Liquid Crystals Today

Captured Orientational Order in Polymer Network Assemblies

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The 'marriage' between low molecular weight liquid crystals and polymers burgeoned in the 1980s with the idea of dispersing liquid crystal droplets in a rigid polymer matrix to create an electrically controllable light scattering medium. The orientation of the liquid crystal droplets, and hence the refractive index match and scattering, can be systematically controlled with an electric field. Today, dispersions of liquid crystals and polymers are found in many forms depending on the concentration of polymer, which can be as large as 70% or as small as 1%. The systems most understood are those of larger concentration where the liquid crystal is segregated out in the form of droplets randomly distributed throughout the surrounding polymer (see page 2). Dispersions of liquid crystals and polymers differ from macroscopic bulk liquid crystals because of the large surface-to-volume ratio and symmetry breaking non-planar geometry imposed by the polymer. Their composite nature profoundly affects the ordering of the liquid crystal, and their susceptibility to external fields makes them suitable for many new electro-optic applications, as well as intellectually challenging to study from the basic science perspective.

Several methods have been designed to disperse liquid crystals in polymer matrices: permeating a microporous filter; emulsifying the liquid crystal in a water soluble polymer; and phase separation techniques to create a dispersion of droplets in non-aqueous polymer materials. The latter two methods have been widely employed in many new commercial products and potentially promising applications (see page 2); for example, privacy windows, reflective displays, projection systems, and most recently, liquid crystal-polymer dispersions have been refined to perform with active matrix technologies. The future of these fascinating materials holds even more promise with further developments and increased interest in reflective display technologies [1], bistable capabilities of dispersed ferroelectric materials [2], and holographic applications where patterned phase separation techniques are employed to create spatial modulations in droplet densities [3].

In the last few years much attention has shifted towards systems of low polymer concentration where the polymer only constitutes 1-5 wt. % of the dispersion. The polymer morphology in the low concentration polymer systems is dramatically different from its polymer dispersed liquid crystal (PDLC) counterpart. Small percentages of photo-curable monomer are dissolved in a liquid crystal and then

Figure 1 *A bistable reflective mode 320 × 320 telephone display prototype using polymer stabilized cholesteric texture (PSCT) technology. The display, developed at the NSF Center ALCOM at Kent State University, is shown removed from its drive circuitry to illustrate its bistable memory.*
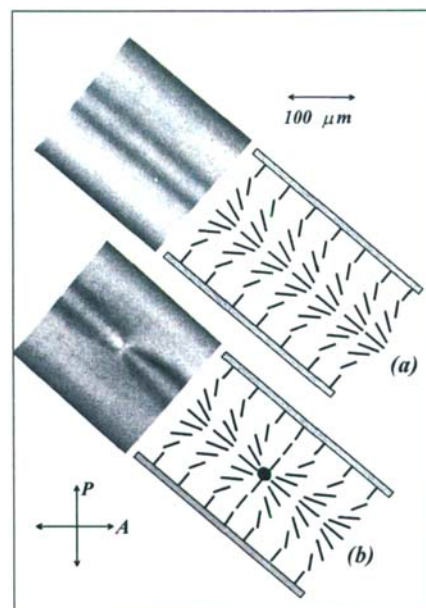
Figure 2 *A black and white photograph of the optical polarizing microscope texture of the escaped-radial nematic director field illuminated by a white light source. Both the continuous director field (a) and the one with point defects (b) are presented. The capillary diameter is 200 µm and has been treated with lecithin to promote homeotropic anchoring. A schematic depiction of the escaped-radial director-field is shown below the photographs.*
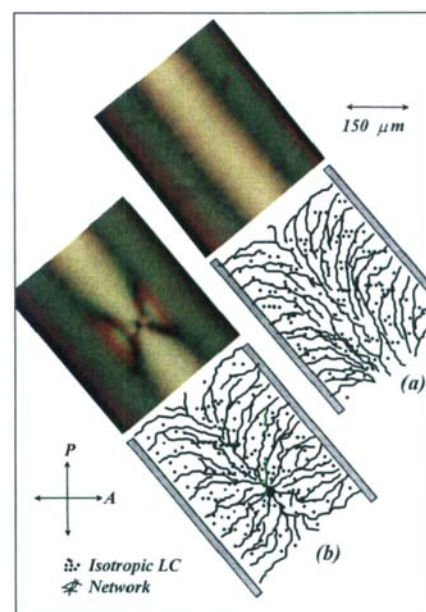
Figure 3 *Colour photographs of the optical polarizing microscope texture of the polymer network (2 wt. %) assembled in the escaped-radial configuration illuminated by a white light source. Both the continuous director field (a) and the one with point defects (b) are presented. The temperature of the sample is 60°C (25° above the clearing temperature of 5CB). The texture at low temperature reveals that the image of the orientational order of the escaped-radial director field was captured. The photograph also reveals that the point defect is captured in the network indefinitely. Model schematic of the polymer network assembly is presented.*

