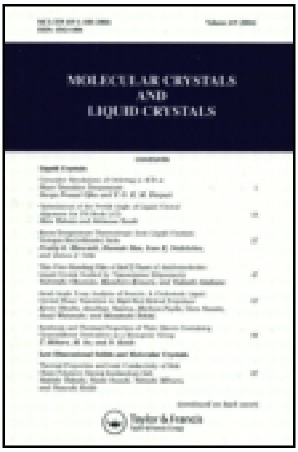

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Influence of Fluorinated Surfactants on the Electro-Optic Switching of Near Infrared Sensitive Polymer-Dispersed Liquid Crystals

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We describe the influence of two fluorinated surfactant dopants on the electro-optical modulation of light scattering by near infrared sensitive polymer dispersed liquid crystals, based on multifunctional acrylates. The molecular configuration and droplet morphology of the obtained samples are found to be bipolar. It is shown that the addition of fluorinated surfactants to the initial mixture may reduce the voltage for the onset of switching and also may enable more efficient liquid crystal reorientation. However, the electrical short of obtained samples is prohibiting achieving complete modulation cycles.

Polymer dispersed liquid crystal (PDLC) materials have demonstrated great potential for electro-optic switching applications [1]. One of the most frequently used methods of creating PDLCs is photopolymerization. Namely, photosensitized mixtures of monomer and liquid crystal (LC) molecules (that are initially miscible, but exhibit reduced miscibility when the polymer is formed) are traditionally employed. As a result, partial phase separation takes place as the photopolymerization proceeds leading to the formation of LC droplets [1]. Spatially modulated refractive index is thus obtained due to the difference ($\Delta n = n_p— n_{LC}$) between the refractive indices of the polymer-rich (n_p) and the LC-rich (n_{LC}) regions formed. The value of n_{LC} is mainly determined by the LC droplets (size, form, spatial distribution) and the configuration of the LC's director ***n*** (the average direction of long molecular axes [2]) inside the LC droplets. The electric field induced modulation of n_{LC} (through the reorientation of ***n***) allows the control of Δn and thus of light scattering.

While traditional material systems have mostly been sensitized to visible or UV light [1], we have focused our efforts on near infra red (NIR) sensitive material complexes that would reduce the cost of fabrication of PDLC and holographic PDLC (H-PDLC) components using NIR diode lasers [3–5]. We succeeded in identifying a specific combination of sensitizer (based on IR140 dye) and multifunctional acrylates to obtain high photosensitivity of the mixture at 823 nm (where cost effective diode lasers are commercially available).

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Unfortunately, the electric field induced modulation of light scattering in those materials was not achieved until recently [6], very likely because of the strong anchoring of LC at droplet polymer interface as well as because of the small and irregular size of LC droplets dispersed in the polymer matrix formed from multi-functional acrylates [7]. At the same time, it has been reported that the addition of specific surfactants to the initial mixture of PDLC can decrease the anchoring of the LC with the polymer and correspondingly can reduce the voltage needed to switch the LC alignment [8,9]. For example, octanoic acid $CH_3(CH_2)_6COOH$ has been used in order to reduce the switching voltage and improve the diffraction efficiency of H-PDLCs.

The present work describes the influence of two fluorinated dopants that we have introduced in our NIR sensitive PDLC materials (see below). Fluorinated materials are known to have low surface energies due to the low polarizability of the carbon-fluorine bond resulting in to relatively weak intermolecular interactions. Fluorinated surfactants can thus be expected to significantly reduce the anchoring energy of LC molecules at the droplet-matrix interface. Our basic material consists of nematic LC mixture E7 (from Merck), dipentaerythritol pentaacrylate (DPEPA, commercial name SR399, from Sartomer), stabilizing monomer 2EEEA (which increases the solubility of the material components used), photo-initiator IR-140, initiator CBr_4 and co-initiator EDMAB. The following two perfluoro-compounds (both from Aldrich) have been tested as surfactant in our PDEPA-based composition in order to reduce the switching voltage.

