Letters

Phase Separation of Polymer-Dispersed Liquid Crystals on a Chemically Patterned Substrate

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The surface-induced structure formation of polymer-dispersed liquid crystals (PDLCs) on a chemically patterned substrate was studied for the first time. The patterns on the substrate were successfully transferred to the PDLC film, resulting in alternating LC-rich and polymer-rich phases. This simple approach offers a new means of organizing micrometer-sized LC domains into well-ordered structures in a polymer matrix of PDLCs.

Polymer-dispersed liquid crystals (PDLCs) are an important new class of materials for potential applications in the areas of light shutters, flat panel displays, privacy windows, microlenses, and so forth.1,2 Such devices require no additional optical elements (i.e., polarizers) for operation, which otherwise place limits on device weight and flexibility.2 They are prepared by demixing polymer and LC, including thermally induced3 and polymerization-induced4 phase separation. The performance of PDLC strongly depends on the final morphology of LC domains in the polymer matrix.2 The size, shape, and distribution of LC domains are generally not only dictated by thermodynamic phase equilibria but are also strongly dependent on phase-separation kinetics and the anisotropic ordering of LC because most polymer systems hardly reach a thermodynamic equilibrium state.5 Thus, a fundamental understanding of the phase equilibrium and phase-separation kinetics of mixtures of polymer/LC is of crucial importance for optimizing the performance of PDLC materials.6–10

Several PDLCs with a controlled LC domain size and distribution have been produced, including holographic PDLCs (H-PDLCs) formed by pattern photopolymerization using two or more interfering laser beams for use in electrically switchable diffraction gratings,11–20 photoenhanced stratification liquid crystal displays (PES-LCDs) formed by photoenforced stratification,21 and phase-separated composite films (PSCOFs) based on

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anisotropic photopolymerization for liquid crystal displays (LCDs).\textsuperscript{22} Surface-induced structure formation in polymer blends has been widely recognized as an inexpensive, highly reproducible way to deliver polymers to specified regions via selective polymer/substrate interaction.\textsuperscript{23–27} Here, we report the formation of ordered structures in a polymer-dispersed liquid crystal (PDLC) film by allowing the polymer and LC to phase separate on a chemically patterned substrate (i.e., concentric Au ring-patterned ITO substrate). The patterns on the substrate were successfully transferred to the PDLC film, resulting in alternating LC-rich and polymer-rich phases as confirmed by polarized optical microscope and Raman spectroscopy measurements. A unique surface-induced phase-separation process was observed for the first time. The time evolutions of the size, number, and total area of LC domains were quantified. This simple approach offers a new means to organize micrometer-sized LC domains into well-ordered structures in a polymer matrix of PDLCs.

Polystyrene (PS; weight-average molecular weight $M_n = 5100$ g/mol and polydispersity PDI = 1.07) was purchased from Polymer Source Inc. A thermotropic liquid crystal (LC), 4-n-pentyl-4'-cyanobiphenyl (5CB; the nematic phase exists at a temperature between 18 and 35 °C),\textsuperscript{28} was purchased from Sigma-Aldrich. The aspect ratio of the length ($\sim 16$ Å) to the diameter ($\sim 4.3$ Å) of 5CB is 3.7, indicating a rodlike molecule. Its director is the long axis of the cyanobiphenyl moiety. PS/5CB 50:50 wt/wt was dissolved in a common solvent, toluene, at a concentration of $c = 2$ wt %, resulting in a homogeneous solution.