assembled via photopolymerization [4]. In most circumstances, the polymer network captures and retains information of the organized liquid crystal environment. The morphology of the polymer network is therefore strongly dependent on the conditions imposed by the liquid crystal (order, alignment, deformations, and defects) prior to assembly. Low concentration polymer network assemblies introduce a volume stabilization effect that has proven successful in many liquid crystal display applications thus far: the bistable reflective mode display [5], normal and reverse mode light shutters [6], volume stabilized ferroelectrics [7], bulk macroscopic alignment [8], modified twisted nematic (TN) [9,10] and super-twisted nematic (STN) displays [11], and amorphous twisted nematic (a-TN) alignment [12]. Perhaps the most impressive technology to date is the bistable polymer stabilized reflective mode display presented in Figure 1. In addition, polymer network assemblies have ameliorated intrinsic problems which have hindered the development of certain liquid crystal display technologies in the past, such as the annoying off-axis haze in light scattering based devices [6], and added stability to the focal conic texture and enhanced viewing angles in reflective cholesteric displays [5]. The polymer network assembly also alleviates mechanical shock problems in ferroelectrics and antiferroelectrics by volume stabilization [7], eliminates the stripe deformations that occur in 270° STN displays [11], and locks-in and immobilizes tilt disclinations in a-TNs [12].

Low concentration polymer network assemblies are classified as soft condensed matter systems with many physical properties and characteristics that are analogous to liquid crystals constrained to random porous glass matrices (Vycor and Aerogel) [13,14]. The first insights into the polymer network structure and morphology were derived from many analytical experimental techniques: electron microscopy [15], birefringence [16], dielectric spectroscopy [17], magnetic resonance [18], diamagnetic and viscosity measurements [19], and small angle neutron scattering [20]. Many of these measurements indicated that the polymer network could be envisioned as fibers or bundles of fibers along the nematic director field [16,19,21]; the fiber diameter and distribution is found to be very material dependent. Investigations of higher concentration of polymer (20-30 wt. %) suggest that the morphology may be thin-layered walls [22]. Most studies to date have focused on networks formed in planar cells. Here we emphasize nematic director fields in non-planar geometries which are utilized as ordering templates to assemble low concentration polymer networks [21,23].

In the early 1970s, Cladis and Kleman [24] revealed that the escaped-radial nematic director field was stable in capillary tubes with homeotropic surface anchoring conditions. The director-field is planar and radial near the capillary walls, and escapes into the third dimension at the cylinder axis. This splay-bend director-field is schematically depicted in Figure 2(a) along with its characteristic optical polarizing microscope texture. In addition, it was also discovered that radial and hyperbolic point defects can alternate along the cylinder axis since both directions of bend are energetically equivalent. A schematic of the escaped-radial director-field with a radial point defect is also shown in Figure 2(b) along with its optical polarizing microscope texture; the point defect has an unambiguous signature in the optical polarizing microscope texture.

We have used the escaped-radial nematic director-field as an ordering template where low concentration polymer networks are assembled. Samples are prepared by dissolving 1-2 wt. % of the diacrylate monomer 4,4'-bisacryloyloxy biphenyl (BAB) and ~ 0.5 wt. % of the photoinitiator benzoin methyl ether (BME) into the room temperature nematic 4'-pentyl-4-cyanobiphenyl (5CB).

