

Electro-optic response and switchable Bragg diffraction for liquid crystals in colloid-templated materials

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We report optical switching studies on nematic liquid crystal incorporated into structures based on self-assembled colloids. We compare the electro-optic responses of liquid crystal imbibed into colloid-templated polymers, liquid crystal imbibed in the interstitial space of colloid crystals, and conventional polymer-dispersed liquid crystals. We characterize the Bragg diffraction of our templated liquid-crystal/polymer composites as a function of electric field and measure switching times. The response of liquid crystal in connected networks differs qualitatively from that of liquid crystal in isolated cavities.

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Photonic crystals of self-assembled colloids have recently generated great interest in the scientific community [1–5]. With suitable periodicities, symmetries, and dielectric contrasts, photonic crystals can exhibit stop bands or full band gaps at optical or near-infrared wavelengths [6,7], making them attractive for applications such as optical switches, filters, and waveguides. By incorporating adjustable dielectric materials, band-gap control or beam switching can be achieved. For example, stop-band shifts have been demonstrated by filling colloidal crystals or crystal replicas with organic solvents [8,9]. Alternately, thermally induced refractive index changes can produce switchable diffraction in self-assembled colloidal hydrogels [10].

Liquid crystals are attractive candidates for incorporation into colloid-templated structures because they exhibit large optical anisotropy, and they can be tuned by applied fields or temperature variation. Indeed, it has been proposed that liquid crystals can alter the photonic band gap [11]. Liquid crystals have been imbibed into the interstitial space of close-packed colloids. Stop-band shifts can then be induced by thermally [9,12] or electrically [12] altering the effective refractive index of the liquid crystal (LC).

We have recently demonstrated the first three-dimensional, electrically switchable Bragg diffraction, utilizing liquid crystal in colloid-based structures [13]. In this paper we study the diffraction from colloid-templated, liquid-crystal filled polymers as a function of electric field. We contrast the electro-optical response of our templated structures against colloid crystals with LC in interstitial cavities and with conventional polymer-dispersed liquid crystals (PDLCs) [14]. We observe a shift toward higher electric fields as well as unexpectedly short relaxation times in the templated samples. Apparently, it is energetically more costly to distort the complex liquid-crystal director pattern in highly connected templated cavities than in isolated, PDLC-like droplets.

We fabricated two classes of colloid-templated samples for our studies. In the first case, a 10- μm -thick flow cell

[5,12] was employed to create crystals of 1.6- μm -diameter SiO_2 colloid (Duke Scientific, CA) between indium-tin-oxide (ITO)-coated glass slides. After drying, the colloid was imbibed with nematic liquid crystal (TL205 [15], obtained from E. M. Merck/EM Industries, NY). We refer to this type of structure as “reverse” filled. In the second case, a crystal was formed by sedimenting the colloid onto a glass substrate. Subsequent drying, filling, and etching [13] created a connected network of spherical cavities in polymer (Norland Optical Adhesive 73, Norland, NJ). The templated polymer was imbibed with liquid crystal and sandwiched between glass slides with transparent electrodes (ITO). The electrode spacing of $\sim 25 \mu\text{m}$ was verified by micrometer measurements and confocal microscopy. We refer to this structure type as “direct” filled.

Our PDLCs were created using polymerization-induced phase separation [14]. In a PDLC, liquid crystal is trapped in micron-sized drops within a polymer matrix. Due to the index mismatch between polymer and unaligned liquid crystal, PDLCs are highly scattering in the absence of an applied field. An applied voltage of $\sim 1 \text{ V}/\mu\text{m}$ reorients the LC director pattern in the droplets. The consequent near index match between liquid crystal and polymer switches the state of the PDLC from scattering to transparent. We utilized the same LC/polymer combinations to make PDLCs and direct samples. High LC volume fractions (55–80%) and appropriate UV curing intensities allowed us to create PDLCs with droplet sizes in the (1–2)- μm range [16,17], as confirmed by optical microscopy. The similar cavity sizes and materials facilitate meaningful comparisons between direct and PDLC samples.

Optical transmission measurements were performed using 633-nm laser light normally incident onto the sample cells. For reverse and direct samples, this meant light was incident perpendicular to planes of close-packed spheres or cavities, respectively. A mechanical chopper, photodetector, and lock-in amplifier were used to measure transmission as a function of sinusoidal applied field (100 Hz), with detector collection aperture $\sim 1^\circ$ for straight-through transmission and $\sim 4^\circ$ for the diffraction spots. The beam was focused to $\sim 25 \mu\text{m}$ diameter to study zero- and first-order transmitted diffraction intensities.

