Switchable Bragg diffraction from liquid crystal in colloid-templated structures

P. Mach[1,2], P. Wiltzius[2], M. Megens[2], D. A. Weitz[3], Keng-hui Lin[1], T. C. Lubensky[1] and A. G. Yodh[1]

[1] *Department of Physics and Astronomy, University of Pennsylvania*
Philadelphia, PA 19104-6396, USA
[2] *Bell Laboratories, Lucent Technologies - Murray Hill, NJ 07974, USA*
[3] *Physics Department and DEAS, Harvard University - Cambridge, MA 02138, USA*

Abstract. – We have incorporated nematic liquid crystal into periodic, polymer host structures templated from self-assembled colloids. Using these composite materials, we demonstrate the first electrically switchable three-dimensional Bragg diffraction. The switchable beam deflection is potentially useful for non-mechanical beam steering and optical beam splitting devices. We compare the electro-optic response of our templated liquid-crystal/polymer composites with conventional polymer-dispersed liquid crystals (PDLCs). Our data reveal a qualitatively different and faster response for liquid crystal distributed within a connected cavity network, as compared to isolated liquid-crystal droplets within a polymer matrix.

Rapid expansion of communications networks is driving intense research and development efforts in the field of optical switching [1]. As the transmission capacity of fibre optics lines continues to increase, new generations of components for handling communications traffic are required. In particular, to reduce cost and complexity it is desirable to develop beam steering schemes capable of re-routing optical signals arriving at a node to multiple destinations, without optical-to-electronic conversion. The possibility for these optical applications has stimulated tremendous interest in photonic crystals [2–4], and in combinations of photonic crystals with active materials [5–9]. In this report, we describe a class of liquid-crystal/polymer composites that offer the potential for efficient optical beam deflection via switchable Bragg diffraction.

A variety of alternatives utilising both "solid-state" and "soft" materials have been explored for deflecting or switching optical beams. Solid-state devices for steering or high-speed modulation of light exploit acousto-optic beam deflection, non-linear optical crystals, or optically pumped carrier shifting in semiconductors [10–12]. Soft devices employ electro-optic or thermo-optic polymers, liquid crystals, and micro-structured composites [13–18]. Although they are generally slower than solid-state–based alternatives, soft-material devices are still

potentially useful for certain applications, for example, to redirect optical signals between various network points, a process that requires only millisecond time scales. Soft materials also offer the advantages of low power consumption, and lower-cost processing methods such as ink-jet deposition, micro-contact printing, and self-assembly [19–24].

With the above-mentioned soft-material qualities in mind, we demonstrate the first three-dimensional, electrically switchable Bragg diffraction, based on templated liquid crystal (LC)-filled polymers. Our polymer replicas are created by exploiting ordering found naturally in self-assembled colloid crystals. Previously, liquid crystals in colloid interstitial spaces [6–8] or columnar pores in silicon [9] have been employed for tunable light filters. Our LC/polymer composites can deflect, split, and shutter optical beams with moderate driving voltages and low power consumption. Our experiments reveal an intriguing qualitative difference between colloid-templated samples and conventional polymer-dispersed liquid crystals (PDLCs): it appears that the highly connected nature of our templated cavities induces a more complex liquid-crystal director configuration, thereby shifting the electro-optic response toward higher electric fields and decreasing switching times.

The switching mechanism for our LC/polymer composite devices is analogous to that of typical PDLCs, which consist of micron-sized liquid-crystal droplets trapped within a polymer host. In an electric field (generally of order $1\,V/\mu m$), the PDLC is transparent because the LC molecules realign and achieve index matching with the polymer [25]. When the aligning field is switched off, the preferred orientation of the LC molecules in the droplets gives an index mismatch with the matrix, and the PDLC changes from a transparent to a strongly scattering state. In a typical PDLC, the LC droplets are randomly distributed in space; they therefore cause diffuse scattering rather than sharp Bragg diffraction of light. To make periodic one- or two-dimensional arrays, other research groups have used holographic PDLC exposure [16, 17], polymer-stabilisation of cholesterics [14], or phase-separation of composite films or emulsions [15, 26] to distribute liquid crystal along planes or lines. In our experiment, we modulate the refractive index in three dimensions; ultimately, the three-dimensional structures should lead to improved wavelength selectivity, diffraction efficiency, and directional control.

Fabrication of our templated LC/polymer samples was a multi-step process, beginning with gravitational sedimentation of $1.6\,\mu m$ diameter silica colloid [27]. The interstitial space of the dried colloid crystal was filled with a UV-curable oligomer. After curing the polymer, the colloid particles were etched out by HF. The resulting thin, porous polymer membrane was transferred to a glass slide covered with a transparent electrode (ITO), dried, and imbibed with TL205 liquid crystal [28]. The samples were capped with ITO-glass to form a sealed cell of approximately $25\,\mu m$ inner thickness. An electric field could then be applied to these cells to study their transmission and diffraction behaviour.

