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Morphology-dependent switching of polymer-stabilized cholesteric gratings

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The use of a fingerprint texture of a cholesteric liquid crystal is demonstrated as a template to direct the formation of periodically ordered micro-size polymer walls. The morphology–property correlation of polymer-stabilized cholesteric gratings (PSCGs) was established for mesogenic and non-mesogenic reactive monomers. These PSCGs are suitable for laser beam steering, control of fibre optic signal and dynamic focus lenses.

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1. Introduction

In a cholesteric liquid crystal a periodically modulated fingerprint texture can be created by the application of an electric field parallel to the helical axis of an initially planar-aligned sample [1]. Using a low concentration of polymer, a uniform, uniaxial grating can be stabilized by blanket UV exposure in the presence of an applied field. Photo-induced polymerization results in the formation of a sub-micron polymer structure [2–4]. We have already demonstrated that these gratings have promising electro-optical properties such as low switching voltage, fast switching and moderate diffraction efficiency [5]. Given these interesting properties and promising performance, a full understanding of the relationship between the morphology of the polymer network and electro-optical properties will assist in the development of high efficiency diffraction gratings.

We have now studied the structure and morphology of polymer-stabilized cholesteric gratings (PSCGs) in which the reactive monomers are polymerized by blanket UV exposure. Using three diacrylate-based monomers, the nematic monomer RM257 (1,4-bis[4-(acryloyloxy)-propoxybenzoyloxy]-2-methylbenzene) and the non-mesogenic monomers 4,4′-bis[6-(acryloyloxy)-hexyloxyl]-1,1′-biphenylene (BAB6) and tri(ethylene glycol) dimethacrylate (TEGDM) (see figure 1), we established the morphology–switching correlation between the polymer network structure and the electro-optical properties of the PSCGs. Morphological and optical microscopy studies indicate that the mesogenic monomer produces more uniform grating domains than do those prepared from non-mesogenic monomers. We demonstrate that these gratings can be stabilized for use in the absence of an applied field. By varying the chiral dopant concentration, the periodicity of the grating can be tuned from 30 to 1.7 μm in a cell with a cell gap of 10 μm. The grating can be switched between a grating-on state and a grating-off state by the application of a moderate field (typically 3–5 V μm^{-1}). Furthermore, we find that the electro-optical properties of these gratings are monomer-dependent and monomer concentration-dependent. The presence of polymer network also significantly improves diffraction efficiencies over those reported for pure cholesteric liquid crystals [6].

2. Experimental

Polymer-stabilized cholesteric liquid crystals were prepared from homogeneous mixtures of the commercial nematic liquid crystal E48 (E. Merck), the commercial chiral dopant R-1011 (E. Merck), the reactive monomers RM257, BAB6 and TEGDM, and the photo-initiator Irgacure 651 (Ciba Additive, 2,2-dimethoxy-2-phenyl-acetophenone) at weight percentages of 94.4% E48, 0.4% R-1011, 5.0% reactive monomer, and 0.2% photo-initiator. The mixtures were loaded in the isotropic phase into commercial liquid crystal cells whose inside surfaces were treated with an indium tin oxide conducting layer and a rubbed polyimide film for homogeneous (planar) alignment of the liquid crystal. At room temperature, the cholesteric helix was oriented perpendicular to the substrates, as expected for planar surface anchoring conditions. When an a.c. electric field applied along the helical axis exceeded a threshold voltage (0.5 V μm^{-1}), the helix was switched to reorient parallel to the substrates and perpendicular to the rubbing direction, yielding a uniform grating in the plane of the substrates.