**Preparation of a Patterned Substrate with Chemical Heterogeneity.** The concentric Au ring-patterned ITO substrate (i.e., chemically patterned) was fabricated using the methods introduced previously by us (Figure 1).\textsuperscript{29–36} A very thin layer of gold (Au, 6 nm) was deposited on a precleaned ITO glass by using an e-beam evaporator (Figure 1b). Then, a drop of poly(methyl methacrylate) (PMMA; $M_n = 534$ kg/mol and PDI = 1.57) toluene solution ($c = 0.25$ mg/mL) was confined between the spherical lens and the Au-coated ITO substrate (i.e., a sphere-on-flat geometry).\textsuperscript{32,33} The concentric PMMA rings were produced on both the sphere and the ITO substrate within 30 min via the controlled, repetitive pinning and depinning of the contact line due to the irreversible evaporation of toluene.\textsuperscript{30–33} Subsequently, the PMMA rings were utilized as templates to prepare the Au ring replica by removing Au between the PMMA rings using an e-beam evaporator (Figure 1b). Then, a drop of polymeric material (PS/5CB 50:50 toluene solution) was confined between the upper sphere used in the experiment.\textsuperscript{32,33} The use of transparent patterns was achieved by removing Au between the PMMA rings and an aqueous solution of the KI/K$_2$CO$_3$ mixture, followed by eliminating the PMMA rings selectively with acetone (Figure 1c). The patterns on the substrate were successfully transferred to the PDLC film, resulting in alternating LC-rich and polymer-rich phases as confirmed by polarized optical microscope and Raman spectroscopy measurements. A unique surface-induced phase-separation process was observed for the first time. The time evolutions of the size, number, and total area of LC domains were quantified. This simple approach offers a new means to organize micrometer-sized LC domains into well-ordered structures in a polymer matrix of PDLCs.

**Surface-Induced Phase-Separation Kinetics of PDLC on a Chemically Patterned Substrate.** A small amount of 2 wt % PS/5CB (50:50) toluene solution (about 30 μL) was drop cast on the ITO substrate. The brown and yellow curves correspond to Au rings and PMMA rings, respectively. The center-to-center distance between adjacent rings is about 20 μm. The scale bar is 70 μm.

Figure 1c shows a typical optical micrograph of the Au ring-patterned ITO substrate used in the studies. The width of the Au rings, $w_{\text{Au}}$, and the center-to-center distance between Au rings, $\lambda_{\text{Au}}$, are about 10 and 20 μm, respectively. Only a small zone of the entire Au ring patterns was shown (Figure 1c). The overall pattern was about 1 cm in diameter, governed by the diameter of the upper sphere used in the experiment.\textsuperscript{32,33} The use of transparent ITO glass with only 6-nm-thick periodic Au rings on the top renders the optical imaging in transmission mode (Figure 1c). Moreover, the effect of physical heterogeneity can be neglected because of the very thin layer of Au rings (i.e., 6 nm). This represents a simple and robust way to produce chemically periodic surfaces.
center of a Au ring-patterned ITO substrate at room temperature, covering both the patterned substrate and the outer bare ITO surface. Because PS and 5CB are incompatible,\textsuperscript{38} demixing between them took place during the solvent evaporation. The sample was left in air for 2 h to allow for the complete evaporation of toluene, which was determined by the stability of the focus under the optical microscope (OM) as well as the constant weight of the sample. After toluene completely evaporated, a uniform PDLC film on the top of the patterned substrate resulted, and a thinner film was found at the outer bare ITO surface (Figure 1S in Supporting Information). The thickness of the PDLC film on the patterned substrate, \( h \), was \( \sim 1.2 \mu m \) as estimated on the basis of \( h = \rho S \), where \( m \), \( S \), and \( \rho \) are the mass of the PS/5CB mixture, the area of the PDLC film formed on the substrate, and the density of the film, respectively. The densities of PS and 5CB are \( \rho_{PS} = 1.05 \) g/cm\(^3\) and \( \rho_{5CB} = 1.008 \) g/cm\(^3\), respectively. The area of the PDLC film was \( 2 \times 2 \) cm\(^2\) according to the digital image. The mass of the PS/5CB mixture, \( m \), was calculated on the basis of the concentration (2 wt%) and the volume of the solution (30 \( \mu L \)) (i.e., \( m = 30 \times 10^{-3} \times 0.8 \times 0.02 = 0.00048 \) g; the density of toluene is 0.8 g/cm\(^3\)). Therefore, the film thickness, \( h \), was \( \sim 1.2 \mu m \) (i.e., \( h = m/\rho S = 0.00048/((1.05 + 1.008)/2) \times 2 \times 2) = 1.2 \times 10^{-4} \) cm = 1.2 \( \mu m \). \( h \) was thinner than the spinodal wavelength of the bulk PDLC phase-separation process, which was \( \sim 3 \) \( \mu m \) as measured by small-angle laser light scattering.\textsuperscript{39} The glass-transition temperature, \( T_g \), of the resulting PDLC film was \( \sim 18^{\circ}C \).\textsuperscript{38} The decrease in \( T_g \) (from \( T_g \) of 64 \( ^{\circ}C \) for pure PS (\( M_w = 5100 \))) was due to the fact that the LC plays the role of plasticizer for the polymer.\textsuperscript{38,40–42}