Figure 1a provides a schematic cross-section of our colloid-templated samples and indicates the relevant geometry for our transmission and diffraction measurements. $633\,nm$ laser light was directed onto the sample cell perpendicular to its surface. The incident light travelled at normal incidence with respect to the planes of close-packed, liquid-crystal–filled cavities. To demonstrate the regular spherical shape and interconnected nature of the cavities, fig. 1b shows a confocal microscope image of a polymer replica filled with rhodamine-dyed ethanol, which enables fluorescence imaging. Clearly, the dyed solvent has percolated throughout the porous network. Point defects and grain boundaries are also apparent. These lead to an effective in-plane crystallite size of roughly $20\,\mu m$. In general, we expect the close-packed planes to have random HCP (rHCP) stacking [20, 21]. In some cases, however, we found FCC domains with (111) planes perpendicular to our incident light beam. Transmission through the sample (*i.e.* path "t" in fig. 1a) was measured as a function of applied field using a standard
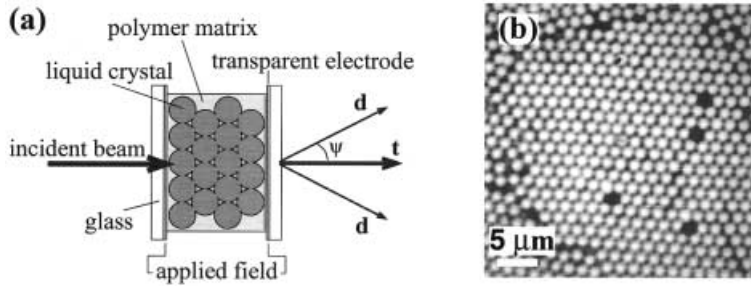
Fig. 1 – (a) Schematic cross-section of liquid-crystal–filled, colloid-templated sample, showing probe beam geometry for transmission and diffraction studies. Path "t" corresponds to transmission measurements performed with unfocused beam, or to zeroth-order diffraction; path "d" indicates beam deflection originating from Bragg diffraction. The diagram elements are not to relative scale. (b) Fluorescence confocal microscope image of filled, colloid-templated polymer.

photodetector/lock-in amplifier arrangement. To characterise the diffraction behaviour of our samples, we used a beam focused to a spot approximately $25 \, \mu$m in diameter. The transmission diffraction pattern, including both zero- and first-order deflections ("t" and "d", respectively, in fig. 1a schematic), was projected onto a translucent screen, and photographed with a digital camera.

To place our results in perspective, we performed similar transmission measurements on conventional PDLC samples. The conventional PDLCs were created using polymerisation-induced phase-separation [25]. Meaningful comparisons with our colloid-templated materials were afforded by using the same LC/polymer combinations in both cases. The LC droplets in the PDLCs were 1–$2 \, \mu$m in size, consistent with previous morphology studies [29, 30], and confirmed by optical microscopy.

In fig. 2, we show representative transmission *vs.* applied electric field responses for PDLC (a) and the colloid-templated LC (b) materials. Both curves exhibit increasing transmission as the LC realigns at higher fields and thus becomes index matched with the polymer matrix [31]. The switching onset for the PDLC, as well as the approach to saturation at higher voltages, are in agreement with previously reported measurements on PDLCs of similar composition [30]. The optical response of the templated sample is shifted toward higher electric fields. Such a shift contrasts with the conventional switching picture for liquid-crystal droplets, described below, which predicts a comparable transmission *vs.* voltage response, or potentially even lower reorientation fields for the colloid-templated samples.