Figure 4 *Optical polarizing microscope photographs of the polymer networks assembled in the escaped radial director field illuminated by a white light source oriented at 45° between crossed polarizers. A magnified point defect captured in a polymer network (a) for a 300 μm cylinder diameter at 60°C. Two capillary tubes side-by-side of 200 μm and 100 μm diameters with only a 1 wt. % polymer network recorded at 60°C (b). A polymer network that was formed in the escaped-radial director field of a 200 μm diameter capillary tube and then extracted into a solvent (c); note that the liquid crystal is completely removed from the network and replaced by an isotropic solvent.*

The clearing temperature of 5CB is 35°C. The mixture is typically heated to 100°C, rigorously agitated for several minutes, and filled into a 100-200 μm diameter capillary tube with treated lecithin walls. The lecithin surfactant enforces homeotropic surface anchoring conditions at the capillary walls. Viewing the sample with optical polarizing microscopy prior to photopolymerization yields the characteristic texture of the escaped-radial configuration presented in Figure 2. The sample is then exposed to UV radiation

to initiate polymerization and assemble the network in the organized environment. The polymerization process is carried out at room temperature (10° below the clearing point of 5CB) where the escaped-radial director field is stable.
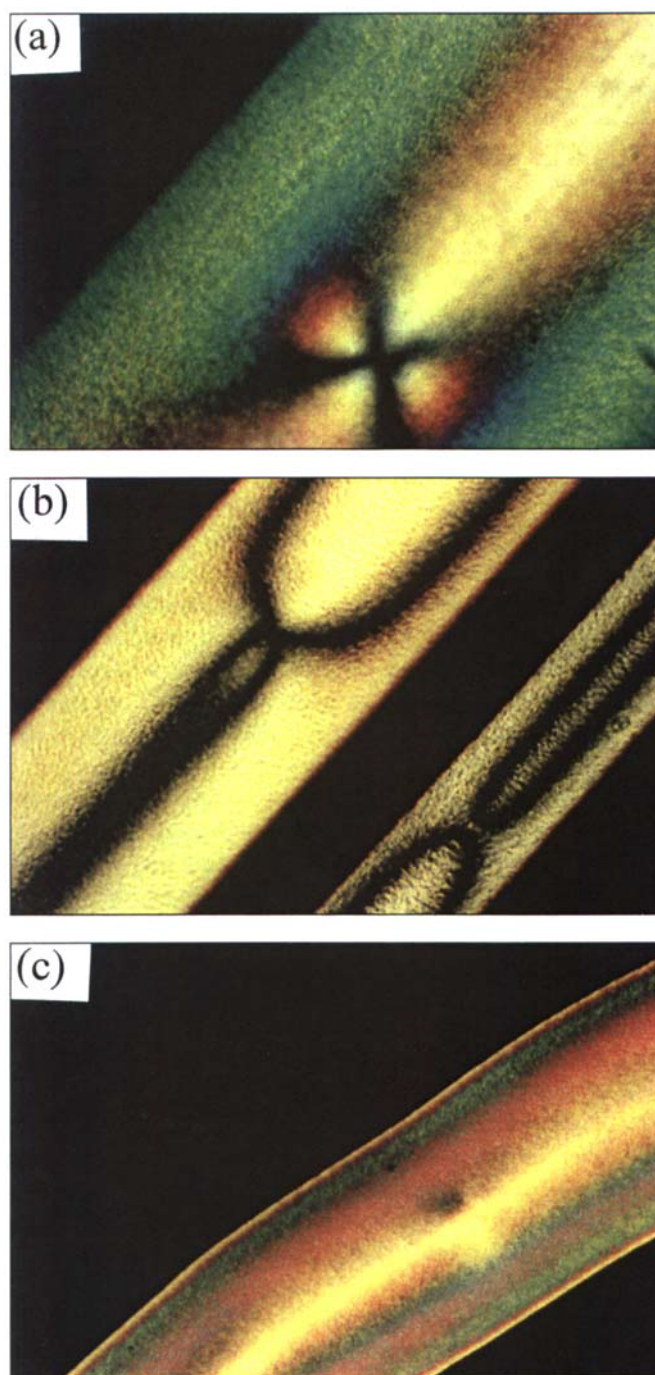
The optical polarizing microscopy texture of the polymer network assembly in the escaped-radial configuration is presented in Figure 3. The major difference between Figures 2 and 3 is that the escaped-radial director-field in Figure 2 was recorded at room temperature (10° below the clearing point of 5CB) and the polymer network assembly in the escaped-radial director-field in Figure 3 was recorded at 60°C (25° above the clearing temperature of 5CB). Figure 3(a) clearly demonstrates that the polymer network assembly has captured and stored the orientational details of the escaped-radial nematic director-field. This is evident from Figure 3 where the birefringence of the polymer network reveals its presence deep in the isotropic phase of the 5CB liquid crystal. This is quite an impressive feature if one considers that only 2 wt. % of polymer can retain the orientation of its ordering template (director-field) at such elevated temperatures in an isotropic environment. The polymer network assemblies were studied and tested at elevated temperatures exceeding 100°C without any signs of degradation. The interference colours that are prevalent in Figure 3 indicate that the birefringence of the liquid crystal-polymer network in the isotropic phase is small and on the order of $\sim 10^{-3}$.