Subsequently, the time evolution of PDLC morphology at room temperature (\( \sim 25^{\circ}C \)) was monitored by polarized OM (Olympus BX51 equipped with a CCD camera; polarizer \( \perp \) analyzer) in transmission mode (Figure 2). The PDLC film was placed in a small, transparent chamber on the OM stage to eliminate temperature fluctuation. It should be noted that the focus and light intensity were not changed throughout the real-time measurement. Generally, the LC droplets in the PDLC film are optically birefringent under the cross-polarized transmitted light condition. They convert linearly polarized light to an elliptical one.\textsuperscript{2} The optical micrograph right after complete solvent evaporation is shown in Figure 2a (\( t = t_0 \)). The 5CB droplets (i.e., bright domains) are randomly distributed on the patterned substrate. The deep-green and dark stripes correspond to the ITO rings and the Au rings, respectively. Locally, they appeared to be parallel stripes.

Because the glass-transition temperature of the PS/5CB mixture, \( T_g^{PS/5CB} \) was 18 \( ^{\circ}C \),\textsuperscript{38} both the 5CB and PS phases were mobile, facilitating phase separation. At \( t = t_0 + 191 \) min, the size of randomly dispersed 5CB domains increased, and the number of domains decreased (Figure 2b). As time progressed, 5CB domains were seen to segregate preferentially to the Au rings and grow into larger droplets (\( t = t_0 + 501 \) min in Figure 2c and \( t = t_0 + 791 \) min in Figure 2d). It has been demonstrated that 5CB absorbed onto the Au surface to form a self-assembled monolayer through the interaction between the cyanide group, CN in 5CB and Au.\textsuperscript{43–45} and a tilted orientation on the Au nanoparticle surface were observed.\textsuperscript{44} In the present study, the strong affinity of 5CB for the Au rings displaced the PS phase toward the ITO parts of the patterned substrate. Thus, the 5CB domains originally located on the Au rings grew larger by the accumulation of 5CB nearby, whereas the domains on ITO rings gradually disappeared (i.e., transported to Au rings) in a process analogous to the evaporation–condensation mechanism in polymer blends.\textsuperscript{46} Phase separation was completed at \( t = t_0 + 1492 \) min as shown in Figure 2e (see the accelerated time lapse video in Supporting Information, Movie 1S, where the intensity fluctuation of 5CB domains may be attributed to (i) the diffusion of 5CB in the PS matrix because the focus and illumination were not changed throughout the real-time measurement and (ii) the change in the orientation of 5CB). As a result, a thin microstructured PDLC film on a chemically patterned substrate was formed, that is, 5CB-rich phase on Au rings alternating periodically with PS-rich phase on ITO rings.

It is noteworthy that a layer of PDLC film covering the patterned ITO substrate was clearly evident in both the digital image and optical micrograph (unpolarized) (Figure 1S in Supporting Information). Moreover, the thickness of the PDLC film was 1.2 \( \mu m \). Taken together, the observed structures were produced by surface-induced phase separation of the PS/5CB mixture rather than the spinodal wavelength of the bulk PDLC phase-separation process.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Time evolution of morphologies of PS/5CB (PS/5CB 50:50 by weight) on a concentric Au ring-patterned ITO substrate. The optical micrographs were taken under a crossed polarizer and analyzer in transmission mode at room temperature. (a) The time at which toluene evaporated completely was taken as \( t_0 \), (b) \( t_0 + 191 \) min, (c) \( t_0 + 501 \) min, (d) \( t_0 + 791 \) min, and (e) \( t_0 + 1492 \) min. The scale bar is 35 \( \mu m \).
\end{figure}
than induced by dewetting. The surface-induced structure formation of PDLC in the present study is similar to the case of PES-LCD formed by photoenforced stratification.21 However, the average size of LC droplets in our study was $10 \mu m$, which was dictated by the width of Au rings (Figure 1c). This is much smaller than the 500 $\mu m$ boxes used in PES-LCD.21 We expect that by using a lower concentration of PMMA toluene solution, PMMA rings with reduced width and periodicity can be readily obtained.32,33 Thus, smaller LC domains on Au rings would result.