- Perfluoro-1-octanesulfonic acid, tetraethyammonium salt $CF_3(CF_2)_7SO_3[N(C_2H_5)_4]$; the abbreviation "PM1" will be used for this molecule further in the text.
- Perfluorododecanoic acid $CF_3(CF_2)_{10}COOH$; the abbreviation "PM2" will be used for this molecule further in the text.

These materials were first used for the preparation of model surfaces by the Langmuir-Blodgett technique. Thus, prior to the fabrication of the PDLC samples, the properties of those molecules (PM1 and PM2) have been studied first onto an aqueous subphase containing 5×10^{-5} M of aluminium ions. In an experiment with a floating monolayer on the surface, we have measured the surface pressure that takes a positive value since the presence of a monolayer on the water reduces the surface tension, Fig. 1. Those monolayers were prepared at 20°C. The surface pressure of the monolayer during the deposition onto solid substrates was maintained at 20 mN/m. The speed of barriers' compression was 2.5 mm/min and the speed of stabilization of the barriers was 1 mm/min. The dipping speed of the substrate was chosen to be about 1mm/min. Under these conditions we obtain well ordered monolayers onto solid substrates. The surface pressure (as defined by the equation $[(P = \gamma_0 - \gamma])$ is the difference between the surface tension of pure water γ_0 and the surface tension after spreading of the monolayer γ. At constant temperature (in our case, 20°C), the curve, representing the surface pressure as a function of molecular area, is called isotherm. The isotherm recorded becomes an important source of information about the stability of the monolayer at the air-water interface, the reorientation of molecules in a two-dimensional system and the phase transitions of molecular states on the interface. The isotherms of PM1 and PM2 show that the two surfactants form very stable and uniform films at the air-water interface.

After this study, the monolayers of molecules (PM1 and PM2) were deposited on glass substrates by vertical dipping and studied by means of an Atomic Force Microscope (model Veeco diDimension V). As one can see in the Fig. 2, two molecules generate different morphologies, but both films are relatively uniform and the characteristic size of

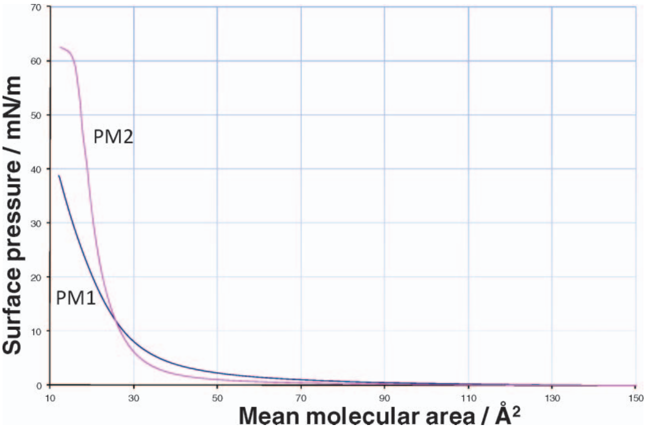

Figure 1. Study of used surfactants as molecular layers onto an aqueous subphase containing 5 × 10^{-5} M of aluminium ions : a) $CF_3(CF_2)_6CF_2SO_3N(C_2H_5)_4$, further called PM1, and b) $CF_3(CF_2)_{10}COOH$, further called PM2.

non-uniformities is below 5 nm. Those substrates where then used to build sandwich-like cells of LC (the molecular coatings facing inside of the cell). The obtained cells exhibited good homeotropic alignment (the director ***n***, was perpendicular to the surface of the cell substrate), see Fig. 3.