The "bipolar" model for the LC director pattern in isolated, ellipsoidal droplets (appropriate for liquid crystal distributed within a Norland PDLC [25, 30, 32]) predicts that the response voltage scales as $(L^2 - 1)^{1/2}/a$, where a is a characteristic droplet size (*e.g.*, semi-major axis) and L is an anisotropy parameter (*i.e.* the semimajor/semiminor axis ratio). The data shown in fig. 2 are taken from a templated sample containing $1.6 \, \mu$m diameter spherical LC domains, and a PDLC with droplet size distribution peaked around $1 \, \mu$m. The relative shift toward higher voltages for the templated sample is surprising because the LC domain sizes, a, are comparable, the raw materials are the same and therefore should give similar anchoring energies, and the colloid-templated cavities are spherical (*i.e.* $L \sim 1$). Apparently, the colloid-templated cavity network produced a more complex defect and disclination line arrangement (as pictured schematically in fig. 2) which requires higher fields for reorientation; the director configuration could be similar to one recently proposed for LC confined
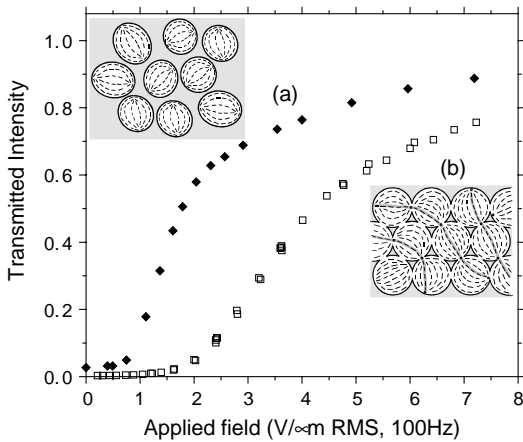
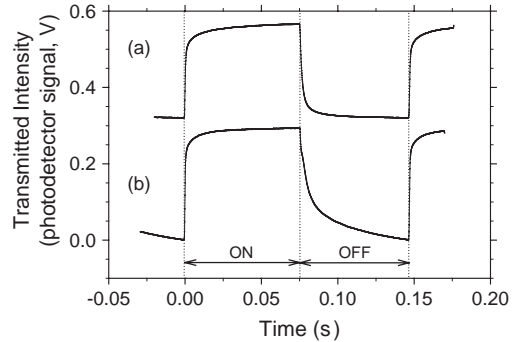Fig. 2   Fig. 3

Fig. 2 – Transmitted intensity *vs.* applied field for (a) PDLC (TL205 liquid crystal, Norland 73 polymer) and (b) colloid-templated structure (TL205 in $1.6\,\mu$m diameter colloid-templated cavities). Transmission is corrected for interface losses. The different arrangements of liquid-crystal molecules within isolated (a) *vs.* connected (b) cavities are indicated qualitatively by the insets; in (b), the grey lines emphasise some possible disclination lines threading through the cavities.

Fig. 3 – Typical time responses for (a) "direct" ($1.6\,\mu$m templated Norland 65, TL205-filled) and (b) PDLC samples (TL205 liquid crystal, Norland 73 polymer, 1–$2\,\mu$m LC droplets). Data were collected using a modulated, $1\,$kHz signal giving a $4.5\,$V/μm (RMS) electric field; curves have been offset for clarity.

within interstitial colloid crystal cavities, where high switching voltages were observed [8]. The qualitative difference between PDLC and templated samples is further corroborated by our preliminary switching time measurements, which reveal significantly shorter fall times for the colloid-templated structures. Representative time response traces, acquired with an amplitude-modulated, sinusoidal driving voltage and digital oscilloscope, are given in fig. 3. At $\sim 4\,$V/μm applied field, a typical response for our templated samples is $\sim 10\,$ms rise and $\sim 5\,$ms fall time. By contrast, for comparable PDLCs, fall times are an order of magnitude longer. The fact that rise times exceed fall times in our templated samples, even as applied fields approach saturation levels, is contrary to expectations based on PDLCs, where fall times are usually substantially longer than rise times [25]. We believe these are further indications of the connected nature of the colloid-templated cavity network [33].

Figure 4 shows photographs of transmission-diffraction patterns at various applied fields for our LC-filled, colloid-templated samples. At zero field (fig. 4a), we observe diffuse scatter, originating from the unaligned highly birefringent LC medium, and defects and disorder within the probe volume. At higher applied voltages (figs. 4b and c), alignment of the LC molecules improves the overall refractive index match, decreases the diffuse scatter, and increases the intensity of the main beam, which is blocked in these photographs. The liquid-crystal alignment produces a diffraction pattern with the symmetry of the underlying templated structure, as is clearly shown in figs. 4b and c. At still higher electric fields ($\geq 3\,$V/μm), a further improved index match between liquid crystal and matrix causes the incident beam to be transmitted directly through the sample cell, thus indicating that within one device, we are able to access straight-through transmission as well as beam-stopping and diffraction.
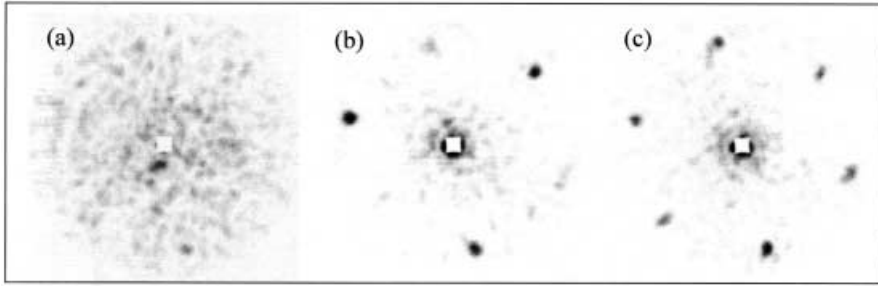
Fig. 4 – Transmission-diffraction patterns from a templated sample ($1.6\,\mu$m colloid-templated Norland 73 polymer, filled with TL205 liquid crystal): (a) with no applied voltage; (b) and (c), applied field of $2.5\,$V/μm (RMS, 100 Hz). (b) FCC-stacked region; (c) rHCP-stacked region. The square blocks the main beam.