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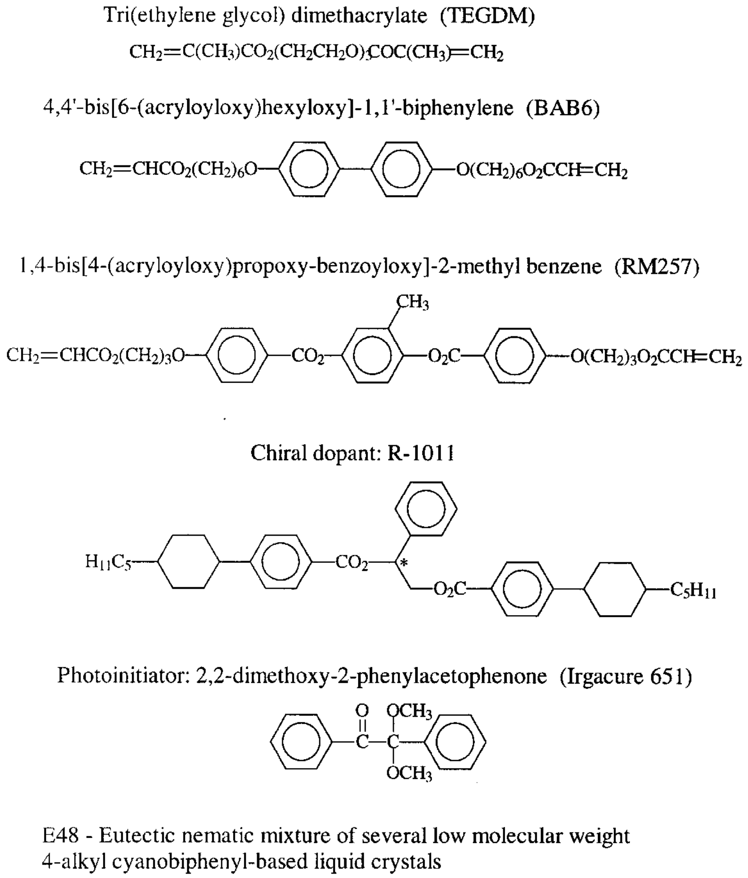

Figure 1. Structures of the chemicals used in this study.

The grating was then stabilized by exposing it to UV radiation from a metal halide lamp ($2\,\mathrm{J\,cm^{-2}}$) in the presence of the electric field.

3. Results and discussion

Figure 2 displays the optical micrographs of polymer networks after evacuating the liquid crystal, and the corresponding SEM photographs of network morphology obtained from gratings stabilized by RM257 (*a*), BAB6 (*b*) and TEGDM (*c*). For the mesogenic monomer RM257, the grating spacing is about 10 μm. Although collapse of the bare polymer networks might be expected, the SEM photographs suggest that sample preparation for SEM does not significantly affect the morphology. The grating structure is remarkably uniform and the spacing is retained. Figure 2 (*b*) shows a grating formed from monomer BAB6. In the case of the non-mesogenic monomers, the grating structure is a more heterogeneous structure in the grating plane; thicker and more fragmented (perhaps damaged during the sample preparation) grating walls are observed. For the same concentration, the thicker walls imply an increased spacing between domains. Figure 1 (*c*) shows the results for gratings formed with TEGDM; comparison with the grating of BAB6 indicates that the periodic optical structure of TEGDM became more distorted. Thin fibres that link adjacent grating walls are observed in all three samples.

To explain the thicker domain walls and larger periodicity of the non-mesogenic network, we may consider the detailed director orientation within the cell. Because of the director twist associated with the cholesteric helix, there will be periodic regions of the cell where the bulk director orientation matches the planar boundary conditions and regions where the bulk and surface orientations compete. In the latter, a splay distortion of the director will propagate between the planar orientations at the two surfaces. Thus, running parallel to the grating direction, there will be a spatial variation of the nematic order averaged over the cell thickness. A mesogenic monomer would presumably have a stronger tendency to nucleate a network in the domains of uniform direction orientation. On the other hand, non-mesogenic monomers would not have the same solubility as the nematic monomer in liquid crystal and could therefore form thicker walled networks, which penetrate into the regions where the director is distorted between the surfaces. For fixed monomer concentration, this would both increase the spacing between network-rich domains and promote a

