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Communications

Polymer Structures Templated on the Pattern-forming State of Achiral Nematic Liquid Crystal

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Introduction

Control of polymer network morphology in a host liquid crystal (LC) - especially the spatial distribution and size of the polymer structures - has been a subject of intense interest both for fundamental studies of phase separation in anisotropic media and for practical applications.[1-3] Local morphology (i.e., submicron length scales) mostly depends on the miscibility or compatibility of the component reactive monomer and liquid crystal in the initial mixture.[4] However, the global morphology - in particular the spatial distribution of polymer structure on the micron or larger scale - can be effectively manipulated by holographic or lithographic techniques.[5,6] In our previous reports, we presented a novel method for preparing both spatially and orientationally ordered polymer networks based on the pattern-forming states of cholesteric liquid crystal as templates.[7,8] This templating approach does not require external patterning agencies and overcomes the limitation of the holo- or lithographic methods to photopolymerizable systems.

In this communication, we demonstrate that the templating effect of a nonachiral pattern-forming state formed in a dual-frequency liquid crystal (DFLC). Using a pattern formation in a pure nematic DFLC and photopolymerization of a reactive monomer, we again obtained spatially organized polymer networks. This result extends the flexibility of the templating effect of LC pattern-forming states from ordinary cholesterics to nonchiral LC systems.

Results and Discussion

The mixture consisted of 94.8 wt% of a dual-frequency liquid crystal MLC 2048 (Merk)), 5.0 wt% of reactive monomer RM 257 (Merk), and 0.2 wt% of photoinitiator Irgacure 651 (Ciba additives) were prepared. The use of reactive monomer, RM257, for LC/polymer composite was previously reported.[7,9] After heating these mixtures to the isotropic temperature of the liquid crystal for a short time, the mixture was cooled to room temperature and then filled into LC cells by a capillary action. Standard electro-optic cells, assembled with indium-tin-oxide coated conductive glass substrates and separated with glass sphere spacers, were used in this study. For homogeneous LC alignment with a small pretilt angle, the inner surfaces of the substrates were coated with polyimide alignment layers, which were uniaxially rubbed and assembled at 180° angle with respect to each rub direction, over transparent electrodes.

Various pattern-forming states were obtained by applying an electric field to the mixtures confined in electro-optic cells as previously described in the reference (10). The polarized optical micrograph of one-dimensional pattern-forming state used in our study is shown in Figure 1. The optical texture consists of uniformly spaced stripes running perpendicular to the surface rub direction (indicated by the inset-arrow) in the plane of substrates. The reactive monomer was then photo-polymerized in the pattern-forming state as a reaction medium. For the radical polymerization, the collimated UV light was illuminated with varied intensity and exposure time: (1) 0.04 mW/cm^2 of filtered 365 nm UV light for 3 h (f = 14 kHz/V_p = 10.2 V), (2) 0.4 mW/cm^2 of filtered 365 nm UV light for 1 h (f = 14 kHz/V_p = 10.2 V), and (3) 2.0 mW/cm^2 of filtered 365 nm UV light at for

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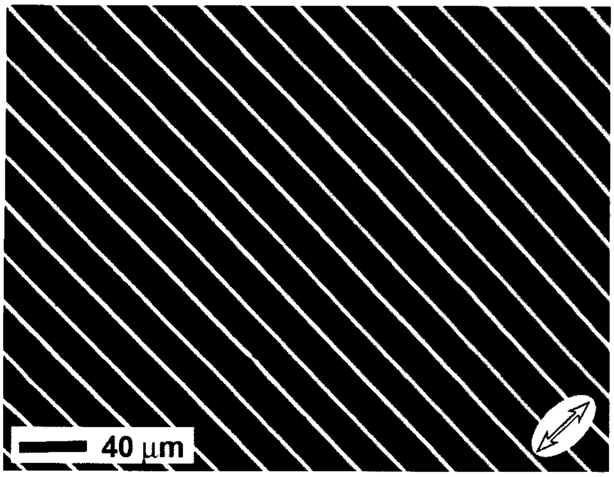

Figure 1. Polarized optical micrograph of the LC pattern-forming state used as a template. The texture was obtained by applying square waveform electric field (f = 14 kHz/V_p = 10.2 V). The surface rub direction is represented by the double-ended arrow.

10 min (f = 14 kHz/V_p = 11.0 V). To examine the network morphology, polarized optical microscopy as well as SEM was used after removal of liquid crystal. The samples were prepared by preferentially dissolving the liquid crystal using a 70/30 v/v mixture of hexane and dichloromethane, with the solvent refreshed seven times over seven days.