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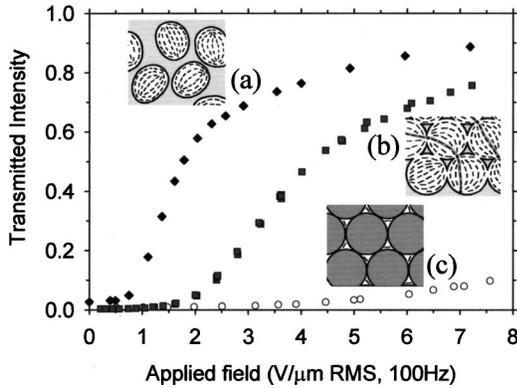


FIG. 1. Plot of normalized transmission intensity vs applied field for three sample categories: (a) PDLC (TL205 liquid crystal, Norland 73 polymer); (b) direct (1.6- μm -templated Norland 73, TL205 filled); (c) reverse (TL205 in 1.6- μm -diameter silica colloid crystal). Transmission has been corrected for interface losses. The different arrangements of liquid-crystal molecules within isolated (a) vs connected (b) cavities are indicated qualitatively by the insets; (c) indicates liquid crystal within interstitial space of a colloid crystal. In (b), the gray lines emphasize some possible disclination lines threading through the cavities.

In Fig. 1 we show transmission data as a function of applied field for all sample categories [18]. The transmission increases with applied field, as the molecules reorient to bring the effective LC refractive index closer to that of the host [19]. The response of the PDLC agrees well with previously reported measurements on similar material combinations [16,17]. We consider in turn the reverse and direct samples.

The response of the reverse sample is by far the weakest, with transmission increasing only a few percent at the highest fields. This observation is consistent with recent work by Kang *et al.* [12], who found that very high fields (≥ 25 V/ μm) were required to achieve significant stop-band shift in LC-imbibed, 200-nm-diameter silica colloid crystals. The weak response was attributed to LC confinement in a constricted interstitial geometry, creating a network of pinned disclination lines, and giving a high surface area to volume ratio. Both of these factors contribute to increase the reorientation field and to reduce the LC volume responding at given voltage, explaining the small transmission changes we see.

The direct samples have higher thresholds than the PDLC, but approach comparable transparency at larger fields. The shift to higher thresholds is surprising, since the conventional switching picture for liquid-crystal droplets predicts comparable or reduced switching voltages for these samples [13].

Figure 2 presents diffraction intensities for both zero- and first orders with increasing field applied to the direct samples. The inset shows a photograph of a typical diffraction pattern, with the threefold symmetry attesting to the fcc, three-dimensional stacking order of the close-packed planes within the probed region [13]. At zero fields, we observe a diffuse scatter similar to PDLC samples, arising from the unaligned highly birefringent LC medium and disorder/defect contributions. As voltage increases, the zero-order in-

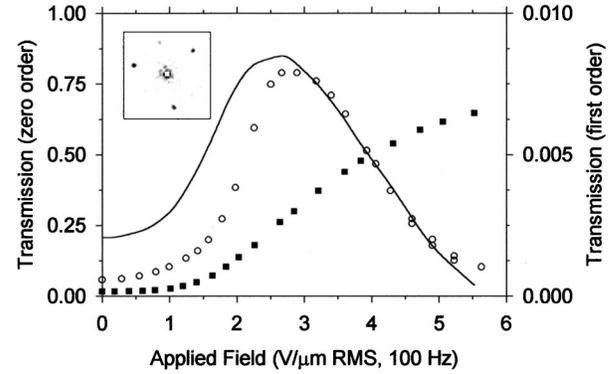


FIG. 2. Transmission vs applied field for zero- and first-order diffraction peaks in a direct sample (1.6- μm colloid-templated Norland 73, filled with TL205 liquid crystal). The curve is a single scattering prediction based on the measured transmission; it reproduces well the observed first-order diffraction maximum. The inset shows a corresponding photograph of the three-fold symmetric diffraction pattern; the zero-order position is blocked by a beam stop.

tensity rises monotonically, analogous to a PDLC but with higher threshold. The first-order diffraction intensity also increases initially, as the LC alignment reduces diffuse scatter. At higher fields, the improving index match continuously decreases the diffractive contrast of the LC-filled cavity lattice. These competing trends combine to produce a clear maximum in first-order diffraction intensity. Such a diffraction maximum can be very useful for light beam switching devices, creating three distinct states: closed, diffractive, and transparent. The low switching field of ~ 2.5 V/ μm is in a range that would be useful for applications.

