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Structure and morphology of polymer-stabilized cholesteric diffraction gratings

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We report a study of polymer network morphology in planar diffraction gratings formed from polymer-stabilized cholesteric liquid crystals. Photopolymerizing a mesogenic monomer yields a regular sawtooth morphology, composed of polymer sheets running at an acute angle between thick, uniformly aligned bundles which reside on the opposing substrates. To explain this morphology and evidence of two grating vectors in the diffraction pattern, we propose a model for the liquid-crystal director where out-of-phase twists at the surfaces gear into an interior twist, which has half the period of the surface twist, via splay distortions running between the substrates. The morphology also changes significantly when a nonmesogenic monomer is substituted or when selectively polarized states of UV radiation are used to cure the polymer. © 2000 American Institute of Physics.

Polymer-stabilized cholesteric liquid-crystal diffraction gratings (PSCDGs) have generated much recent interest as a promising approach to producing on–off electrically switchable, thin-film diffractive optics.1–4 These gratings, formed by stabilizing the “fingerprint” texture of a cholesteric induced in a standard electro-optical cell, can function in either the Bragg or Raman–Nath (phase grating) limits.2,3 They are particularly suited to beam steering/optical routing or sensor protection applications requiring operation in transmission, high efficiency, and millisecond (or less) response to low voltages. However, the specific morphology of the polymer network, and its precise connection to the electro-optical properties of the composite system, remain open issues. In this letter, we present the detailed study of the network morphology in PSCDGs, and infer a model for the director configuration of the host liquid crystal in which a combination of twist and splay distortions produces a structure with different surface and bulk grating vectors. We also investigate the effect of monomer mesogenicity on the network morphology and on the observed diffraction, and variations in these properties due to selective polarization in the UV-initiated polymer cure.

For a mesogenic monomer, we find using scanning electron microscopy (SEM) that the cured network is anchored on the cell substrates by a regular array of thick, uniformly aligned polymer bundles, which are connected by a sawtooth pattern of less dense walls alternating between the substrates. The bundles have substantial optical birefringence, confirming a high degree of anisotropy and a high density of polymer. The overall network morphology, and features observed in the optical diffraction pattern, are consistent with a liquid-crystal director structure in which the expected cholesteric twist (optical pitch \( P \)) running parallel to the substrates in the cell interior is complemented by twisted surface regions with optical pitch \( 2P \). In addition, we deduce that the surface twists are phase shifted by \( P \) with respect to each other. The polymer structure also depends on the state of UV polarization. When exposed anisotropically to polarized UV at a wavelength corresponding to the maximum dichroic anisotropy of the host liquid crystal, the sawtooth walls develop large holes, and the residual fibril structures are thicker. For a nonmesogenic monomer, although the polymer network still shows a regular pattern of phase separation, the sawtooth cross section has basically collapsed into a series of ridges, and there is dramatic structural asymmetry between the two surfaces. The bare network is also substantially less birefringent.

Our samples were mixtures of the nematic liquid-crystal BL006 (Merck), chiral dopant R-1011 (Merck), and the photoinitiator Irgacure 651 (Ciba Additive Corp.). We used two reactive monomers, nonmesogenic 1,6-hexanediol diacylate HDDA (Aldrich) and the nematic mesogen RM257 (Merck). The sample components were mixed in the following weight ratio: BL006 (94.35), R-1011 (0.40), monomer (5.00), and photoinitiator (0.25). The mixtures were filled into 10-\( \mu \)m-thick antiparallel rubbed commercial electro-optic cells. The inset at the top of Fig. 1 shows the measured dichroic ratio for the undoped nematic mixture. After filling the cells with cholesteric mixtures, fingerprint textures were obtained by applying an electric field (typically, 0.4 V/\( \mu \)m at 1 kHz).2–4 The planar grating textures were then stabilized by photopolymerizing the monomer using 353 nm (peak dichroic ratio) filtered light from a collimated Xe lamp. The polarization of the UV light was carefully controlled to be either purely parallel (PA) or perpendicular (PE) to the helical axis of the cholesteric (equivalent to the grating vector), providing either a uniform, isotropic (PA polarization) or periodic, anisotropic (PE polarization) absorption profile across the sample. Diffraction patterns from the samples were recorded using normally incident PE HeNe laser light and a charge-coupled-device detector. No analyzer was used. To facilitate both optical and SEM imaging of the bare polymer network, we evacuated the liquid crystal from the stabilized samples by soaking the cell in a hexane/dichloromethane co-solvent (70:30 v/v).

Figure 1 displays the diffraction patterns obtained from gratings stabilized by HDDA and RM257 networks, for both PA- and PE-polarized UV cure. Diffraction orders corre-
responding to harmonics of an optical periodicity $P = 5 \mu m$, equal to the grating spacing obtained from a direct image of the sample interior, are labeled with integers. In addition, half-integer peaks, corresponding to an optical period $2P = 10 \mu m$, are observed. The relative intensity of the latter is sensitive to the UV cure polarization in the case of nonmesogenic HDDA, and is basically insensitive for samples containing RM257. Specifically, we find that the ratio of integrated half order to total diffracted intensity is 0.30 for PA-polarized UV and 0.25 for PE polarization in the RM257 samples, compared to 0.40 $\sim$PA$\sim$ and 0.12 $\sim$PE$\sim$ in the HDDA samples. In addition, as shown, a small applied field ($\sim 1 V/\mu m$) abruptly and sharply reduces the amplitude of the half-order peaks, leaving a grating structure dominated by a single period $P$. These results suggest that the grating contains a composite structure, with distinct optical periods $P$ and $2P$.