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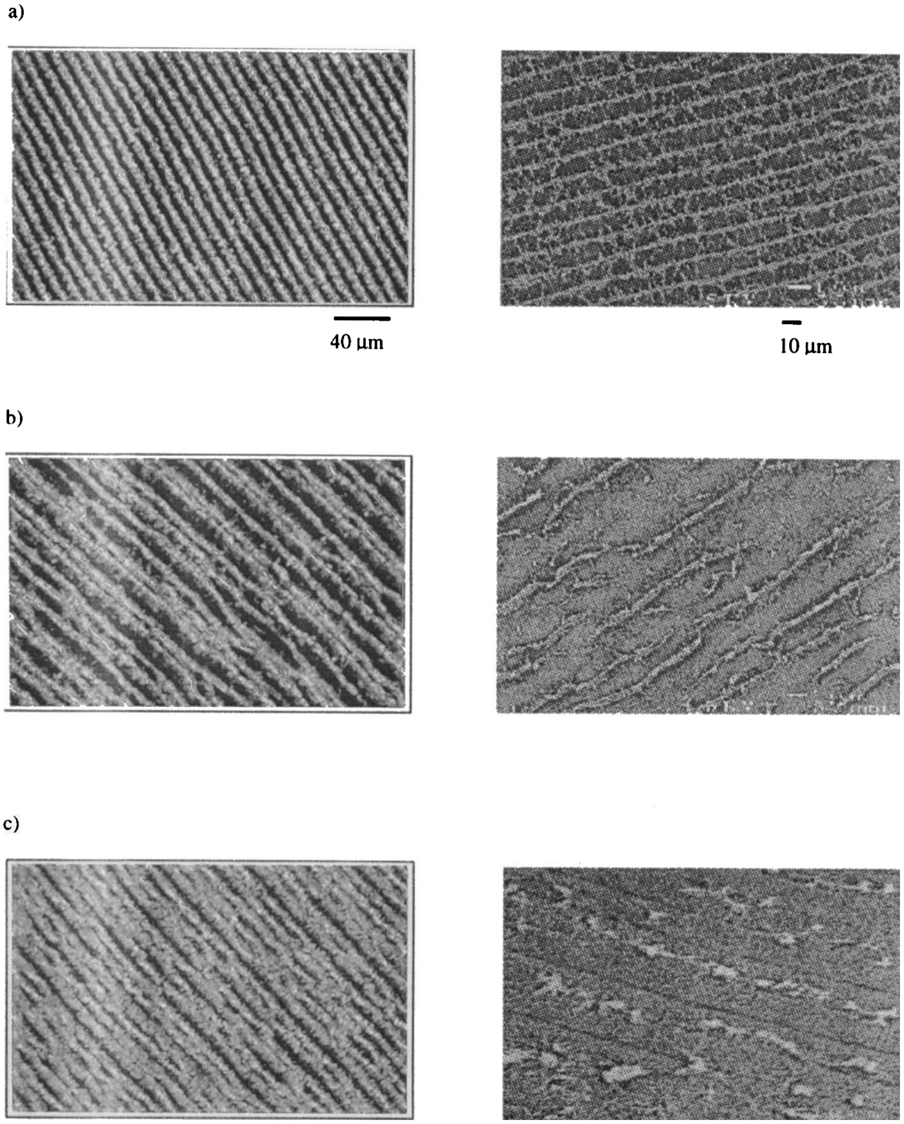

Figure 2. In the lefthand panels, optical micrographs of the PSCGs of RM257 (*a*), BAB6 (*b*) and TEGDM (*c*), after evacuating the liquid crystals, are presented. The corresponding SEM photographs of polymer morphology are shown in the righthand panels.

more fragmented structure within the grating planes. Perhaps one could develop finer control over the composite grating morphology by more systematic or time-dependent manipulation of the director orientation and by variation of the polymerization conditions.

Figure 3 shows the voltage dependences of the diffraction intensities for the zeroth order of all the PSCGs. The plots indicate the dynamic response of PSCGs in response to an applied square wave voltage from grating-off state to grating-on state, with the amplitude and offset from zero optimized for maximum contrast between the off and on states. The vertical axis is the intensity of undiffracted laser light incident normally on the grating. No analyser is used for the transmitted light. In general, both fast, presumably liquid crystal-dominated, and slow, presumably polymer-dominated, responses are observed. However, the response times and contrast ratios vary significantly for the three monomers. Interestingly, the PSCG prepared from non-mesogenic monomer TEGDM displays the highest contrast ratio of ~6:1 between the off and on states. The contrast is somewhat lower (~4.4:1) for a PSCG prepared from mesogenic monomer RM257, but the dynamic response is dominated by the fast component (~1.5 ms time constant) and is the fastest among the three PSCGs. This fast response between the two states suggests both minimum dynamic distortion of the network and strong anchoring of the liquid crystal to the network structure. PSCGs prepared from BAB6 showed intermediate contrast ratios and response times.

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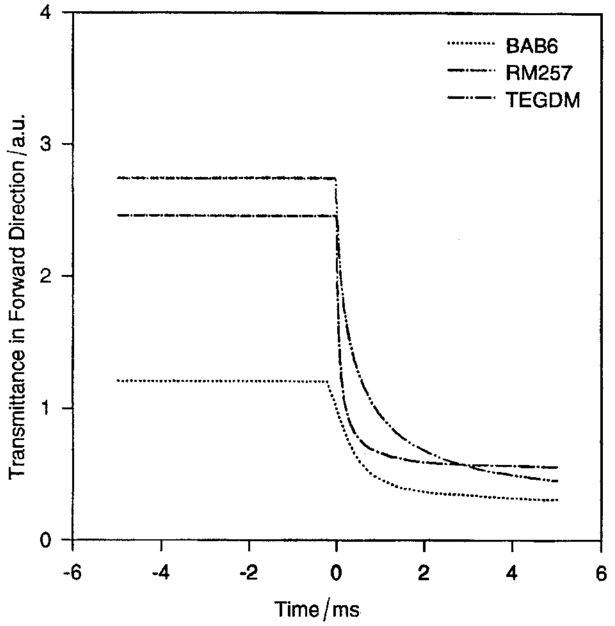

