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The electro-optical response of nematic emulsions

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Switchable nematic emulsions are micron-sized droplets of nematic liquid crystal, floating in isotropic fluid matrices. Such droplets can be switched from an opaque (off) to a transparent (on) state by application of very low electric fields. It is known that the electro-optical properties of liquid crystal dispersions are affected by several parameters, including the liquid crystal loading. The electro-optical response of nematic emulsions has been investigated as a function of liquid crystal weight percentage. Almost transparent films with a reduced contrast ratio are obtained with lower liquid crystal contents. A macroscopic phase separation is observed when liquid crystal content exceeds 45 wt %. On the contrary, large contrast ratios and very low switching fields can be obtained if liquid crystal ranges from 25 to 35 wt %. Consequently, nematic emulsions prepared in this liquid crystal range can be used as promising systems for electro-optical applications. In addition to technological developments, these results can help computational and basic studies of phase separation in novel multiphase liquid crystalline materials.

1. Introduction

Nematic emulsions are composite materials formed by micron-sized droplets of nematic liquid crystal dispersed in a fluid isotropic matrix [1–3]. They have attracted the interest of many researchers for the particular properties of liquid crystals in restricted geometries [4–8]. The structure and defects of liquid crystals and the non-classical interactions between the anisotropic droplets dispersed in host matrices represent some of the investigated fields. Recently, we have proposed dispersions of nematic liquid crystal droplets in monomer mixtures for new electro-optical devices [9–11]. Thin films with micron-sized droplets can be switched from an opaque state to a transparent state by application of a suitable electric field. The behaviour of switchable nematic emulsions operating in a reverse mode that is droplets characterized by a transparent (off) state and an opaque (on) state has been recently presented [12]. In both cases, the operation principle is the electrically controlled reorientation of liquid crystal directors, which changes the scattering cross section of droplets and, consequently, the transmittance values of films. Obviously, the highest values of on-state transmittance in direct-mode operating emulsions can be obtained if a match between the ordinary refractive index of liquid crystal and that of the monomer matrix is fulfilled. Such switchable nematic emulsions are stable over a long time due to the high viscosity of the monomer matrix and their switching fields are very low (few tenths of V μm^{-1}). Their rather long relaxation times, due to the low restoring forces acting on liquid crystal directors, have been decreased to some tens of milliseconds by means of either a few per cent of surfactant molecules [13] or chiral dopants [14]. Consequently, it has been suggested their use as light shutters, switchable windows, displays and other devices is an alternative to conventional liquid crystal technology. In fact, nematic emulsions require no polarizer, are easier to prepare, and use less expensive raw materials. They have been also proposed as bifunctional devices, i.e. films that are able to change both their transparency and colour, by addition of photochromic molecules, which are able to change their absorption spectrum upon exposure to sun light [15, 16]. The presence of polymerizable chemical groups in the matrix components has allowed development of a new procedure to obtain direct-mode polymer dispersed liquid crystals [17, 18], reverse-mode operation shutters [19], electrically switchable diffraction gratings [20] and bifunctional electro-optical devices [21]. For every practical application described above, it is important to design the switchable devices with particular electro-optical characteristics concerning switching fields, contrast ratios, relaxation times, etc. It is known that liquid crystal dispersion performance depends on several parameters, e.g. droplet number

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density, droplet size, refractive index values and film thickness [22]. As a consequence, it is important to study the electro-optical properties of particular sections of their phase diagram. In addition, the phase diagrams of liquid crystal dispersions are complex and difficult to model since they depend on polymer chemistry, polymer structure, liquid crystal composition and evolved phases. Furthermore, the kinetics of the process causing phase separation to occur plays an important role. The knowledge of how the variation in composition and temperature can lead to different morphologies and electro-optical properties can help the computational and basic physics in the interpretation and prediction of phase diagram and device properties which will be found both in liquid crystal dispersions and in more general multiphase liquid crystalline materials such as carbon–mesophase carbon composites, filled nematics, colloidal nematics and ferronematics.

In this paper we report an investigation of the influence of liquid crystal loading on the electro-optical properties of switchable nematic emulsions. We will show that the increase of liquid crystal content dramatically affects the electro-optical performance of nematic emulsions and that excellent electro-optical devices can be obtained in a restricted liquid crystal range.

