, each current competes to generate various solidified polymeric structures. For the case of $h=50$, the LC molecules are more attracted to the alignment layer and the LC/polymeric boundary becomes sharp, compared to the case of $h=0$. For the case of $h=-20$, the polymer layer formed on the alignment layer, which is the opposite result that was found by numerical simulation and is shown in Fig. 4. This means that if a long range surface directed current can be generated, then various kinds of solidified microstructures inside the cell can be constructed.
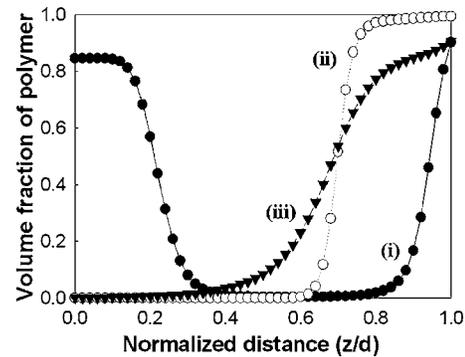
In summary, the surface effects on anisotropic photopolymerization induced phase separation have been analyzed by experiments and numerical calculations. It was observed that the optical texture and cross sectional polymeric structure in PSCOF depend on the competition between the entropic diffusion and surface directed current during photopolymerization. A simple one-dimensional theoretical approach that considered surface effects was carried out on the basis of a previous kinetic model. The formation of polymer layer in the presence of surface effects can be understood as competition between entropic flow and surface directed flow of polymer and liquid crystal.

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