It was confirmed using a polarized optical microscopy that for all three samples obtained at different polymerization conditions, a spatial period and local orientational order of the host pattern-forming state are precisely transferred to the polymer networks. The average optical axis of local networks is perpendicular to the stripe (i.e., parallel to the surface rub direction). The SEM images obtained from these samples demonstrate further details of the network morphology as well as spatial pattern formation of the polymer network. Figure 2 shows network morphologies polymerized with a weak UV-light (condition 1). Figure 2(a) formed at the absence of electric field exhibits a nodular *fused-grain* morphology, which shows a long-range orientational order of dense polymer strands. However, no spatial pattern is observed in this case. This can be explained by considering a uniform director orientation parallel to the surface rub direction (denoted by double-ended arrow). Since a non-chiral nematic mixture was confined between homogeneously aligned surfaces and no electric field was applied, only orientational order of the host LC was replicated by the polymer network.[9] It should be noted that the long axis of an individual grain is oriented along the surface rub direction (equivalent to the average optical axis of host LC). Moreover, it was confirmed (by combining this result with a polarized optical micrograph) that the average optical axis coincides with its long axis. As a result, the orientation of grains can be used as a measure of the local director orientation for both liquid crystal host and polymer network.

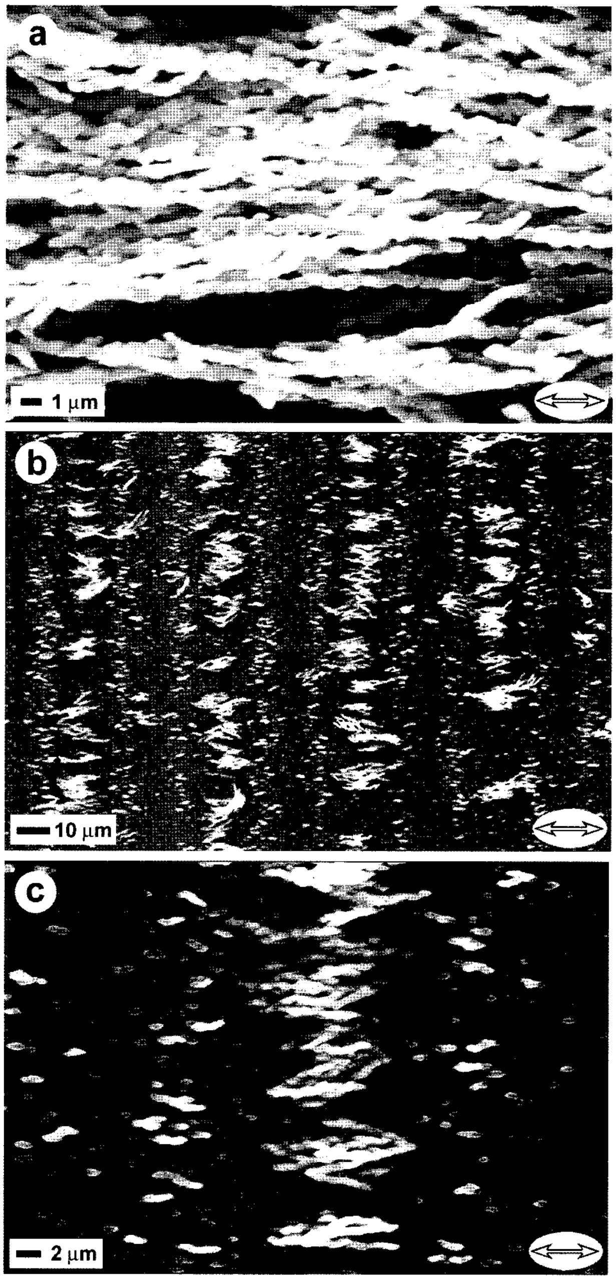

Figure 2. The SEM micrographs of network morphologies formed in (a) homogeneously aligned and (b), (c) the pattern-forming state of the nematic dual frequency LC MLC 2048 using 365 nm UV light (0.04 mW/cm^2 for 3 h). In (a) the polymer strands exhibiting fused-grain morphology run parallel to the optic axis of the host LC (i.e., parallel to the rub direction indicated by the inset arrow). In (b) and (c), the oval particles and nodular strands form a spatial pattern in which the period was accurately templated by the host LC.

To make a comparison, the polymer network formed in the pattern-forming state is shown in Figures 2(b) and 2(c). Although the same *linked-grain* morphology is observed, the periodic pattern is apparent in this case and the period of polymer pattern is equivalent to that in host pattern-forming state. Two weak surface-localized stripes are located in-between strong bulk stripes, consisted of multiple strands of linked-grains, running parallel to the rub direction. Essentially the same structures are observed on both substrates, indicating that the discontinuity of polymer stripes was caused by mechanical stress and split into opposite substrates during the cell opening process. The image viewed at larger magnification (Figure 2(c)) clearly demonstrates that the nodular strands and oval particles on the surface are oriented perpendicular to the stripe in the plane of substrate, accordingly parallel to the rub direction. This strongly indicates that the average director of the pattern-forming state is parallel to its modulation axis (perpendicular to striped domains).