2. Experimental

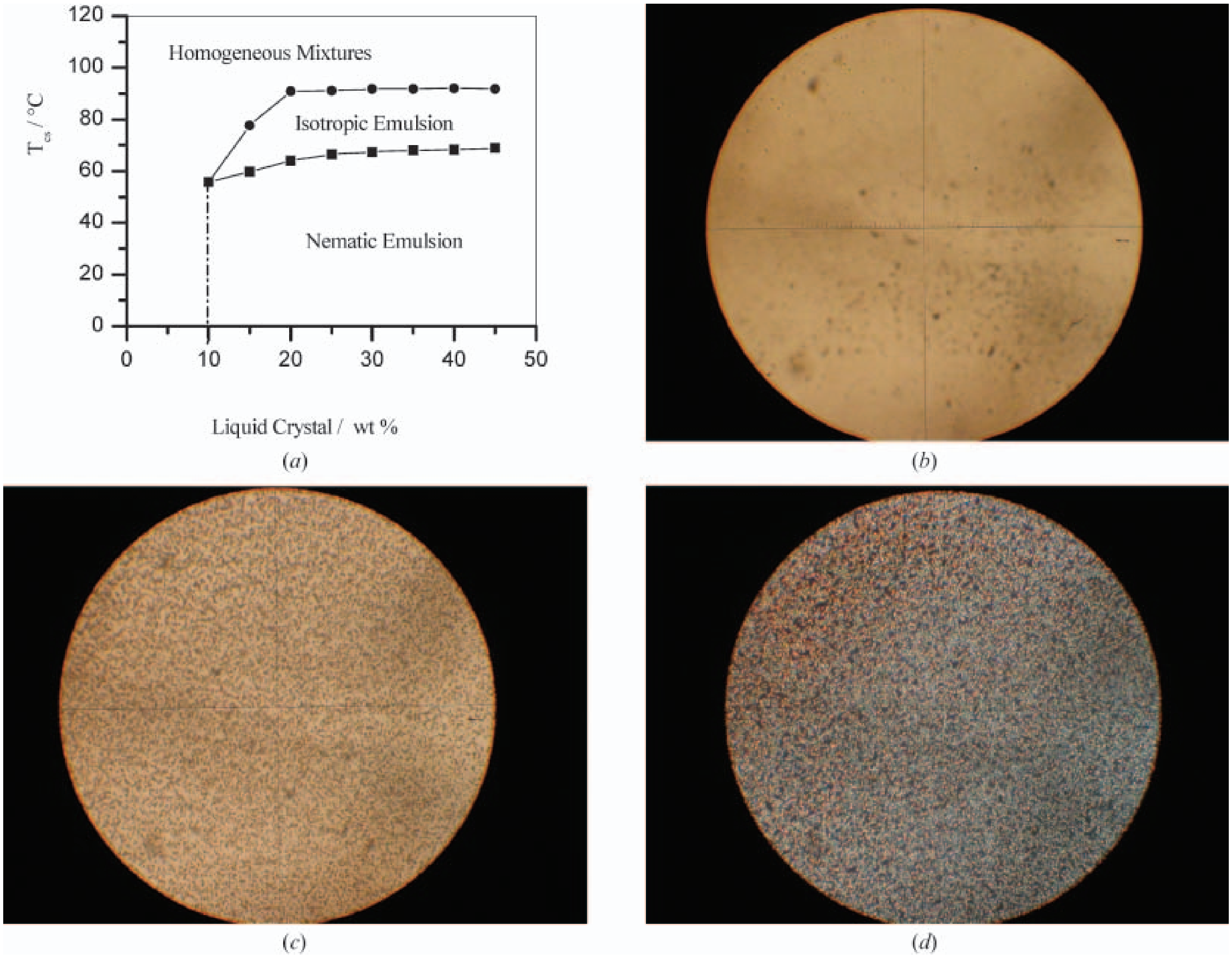
Nematic emulsions were prepared with TL202 (a nematic liquid crystal with a positive dielectric anisotropy from Merck) and a mixture of bisphenol A glycerolate diacrylate (BAGD, from Aldrich) and CN945B85 (an aliphatic urethane triacrylate, 85% in hexanediol diacrylate from Cray Valley-Total). The weight ratio between the two monomers was fixed at BAGD:CN945B85=39:61, since it gives a refractive index of liquid crystal saturated matrix matched with the ordinary refractive index of droplets [9]. TL202 concentration was varied in the range 10–45 wt %. Such values represent the boundary contents for the onset of phase separation of liquid crystal in droplets and for macroscopic phase separation between liquid crystal and monomer matrix, respectively. Samples were prepared by weighing the appropriate amount of components and stirring the mixtures at 100°C. Then, a small quantity was introduced by capillary in home-made cells with ITO conductive substrates at a temperature well above the critical solution temperature, i.e. the temperature above which a homogeneous single phase is observed. Cell thickness was about 30 μm. Uniform, micron-sized emulsions were obtained by cooling samples at a controlled rate of $50^{\circ}\mathrm{C\,min}^{-1}$. The electro-optical properties of emulsions were investigated in the nematic range at room temperature ($T=20.0^{\circ}\mathrm{C}$) with the experimental set-up described in a previous work [22]. The sample temperature was kept constant by a programmable hot stage, the stability of which was better than 0.1°C (Linkam PR600). The intensity of light measured with no sample in place was assumed to be the full scale intensity. The switching fields, $E_{10\%}$ and $E_{90\%}$, are defined, respectively, as the electric fields required to reach 10% and 90% of the maximum transmittance. The decay time, τ_{decay}, defined as the time required for the optical transmittance to drop 10% of its maximum value after the field removal, was determined by monitoring the drive signal ($\nu=1\,\mathrm{kHz}$, $E_{\mathrm{rms}} \approx 2\,\mathrm{V\,\mu m}^{-1}$) and the response of the photo-diode.