Figure 3(b) also reveals a very interesting aspect associated with polymer network assemblies; the polymer network has captured the point defect in the escaped-radial director-field. The point defects in the escaped-radial director-field (see Figure 2(b)) typically annihilate one another within minutes. The polymer network assembly, however, has captured this metastable state indefinitely (see Figure 3(b)). The low concentration polymer network essentially retains the information of the director-field just prior to photopolymerization. A point defect that has been stored in a polymer network has a characteristic black cross when viewed between cross polarizers of an optical microscope as shown in Figure 4(a). The polymer network is even capable of capturing the orientational order and defects of the director-field with only 1 wt. % of polymer. Figure 4(b) shows the captured escaped-radial director-field with defects at 25°C above the clearing point of 5CB with a 1 wt. % network.

For better perspicuity on the transfer of orientational order and disorder to the polymer network, two additional experiments were performed: (1) the polymer network assembly was carefully extracted from the liquid crystal environment after photopolymerization and (2) the polymer network was assembled above the clearing point of the liquid crystal 5CB. The polymer network formed in the escaped-radial director-field was carefully extracted into a solvent [21]. It was submerged in the solvent for several days to ensure that all liquid crystal initially surrounding the network was replaced by the solvent. The sample was then viewed between crossed polarizers of an optical microscope at 25°C (see Figure 4(c)) and the resulting texture reveals that the network has retained the orientational information of the nematic director-field which manifests itself in the optical birefringence. Next we assembled the polymer network above the clearing point of the 5CB compound. After photopolymerization, the optical polarizing microscope texture revealed a highly scattering structure below the clearing point and a completely black texture for all angles above the clearing temperature; thus confirming the transfer of disorder to the network.

There are subtle changes in the microscope texture of the polymer network in the escaped-radial director field (see Figures 3,
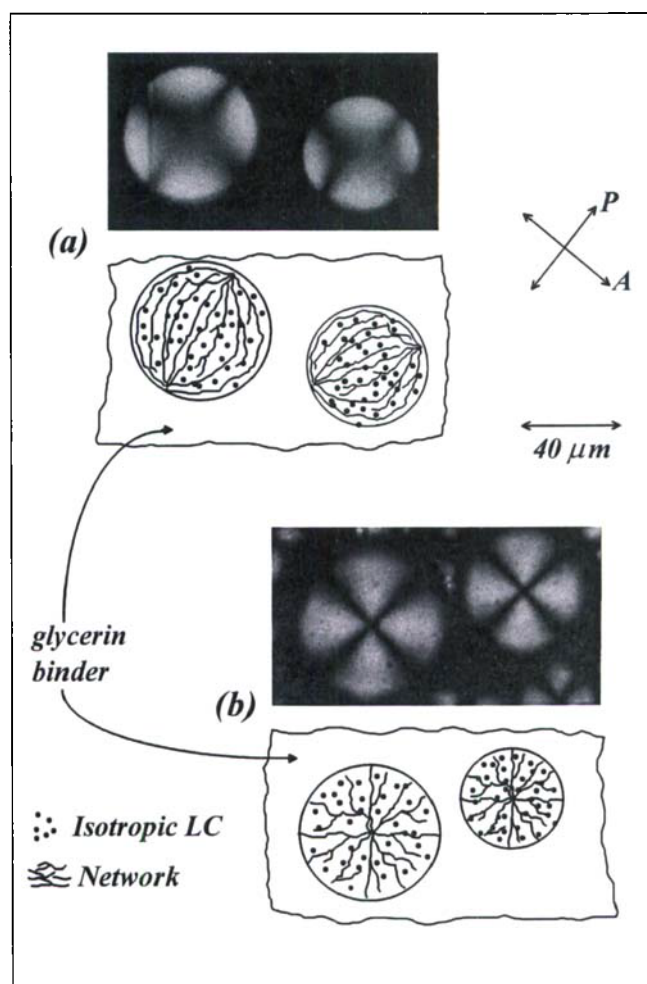