Figure 3. The dynamic response of PSCGs prepared from three different monomers in response to an applied square wave voltage from grating-off state to grating-on state, with the amplitude and offset from zero optimized for maximum contrast between off and on states.

Figure 4 shows the monomer concentration dependence of diffraction patterns obtained from gratings stabilized by 3 and 5 wt % of RM257. For an 0.4 wt % chiral dopant concentration, diffraction orders corresponding to harmonics of an optical periodicity of 5 μm were obtained. Moreover, lower intensity peaks corresponding to an optical period of 10 μm are also observed. These results suggest that the grating contains composite structures of liquid crystal and polymer micro-wall. Figures 4(*a*) and 4(*b*) show the first order diffraction pattern of a 3 wt % RM257 sample switched between the grating-on and grating-off state (2.0 V μm^{-1}). The intensity of first order peaks was reduced upon the application of electric field. As shown in figures 4(*c*) and 4(*d*), higher monomer concentration (5 wt % of RM257) results in a multiple order diffraction pattern switched between grating-off and grating-on states (5.5 V μm^{-1}). The multiple order diffraction pattern abruptly reduces the intensity amplitude in the presence of the electric field.

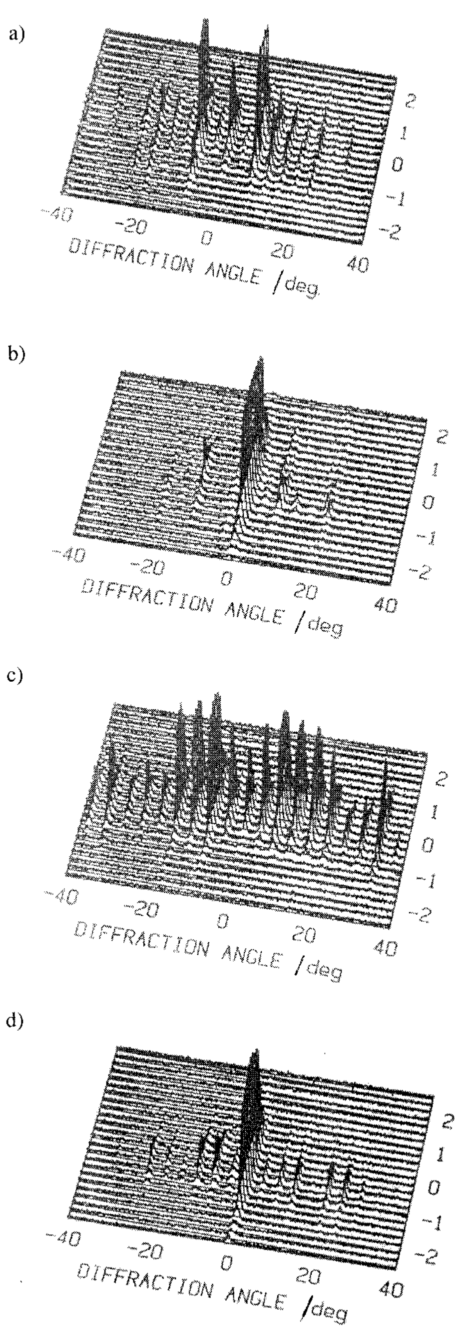

Figure 4. Diffraction patterns of PSCGs at zero applied field, prepared from 3 wt % RM257 (*a*) and 5 wt % RM257 (*c*), and the diffraction patterns of the PSDGs at 2 V μm^{-1} (3 wt % RM257) (*b*) and 5.5 V μm^{-1} (5 wt % RM257) (*d*).

4. Summary

We have demonstrated the use of a cholesteric liquid crystal fingerprint texture as a template to direct the formation of periodically ordered micro-size polymer walls. The morphology–property correlation of PSCGs was established for mesogenic and non-mesogenic reactive monomers. The dynamic of the electro-optical response of the PSCGs studied is around 1–4 ms. First order and multiple order diffraction pattern of PSCGs were obtained by varying the monomer concentration. These PSCGs are suitable for optical beam steering and directed energy control devices.

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