The diffracted intensity can be quantitatively predicted from the measured extinction of the forward beam. According to Lambert-Beer's law, the transmission through a sample of thickness L is $I/I_0 = \exp(-L/l)$, where I_0 and I are the incident and transmitted intensities, $l = (n\sigma)^{-1}$ is the mean free path, and n is the density of scatterers. The optical extinction cross section $\sigma = \sigma_{\text{periodic}} + \sigma_{\text{random}}$ has two contributions: diffraction and random scattering from defects in the matrix or liquid-crystal director pattern. In single scattering approximation, the diffraction peak intensity will be $I_0 n \sigma_{\text{diff}} L$, where σ_{diff} is a diffraction cross section. Because of their common diffraction origin, σ_{periodic} and σ_{diff} will have similar refractive index dependence and the ratio $\sigma_{\text{diff}}/\sigma_{\text{periodic}}$ will be nearly a constant. Taking into account that the diffracted light also experiences extinction by a factor I/I_0 , we can then approximate the diffracted intensity as $(\sigma_{\text{diff}}/\sigma_{\text{periodic}}) I \ln(CI_0/L)$, with $C = \exp(-n\sigma_{\text{random}}L)$. The corresponding curve is plotted in Fig. 2. It reproduces the observed diffraction maximum, and accurately traces the intensity at high fields. At low fields, the unaligned liquid crystal increases the random scattering cross section σ_{random} . Indeed, the measured intensity is overestimated, showing the character of the scattering changes as the field is lowered.

The connectivity of the liquid-crystal cavity network has consequences for the switching times. We have measured the switching times of our direct and PDLC structures, using an

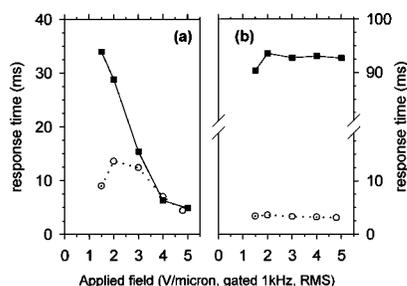


FIG. 3. Measured rise (a) and fall (b) times. Solid symbols are for a PDLC (TL205 liquid crystal, PN393 polymer, $\sim 2\text{-}\mu\text{m}$ LC droplets); open symbols are for a direct sample (TL205 in PN393 polymer, with $1.6\text{-}\mu\text{m}$ colloid-templated cavities). Rise times are measured from turn on to 90% of the asymptotic photodetector signal level. Fall times are measured from turn off to the 10% level of asymptotic signal.

amplitude-modulated high frequency sinusoidal voltage [17,20], photodetector, and digital oscilloscope.

In conventional PDLCs, fall times typically exceed rise times, since relaxation is driven only by elastic energy, with no electric field. The fall time is proportional to $R^2/(L^2 - 1)$, where R is a characteristic size (semimajor droplet axis) and L reflects droplet shape anisotropy (semimajor/semiminor axis ratio). This model predicts that isolated, spherical liquid-crystal droplets should have anomalously long fall times [14,21].

Figure 3 provides a comparison of rise and fall times for various applied electric fields for both the PDLC and direct structures. For the PDLC, the shorter rise vs fall times agree

with expectations. By contrast, our direct samples, which have spherical cavities as their constituent building blocks, exhibit a rapid relaxation, faster than corresponding rise times, and in contradiction to the prediction above. Figure 3(b) also shows a notable difference between the sample categories, namely, significantly shorter fall times for direct vs PDLC structures. These data are an indication of LC domain connectivity; elastic energy built up within an interconnected director/defect configuration under applied field could significantly exceed the elastic energy in a collection of independent, bipolar LC droplets, and, therefore, drive a faster relaxation response.

In summary, we have characterized the electric field response of three-dimensional, switchable transmission Bragg diffraction obtained from liquid crystal within colloid-templated polymer structures. We observe contrasting trends in intensity vs applied field for zero- and first-order diffraction. We have compared our direct samples against LC imbibed into interstitial spaces of colloid crystals, and against conventional PDLCs. Switching times for the templated samples differ from the expected response for liquid crystal within isolated spherical PDLC droplets. A complex director configuration for liquid crystal distributed in a connected network of spherical cavities may give rise to these differences.

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 [15] TL205 is a multicomponent mixture, exhibiting a nematic phase at room temperature. In a simplified picture, the constituent TL205 molecules can be thought of as ~ 30 Å-long organic rods. The characteristic refractive indices are $n_o = 1.53$ along the short molecular axes, and $n_e = 1.75$ along the long axis (Merck data). TL205 has a positive dielectric anisotropy, and will undergo molecular long axis alignment along an applied electric field.
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 [18] Results similar to those in Fig. 1 have also been obtained for other material combinations, such as TL205 in PN393 (E. M. Merck) polymer.
 [19] For the PDLC and direct samples, index match is possible at high fields ($n = 1.56$ for Norland 73); for the reverse sample (silica $n = 1.45$), complete index match cannot be attained.
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