The observed diffraction patterns had both threefold (fig. 4b) and sixfold (fig. 4c) symmetry, depending on which area of the sample was probed. These symmetries enable us to convincingly identify the crystal structure. A simple two-dimensional close packing leads to sixfold symmetric Bragg rods in reciprocal space. Perfect three-dimensional crystals yield Bragg spots. In our scattering geometry, with our probe wavelength and crystal periodicity, we do not exactly intersect the reciprocal space spots of the perfect crystals. Both finite-size effects and stacking faults (which in the limit of random sequences give rise to an rHCP crystal) in our system spread the Bragg spots into modulated Bragg rods that we detect. The symmetry of the diffraction patterns depends on the stacking sequence. HCP and rHCP sequences produce sixfold patterns such as that of fig. 4c. FCC sequences produce threefold patterns such as that of fig. 4b with three intense spots arising from smeared $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$ Bragg peaks, and three less intense spots arising from $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ Bragg peaks, or vice versa. The expected diffraction angle is $\theta = \sin^{-1}[(2/\sqrt{3})\lambda/(n_{\text{eff}}d)]$, where d is the LC cavity diameter, λ is the incident wavelength, and n_{eff} is the refractive index of the sample; n_{eff} is weighted with appropriate LC/polymer volume fractions, approximating the LC contribution with an isotropic average: $n^2_{\text{LC}} = (2n_{\text{o}}^2 + n_{\text{e}}^2)/3 = (1.60)^2$; $n^2_{\text{eff}} = (0.74n^2_{\text{LC}} + 0.26n^2_{\text{polymer}}) = (1.59)^2$. After accounting for refraction of the diffracted beam as it exits the sample cell, we determine the effective first-order deflection angle (Ψ in fig. 1a) to be 27.6°; our measured angle of $27 \pm 1°$ is in agreement with this prediction.

We note that, while normal-incidence stopband measurements of the type previously reported on LC-imbibed colloids [6–8] can probe variable refractive index effects, they do not inherently detect the underlying three-dimensional arrangement of the templating colloid. In other words, they do not differentiate from a tunable dielectric stack of similar layer spacing. By contrast, the information provided by our transmission diffraction patterns, in particular the threefold symmetry characteristic of FCC stacking, reveals experimentally the true three-dimensional nature of the electrically switchable Bragg diffraction, which originates from order in the colloid crystal template.

Besides the intriguing diffraction and electro-optic switching of the samples discussed above, our LC-colloid composites may have technological appeal as well. From an applications point of view, our devices require relatively moderate switching voltages of $\sim 100\,$V, and have low, approximately one microwatt power consumption. In comparison, solid-state lithium niobate modulators can require voltages of kilovolt order, unless periodically poled [11], while acousto-optic beam deflectors operate at milliwatt power levels [10].

In summary, we have used self-assembled colloids to generate periodic polymer hosts for nematic liquid crystal. Our templated liquid-crystal/polymer composites exhibit electrically switchable Bragg diffraction; the diffraction symmetry reflects the three-dimensional order of the LC distribution. This switchable diffraction may be useful as a non-mechanical method for optical beam steering. Comparisons of our templated LC/polymer composites with conventional PDLCs reveal a qualitatively different electro-optic response for liquid crystal in connected *vs.* isolated cavities, which may give the practical advantage of faster switching times.

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[28] TL205, obtained from Merck/EM Industries, NY, is a multi-component mixture, exhibiting a nematic phase at room temperature. In a simplified picture, the constituent TL205 molecules can be thought of as $\sim 30\,$Å long organic rods. The characteristic refractive indices are $n_{\mathrm{o}} = 1.53$ along the short molecular axes, and $n_{\mathrm{e}} = 1.75$ along the long axis (Merck data). TL205 has a positive dielectric anisotropy, and will undergo molecular long-axis alignment along an applied electric field. The polymer component of our samples is Norland Optical Adhesive #73, which has a refractive index of 1.56.
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