Then samples of un-doped (by PM1 or PM2) "PDLC" films, containing a single *monolayer* of large LC droplets (only one droplet of LC exist on the optical path) that are more suitable for observations by polarizing microscope, have been fabricated in order to study the LC interaction with the confining polymer interface (walls) and the corresponding director configuration. Such monolayer films were fabricated between two non-coated microscopic slides to reduce their influence on the LC alignment. The thickness of those monolayer PDLC films was 6μm and the diameter of LC droplets (measured in the plane of the film) was in the range from 1 μm to 15 μm. The obtained big droplets were flattened in the plane of the film and revealed a shape of oblate spheroid [1]. Finally, multilayer structures of small droplets (multiple LC droplets exist in the optical path, with diameters between 1-3 μm) were prepared between two ITO-glass substrates (as standard PDLCs).

Fig. 4 illustrates the bipolar structure of the LC alignment, found within the droplets, showing the "planar" orientation of LC on the polymer interface. Upon introduction of the surfactants PM1 or PM2 into the original composition, no noticeable differences were observed by polarizing microscopy and the bipolar structure was preserved in the LC droplets. The electro-optical response (namely the electrically controlled light scattering) of multilayer PDLCs has been studied by the measurement of light transmission through the sample as a function of applied voltage. In order to fabricate those PDLC structures (with LC droplets of diameters less than 1–3 microns), the concentration of LC in the pre-polymerized solution was increased up to 40-50% from the 23.8% typically used for our H-PDLCs. Namely, three mixtures were prepared (all without IR-140 to facilitate this particular study):

Mixture 1 (with PM1): DPEPA + 2EEEA + initiator + co-initiator + PM1 (1.7%) + E7 (45%)

Mixture 2 (with PM2): DPEPA + 2EEEA + initiator + co-initiator + PM2 (1.7%) + E7 (48%)

Mixture 3 (reference): DPEPA + 2EEEA + initiator + co-initiator + E7 (50%).