Evolution of LC Domains and Chemical Composition of PDLC on a Chemically Patterned Substrate. The time evolution of the average size (in terms of LC domain area), number, and total area of 5CB droplets on Au rings was quantified using ImageJ software (Figure 3). The initial diameter of the droplets was much less than half of the Au ring width, $d_{Au} (d_{Au} \approx 10 \mu m) (t = t_0 = 0 \text{ min and } t = 191 \text{ min in Figure 2a,b, respectively})$. As time progressed, the droplets on Au rings condensed together and increased successively in size, forming domains of $5-10 \mu m$ in diameter ($t = 501$ and 791 min in Figure 2c,d, respectively). The final size of the domains was determined by the Au ring width ($t = 1492 \text{ min in Figure 2e}$). The number of droplets on the Au rings decreased with time (Figure 3b), and the total area covered by the 5CB droplets on the Au rings increased with time (Figure 3c). It is clear that a longer time was needed for the large 5CB domains on the Au rings to merge (and on the ITO rings to transport to the Au rings) as a result of a longer distance of movement.

The resulting PDLC film was composed of alternating stripes of 5CB-rich and PS-rich phases. To confirm this, the chemical identification of PDLC on the patterned substrate was performed using spatially resolved Raman spectroscopy (Renishaw inVia Raman microscopy, excited with a 488 nm Ar+ laser at 10 mW).
The Raman spectrum of pure 5CB is shown in Figure 4a. The vibrational frequencies of 1607 and 2228 cm\(^{-1}\) correspond to ring stretching from the benzene derivative (doublets) and a CN stretch, respectively. The chemical structure of 5CB is shown in the inset. The CN group in 5CB is unique as compared to PS and possesses a strong Raman cross section. Thus, Raman line scanning was conducted in the direction perpendicular to the Au rings as indicated by a line in the inset (Figure 4b) by focusing on the CN stretch vibrational spectrum in the frequency region from 2210 to 2250 cm\(^{-1}\). The CN stretch peak intensity at 2228 cm\(^{-1}\) along the scanning direction is shown in Figure 4b. The spectra from four different spots on each Au ring and the ITO ring were acquired after 10 s of exposure to the laser beam. The width and periodicity of the Au rings were \(\sim 10\) and \(\sim 20\) \(\mu\)m, respectively, as clearly evident in Figure 4b. The CN stretch intensity difference \(I_{CN, Au}/I_{CN, ITO} = 7\) was consistent with optical microscopy observation where the majority of 5CB was deposited on Au rings (Figures 2 and 3). The low value of the intensity difference \(I_{CN, Au}/I_{CN, ITO}\) may also be partially attributed to the fact that a small amount of 5CB resided in the PS matrix on the ITO rings (i.e., 5CB in the PS-rich phase). We note that FTIR spectroscopy has also been successfully applied to study PDLC formation.\(^{47-49}\)

In summary, we have demonstrated that chemically patterned surface-induced phase separation of PDLC could afford a unique means to control the distribution of LC and organize micrometer-sized LC in a well-ordered fashion in a polymer matrix over a large area with no need for photirradiation. Because of the strong chemical affinity between LC and Au, the LC droplets wet, grow, and coalesce preferentially along the Au rings. The patterns on the substrate were transferred to the PDLC film as a direct consequence of the incompatibility of PS and 5CB, the preferential interaction between 5CB and Au,\(^{43-45}\) and the comparable pattern size with respect to the length of the domain morphology on the homogeneous substrate. The preferential affinity of 5CB to the Au rings induced a surface spinodal wave that suppressed spinodal decomposition of the bulk because of the fact that the thickness of the PDLC film was smaller than the spinodal wavelength, enabling the transfer of surface patterns to the PDLC film in a way similar to the case of polymer blends.\(^{27}\) The film thickness,\(^{23,24,50}\) the molecular weight of the polymer,\(^{26}\) and the variation of width and periodicity\(^{23,27}\) of the Au rings are expected to influence the structure formation of PDLC on the patterned substrate. These experimental parameters are currently under investigation and will be optimized to yield ideal pattern transfers of PDLC.

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**Supporting Information Available:** Digital image and optical micrograph of a PDLC film on the Au ring-patterned ITO substrate and movie of surface-induced structure formation of PDLC on a concentric Au ring-patterned ITO substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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