To confirm this inference, we also performed real-space imaging of the bare polymer network, using polarized light microscopy and SEM. Figure 2 shows results with polarized light, with the focus carefully adjusted to a position just below the top substrate. As revealed in Fig. 2(a), anisotropically exposed RM257 (PE polarization) produces a strongly birefringent, regular stripe texture of network-rich domains. The domain spacing is $P = 5 \mu m$. A similar pattern, with greatly reduced birefringence, is found for the case of anisotropically exposed HDDA [Fig. 2(b)]. By careful examination, one discerns that the true period of the structure is $2P = 10 \mu m$. This result is particularly manifest in the HDDA picture, where one can see clearly that the image intensity of the individual domains alternates. Moreover, since we find that the position of the more and less intense domains shifts laterally by $P$ (or, equivalently, interchanges) as the focus is shifted to the bottom substrate, we conclude that the $2P$ structures are anchored at opposite surfaces with a $P$ phase shift between them.

Representative SEM data obtained on multiple samples, and a model for the PSCDG structure deduced from them, are presented in Fig. 3. In Fig. 3(a) the polymer network for mesogenic RM257 (and for PA-polarized UV exposure) zigzags between the cell surfaces in a sawtooth pattern; the magnified inset shows that the region under a sawtooth is largely void of polymer. The mainframe of the structure is composed of densely packed polymer bundles, localized and uniformly spaced (period $2P = 10 \mu m$) at the cell surfaces, and running parallel to the rubbing direction. These bundles are connected between opposite surfaces by homogeneous sheets composed of fine polymer fibrils. The sheets make an acute angle with respect to the surfaces, which is consistent with a $P$ phase shift of the structure between the surfaces. Knowing the angle at which the SEM profile was taken with respect to the substrate, and the period of the sawtooth structure, we are able to confirm that the height of the structure is indeed consistent with the $10 \mu m$ cell gap. Also note that on a cross section taken halfway between the substrates, the period of the polymer domains is $half$ of the surface value. In Fig. 3(b), we observe that PE-polarized UV exposure reduces the homogeneity and density of fibrils in the connecting sheets of the sawtooth structure; there are noticeable voids in
the sheets, and the residual fibrils are thicker and less homogeneously aligned.

To explain these observations, we propose the model in Fig. 3(c). The central feature of the model is that the optical pitch of the twisted director changes from a value \( P \) in the cell center to twice this value (2\( \text{P} \)) at the surfaces. The surface twists are phase shifted by \( \text{P} \) with respect to each other and are efficiently connected by splay distortions across the cell, as indicated. The shaded regions show how this structure can template the growth of polymer domains in the observed sawtooth profile, and thereby lead to stabilization of both \( \pi \) (surface) and 2\( \pi \) (interior) director twist. In the case of mesogenic RM257, we conjecture that the monomer molecules prior to photopolymerization are preferentially localized in regions through which distortion of the liquid-crystal director is minimal [e.g., the zig-zag shading indicated in Fig. 3(c)]. Since in zero field the liquid-crystal director lies in the plane of the substrates, and since we operated at the minimum field required to distort this orientation and produce a fingerprint texture, it is reasonable that, as shown, these regions possess average planar orientation. For this configuration, the regions of minimum UV absorption for PE polarization would lie between the polymer domains shown schematically in Fig. 3(a). Then, phase separation processes driven by UV intensity gradients and the “mesogenic” potential of the host could compete in localizing the polymer network, degrading the homogeneous sawtooth structure in Fig. 3(a) and producing the structure in Fig. 3(b). Alternatively (or perhaps simultaneously), enhanced polymer growth along the direction of UV polarization may contribute to the morphological differences between Figs. 3(a) and 3(b). In this case, PE polarization (along the helical axis) would promote thicker bundles in the mainframe and fibrils running perpendicular to the mainframe within the sawtooth faces [as in Fig. 3(a)], while PE polarization would produce thinner bundles and more heterogeneity in the fibril orientation [effects apparent in Fig. 3(b)]. Finally, we point out that localization of the mainframe in regions where the liquid-crystal orientation is homeotropic (obtained by uniformly rotating the director in Fig. 3(c) by 90° into the page) does not alter the essential aspect of our scenario for the origin of the sawtooth morphology.

Figure 3 also shows the network profile for PE-polarized exposure of HDDA. Although patterned phase separation is still apparent, the basic sawtooth profile observed for RM257 appears considerably weakened and partially collapsed into a more ridge-like structure on the substrate farthest from the UV source [Fig. 3(d)], and barely visible beneath a thick layer of isotropically distributed polymer on the near surface [Fig. 3(e)]. This indicates that the nonmesogenic monomer is relatively free to diffuse toward the surface on which the UV is incident, and that phase separation induced by gradients in host orientational order near this surface is much less effective for HDDA than for RM257. We find that the near-surface templating is even weaker for the case of PA-exposed HDDA, but the morphology on the far surface is similar to the PE case. However, as noted in Fig. 1(a), there is a significant difference in the diffraction patterns for the two cases. Perhaps some morphological features are lost in preparation of the samples for SEM or are too subtle to pick out.

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