Figure 5 *Black and white optical polarizing microscope photographs of captured bipolar (a) and radial droplets (b) illuminated by a white light source. The temperature of the sample is 40°C (~5° above the clearing point of 5CB).*

4(a) and (b)) as the temperature is increased from the clearing point of 5CB (35°C) to elevated temperatures exceeding 100°C. The polymer network assembly void of liquid crystal (see Figure 4(c)) suspended in a solvent is invariant with changes in temperature. We can therefore safely attribute the optical anisotropy observed in Figures 3, 4(a) and (b) to residual nematic order in the isotropic phase induced by the internal surfaces of the polymer network and the ordered polymer network itself. We are currently pursuing this approach to model the details of the internal surfaces, orientational order, and distribution of the polymer network assembly [21]. By estimating the birefringence of the polymer network in the solvent, DnPN, from its optical interference pattern when viewed between crossed polarizers of an optical microscope, the orientational order parameter can be estimated using the simple expression DnPN=cSDnOP. Using a concentration c=0.02, and the birefringence of the completely ordered bulk polymer, DnOP~0.35, the order parameter is ~0.1. The value of S is substantially lower than that of the liquid crystal where it was assembled. Recent experiments disclosed by Fung [16] have revealed that S can be significantly larger for the polymer 4,4'-Bis[6-(acryloyloxy) hexyloxy]biphenyl (BAB6). These differences are attributed to the degree of ordering of the BAB or BAB6 in the nematic director field prior to photopolymerization.

Many nematic director fields with various types and combinations of elastic deformations can serve as ordering templates for polymer

network assemblies. In Figure 5 we demonstrate the formation of a polymer network in spherical liquid crystal droplets suspended in a viscous glycerin. Prior to photopolymerization, the BAB/BME/5CB mixture is emulsified into a glycerin binder [23]. The sample is agitated to form a collection of supramicrometer droplets and then subsequently photopolymerized. The glycerin matrix prefers homogeneous anchoring of the liquid crystal molecules, and a glycerin matrix doped with small amounts of lecithin promotes homeotropic surface anchoring conditions. The polymer networks assembled in bipolar droplets are presented in Figure 5(a) and those assembled in radial droplets are presented in Figure 5(b). The photographs were taken at a sample temperature of 40°C, five degrees above the clearing point of 5CB; the network has therefore recorded the details of the bipolar and radial ordering templates.

During the past few years we saw what began as a few novel ideas for light shutters and reflective displays evolve into an exciting area of basic science and technology. Low concentration polymer networks assembled in the organized environment of a nematic director field are rich in physical phenomena and have provided researchers with an opportunity to explore finite size and confinement effects in complex composite systems not previously possible. The simple experiments presented here indicate that the cross-linked polymer network mimics the deformations, orientation, and defects of the liquid crystal state where it was initially assembled. An even more impressive aspect of these dispersions is their success rate in applications: ranging from stabilizing the focal conic texture in cholesteric displays to enhancing the electro-optical performance of conventional TN cells, and their intrinsic ability to alleviate some of the barriers associated with ferroelectrics, 270° STNs, and a-TN alignments. Studies on polymer network assemblies are still in their infancy, and as research and development in basic and applied materials science progresses in the coming years, many more unique applications and uses of these fascinating materials will certainly become evident.

Acknowledgements

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