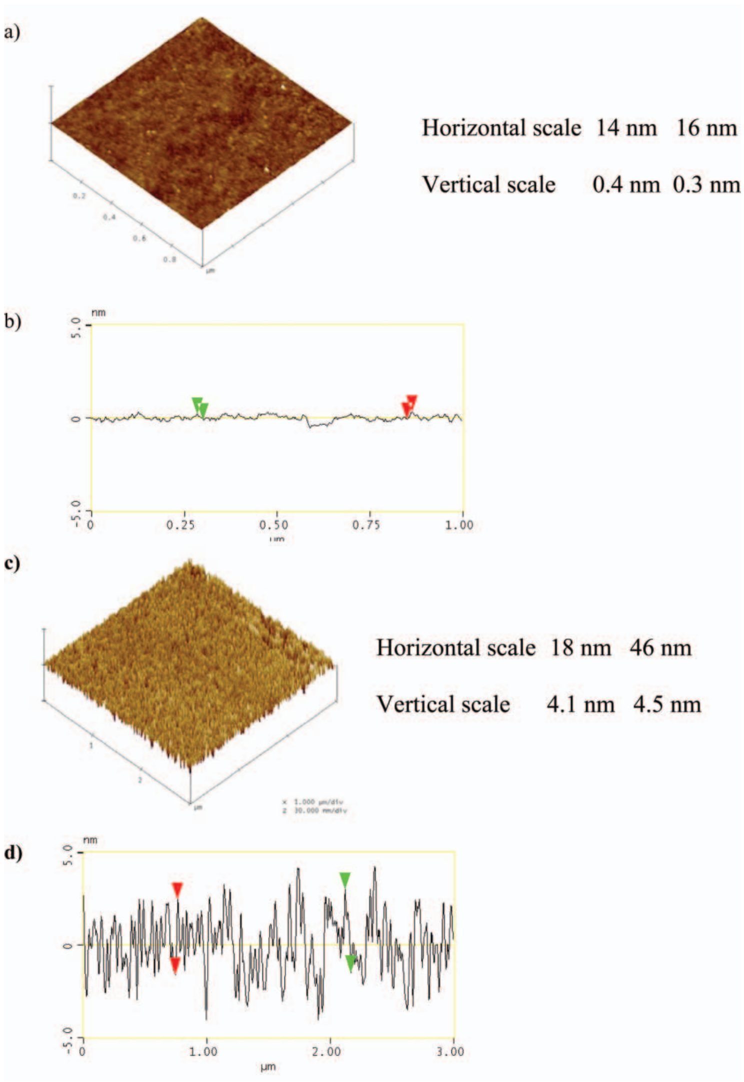

Figure 2. Atomic Force Microscope studies of thin molecular layers deposited on glass substrates: a) & b) with PM2 molecules; c) & d) with PM1 molecules.

Each mixture was placed between two ITO-glass substrates with a 3μm Mylar spacer and uniformly irradiated with UV light (UV curing light gun, model ELC-410, from Edmund Optics) at room temperature. Samples, polymerized in this way, were inspected with an optical microscope and found to display PDLC structure of multilayers of LC microdroplets with an average diameter of the order of 1–3 μm.

The transmission of the probe beam (obtained from a CW He-Ne laser, operating at 543 nm) through each sample was measured as a function of a square-like AC voltage applied at a frequency of 1 kHz. No analyser was placed in front of the detection system, which was placed at 25cm behind the PDLC sample. A 0.8 mm diameter diaphragm was

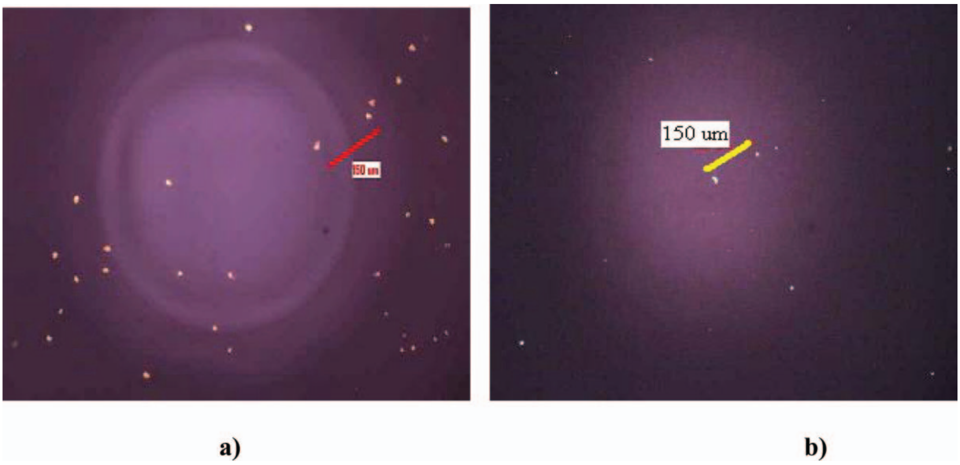

Figure 3. Microphotography of homeotropic liquid crystal cells (placed between crossed polarizers) fabricated by using glass substrates coated (by Langmuir Blodgett technique) with molecules a) PM1 and b) PM2. The small tilted bar in the center shows ≈150 μm scale.