The network formed using a ten times stronger UV radiation (condition 2) shows no significant difference. The grains are slightly better defined in the strands, but general morphology and pattern formation are very similar to previous case. In contrast, the sample irradiated with a fifty times stronger UV light (condition 3), exhibits a very fine grain texture, whose average orientation is again parallel to the surface rub direction (indicated by inset-arrow in Figure 3(a)). The network appears much smoother and grains are less noticeable. The polymer network formed in a patterned LC host consists of strong stripes with a single 40 μm-period. No surface pattern is observed in this case. The fine nodular strands are now bent and forms micro-arches, facing normal to the rub direction. Similar amount of patterned network was also observed on the opposite substrate. In all cases, the period of polymer patterns on the SEM images is doubled compared to the LC template and observed on both substrates. To obtain the same pattern observed by optical microscopy, we can deduce that the polymer stripes anchored on opposite substrates are simply interdigitated.

It is important to notice that the applied voltage, in the third condition, is higher ($V_p = 11.0$ V) than other cases ($V_p = 10.2$ V) at the same frequency. As reported earlier,[10] the modulation intensity of director in the pattern-forming state is very sensitive to the applied electric field. With the increased voltage, the director undulation perpendicular to the stripe domain (primarily bend-mode distortion) is amplified, so that the templated network are significantly bent as seen in Figures 3(b) and 3(c). Consequently, we believe that the spatial distribution of network is caused by the director distortion of the host LC pattern-forming state. As we reported earlier,[7,8] the gradient in elastic distortion of host LC defines a global morphology of the polymer network. On the other hand, the difference in grain size is influenced by the intensity of UV light used for photo-polymerization.[11] The local morphology of polymer networks may also be affected by a monomer structure and its miscibility to the LC host.[4]

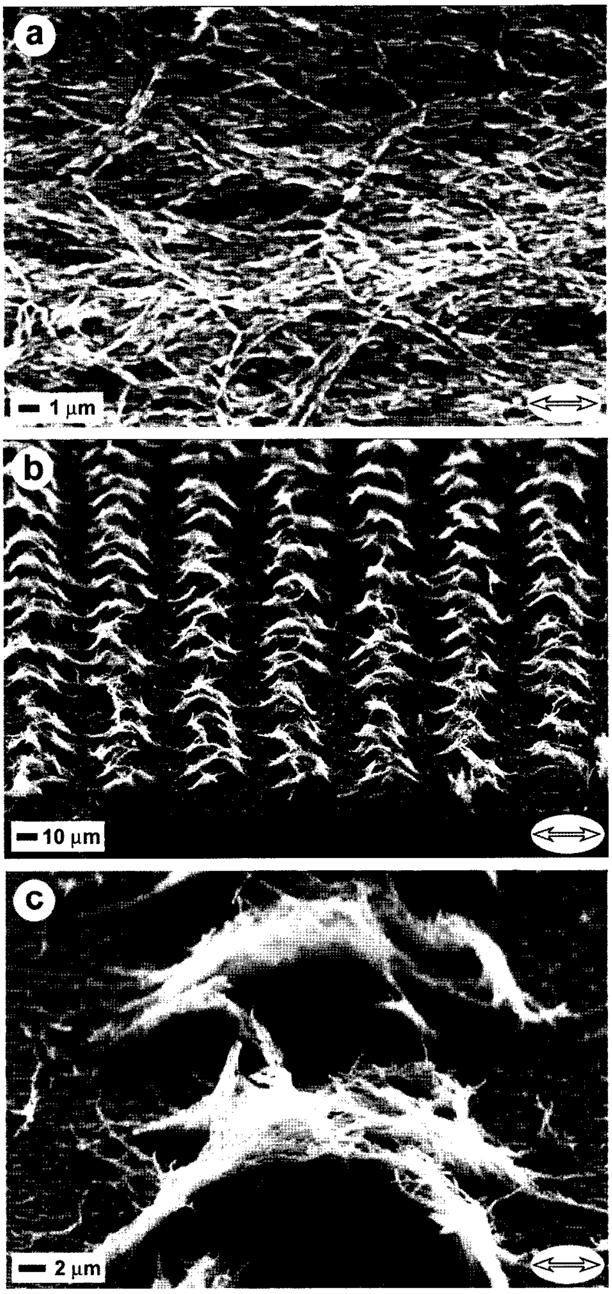

Figure 3. The SEM micrographs of network morphologies formed in (a) homogeneously aligned and (b), (c) the pattern-forming state of the nematic dual frequency LC MLC 2048 using 365 nm UV light (2.0 mW/cm^2 for 10 min). In this case of a strong UV radiation, the grain size is much smaller than that formed in a weak UV intensity. The polymer network (b and c) formed in the pattern-forming state exhibits a spatially organized network structure templated by the host LC.

In conclusion, we have presented examples of polymer network morphologies templated on one-dimensional pattern-forming states of nonchiral liquid crystal mixture. The polymer patterns were obtained by photo-polymerizing a small amount of reactive monomer in the pattern-forming state of host LC, as a reaction medium, which is formed near the inversion frequency for the dielectric anisotropy of a nonchiral "dual frequency" LC material. We have demonstrated that the chirality of the system is not always required for templating polymer networks. Instead, a periodic director distortion and its modulation density are an important factor for the templating effect.

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