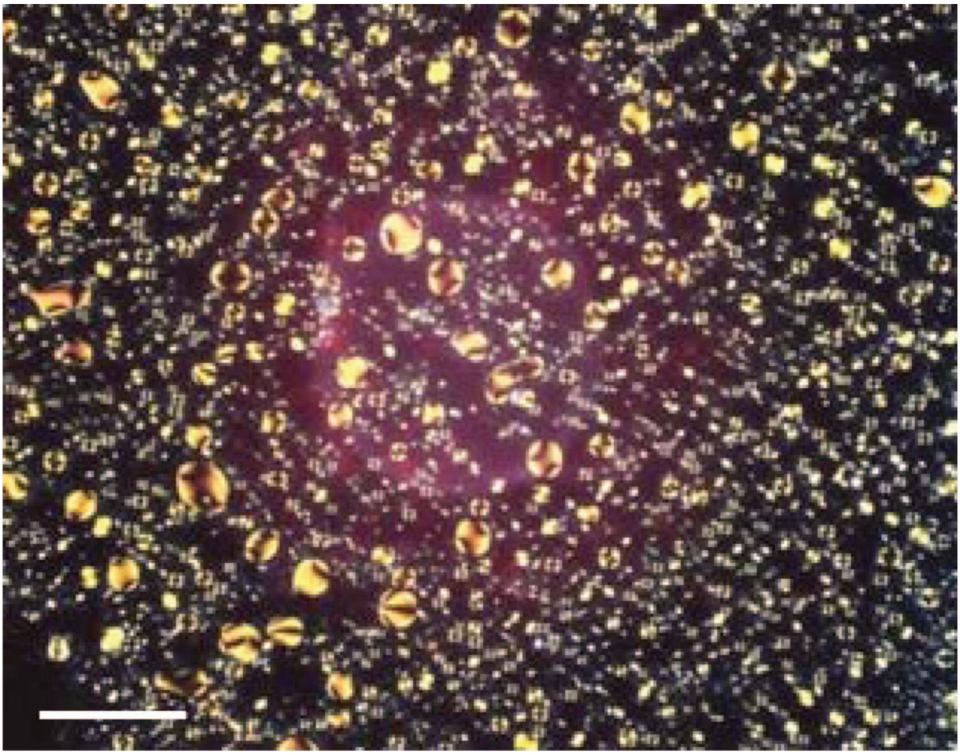

Figure 4. Bipolar LC droplet "monolayers" of our PDLC matrix (of thickness 6 μm.) placed between crossed polarizers of the microscope. Largest droplets have diameters at the order of 15 μm (the white horizontal bar shows approximately 50 μm scale). A similar morphology is observed in the presence and absence of perfluorinated surfactants.

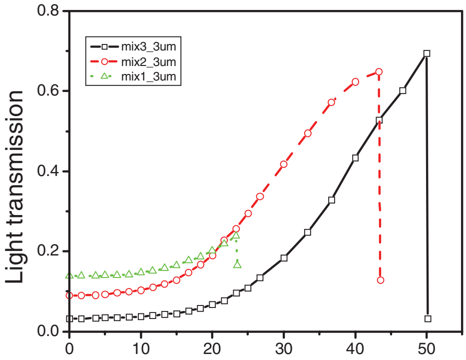

Figure 5. Light transmission (in arbitrary units) versus electric field V/μm for three PDLC samples made of different chemical compositions (see the text for more details) of thickness 3 μm.

used to limit the surface of the active area of detection. The magnitude of the voltage was increased in discrete steps and the probe's transmission was monitored at each voltage.

Fig. 5 presents the results of the above mentioned measurements. The applied voltage is divided to the sample thickness in order to obtain electric field values. As one can see, there are no striking differences in the general appearance of the three curves. Electric fields of the same order of magnitude (15–25 V/μm) are required for all samples to change the light scattering. However, approximately 20-27% smaller field is required for the Mixtures 2 (compared to Mixture 3) to induce similar changes in light transmission. It can also be noted that the curve for Mixture 2 has a tendency to saturation at lower field (starting from 40 V/μm) whereas the curve for Mixture 3 continues to rise and the curve for Mixture 1 demonstrates the lowest slop. In fact, we attempted to measure S-shaped curves for all of the samples. Such curves include the range of complete saturation of light transmission and are required to define correctly the 10% and 90% levels, which correspond to the "threshold field" and the "field of saturation," respectively. Unfortunately, it was not possible to obtain complete saturation because of electrical shorting accompanied by an abrupt drop in transmission.

Indeed, our PDLC materials had very weak resistance to short circuit. The addition of PM1 or PM2 into the mixtures increases the risk of short circuit, very likely because of the presence of surfactant aggregates or because of increased conductivity arising from the ionic nature of the surfactant molecules. In fact, both of those surfactants degraded the uniformity of samples that was found to be related to the poor miscibility of those surfactants in the initial mixture, before polymerization. This aspect was additionally studied. One can see from Fig. 6 that PM1 and PM2 are not completely soluble in the monomer mixtures prepared at ambient temperature; they exhibit flakes of PM2 and PM1. Upon heating, the mixtures become homogeneous at the melting points of the surfactants: 184–190°C for PM1 and 107–109°C for PM2. At these high temperatures the mixtures are uniform and transparent. After cooling to room temperature, the mixtures once again become non uniform. A fine suspension of surfactant is observed in both mixtures.

To summarize, only a small reduction of switching voltages was achieved by the use of fluorinated surfactants. We believe that the observed low efficiency is related to the extremely low solubility of surfactants used in our PDLC mixtures (leading to aggregations and electrical shorting). This is the reason why we were not able to continue the characterization process, including contrast, response-time, etc. The solubility problem must be

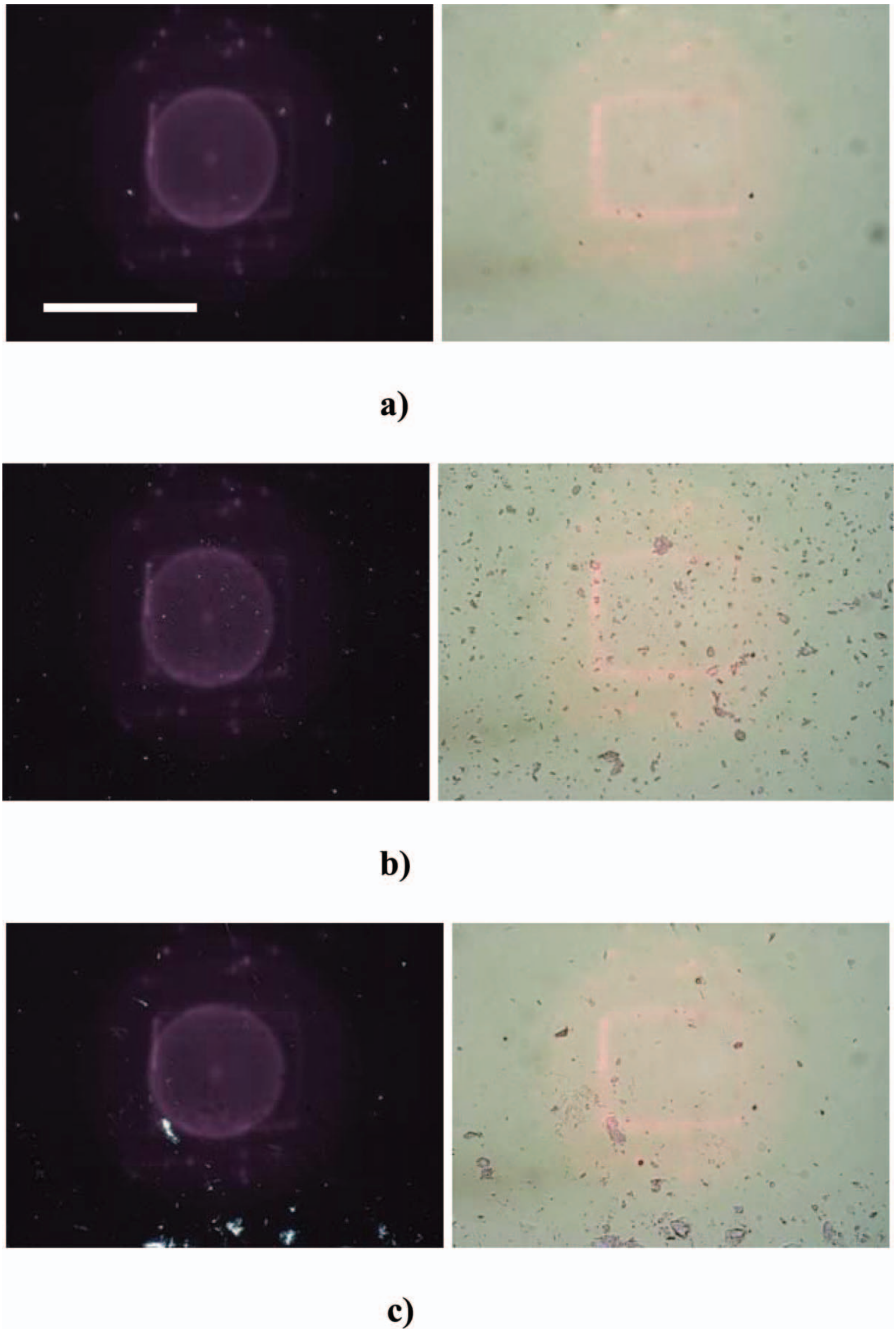

Figure 6. Mixtures of H-PDLC with LC E7 before polymerization at room temperature, between crossed polarizers of the microscope (on the left) and without analyzer (on the right) **a)** without surfactants; **b)** with PM1; **c)** with PM2. Largest aggregations (see on the right) have diameters at the order of 8 μm - 10 μm (the white horizontal bar shows approximately 50 μm scale).

resolved before significant improvements in switching characteristics could be achieved. It must be however noted that their high solubility in the LC or the polymer matrix is not desirable either. In an ideal scenario, the surfactant should be miscible with the initial monomer-LC solution, but should spontaneously assemble at the surface of the LC droplets as the phase separation proceeds with photopolymerization. Electrical properties (conductivity, ionic purity, etc.) of mixtures, based on DPEPA and surfactants, should be additionally studied to allow the application of higher voltages.

Acknowledgment

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References

[1] Drzaic, P. S. *Liquid Crystal Dispersions*; World Scientific, Singapore, 1995, pp. 30–59.
[2] De Gennes, P. G. *The Physics of Liquid Crystals*; Oxford University Press, London, 1974.
[3] Pilot, P., Boiko, Y. B., Galstyan, T. V. (1999). *Near-IR (800 to 855 nm) sensitive holographic photopolymer-dispersed liquid crystal materials*, Proc. SPIE 3635, pp. 143–150.
[4] Galstian, T., & Tork, A. *Photopolymerizable composition sensitive to light in a green to infrared region of the optical spectrum*, U.S. patent 6,398,981 (June 4, 2002).
[5] Bouguin, F., & Galstian, T. V. *In-situ recorded holographic lenses for near-infrared diode lasers*, Proceedings of SPIE — 4342 Optical Data Storage 2001, Terril Hurst, Seiji Kobayashi, Editors, January 2002, pp. 492–501.
[6] Harbour, S., Simonyan, L., & Galstian, T. (2007). Electro-optic study of acrylate based holographic polymer dispersed liquid crystals with broad band photosensitivity, *Optics Communications*, *277* (2), 225–227.
[7] Tondiglia, V. P., Natarajan, L. V., Sutherland, R. L., Neal, R. M., & Bunning, T. J. (1998). *MRS Proc. 479*, 235.
[8] Liu, Y. J., Sun, X. W., Dai, H. T., Liu, J. H., & Xu, K. S. (2005). Effect of surfactant on the electro-optical properties of holographic polymer dispersed liquid crystal Bragg gratings, *Optical Materials*, *27*, 1451–1455.
[9] Sutherland, R. L., Hagan, B., Kelly, W., & Epling, B. *Switchable polymer-dispersed liquid crystal optical elements*, US Patent 6,867,888 B2, Mar 15, 2005.