3. Results and discussion

Figure 1a shows the phase diagram of the BAGD+CN945B85/TL202 system as a function of liquid crystal content. It was determined by observation of thin films by an optical microscope between crossed polarizers. At low temperatures we observed the existence of nematic emulsions (figure 1d). The liquid crystal-rich phase is separated in droplets from a monomer mixture-rich phase. Droplets show a bipolar configuration, i.e. liquid crystal molecules prefer a tangential alignment at droplet interfaces.

The phase separation in droplets starts from 10 wt % of liquid crystal. If the temperature is increased, liquid crystal droplets begin to increase in size and their number density reduces. This effect can be attributed to a change of mutual solubilities of components. Depending on liquid crystal loading, droplets lose their nematic properties at a particular clearing temperature, T_{c}, but do not disappear at all (see figure 1c). Such isotropic droplets do exist without any electro-optical response until the critical solution temperature, T_{cs}, i.e. until the temperature is reached for which a single homogeneous phase is observed (see figure 1b). A macroscopic phase separation of liquid crystal from monomer matrix is observed for liquid crystal concentrations larger than 45 wt %.

At room temperature (20°C) the electro-optical behaviour of emulsions is quite different, as shown in figure 2. The electric field dependent transmittance shows very small changes for a liquid crystal content as large as 10 wt % (data not shown). If liquid crystal loading is furtherly increased, the off-state transmittance decreases whereas that for the on state is almost constant due to the match between refractive indices of monomer matrix and liquid crystal droplets. The decrease of off-state transmittance can be attributed to



(*a*) (*b*)

(*c*) (*d*)

Figure 1. Phase diagram (a) of the investigated system and optical microscope images of the (b) homogeneous mixture, (c) isotropic emulsion and (d) nematic emulsion. The monomer weight ratio was fixed at BAGD:CN945B85=61:39. The investigated liquid crystal loading was 10–45 wt %, representing the boundary values for the onset of liquid crystal droplets and for a macroscopic inhomogeneous phase separation.

the increase of droplet number density and size, as confirmed by optical microscope observations.

Such results are in agreement with the theoretical prediction of the anomalous diffraction approximation (ADA) for the transmittance of a nematic droplet surrounded by a homogeneous matrix. According to ADA, which holds in the limits $kR >> 1$, $\left(\frac{n_{\text{droplet}}}{n_{\text{matrix}}} - 1\right) \ll 1$, and neglecting multiple scattering, the transmittance behaves as follows [23]:

$$T = \exp(-\beta\sigma d), \tag{1}$$

where

$$\sigma = 2\pi R^4 k^2 \left(\frac{n_{\text{droplet}}}{n_{\text{matrix}}} - 1\right)^2 \tag{2}$$

and β is the number density, σ is the droplet scattering cross-section, d the film thickness, k is the impinging light wavevector, R the droplet radius, n_{droplet} and n_{matrix} are, respectively, the refractive index of droplet and monomer matrix. Samples with 35 wt % of liquid crystal concentration show an increase of the off-state transmittance and decrease of the on-state one due, probably to the start of coarsening between droplets. Such a coarsening reduces the droplet size homogeneity and then evolves in the macroscopic phase separation for liquid crystal concentration larger than 45 wt %.

The strong dependence of T_{off} on liquid crystal content (see figure 2) strongly affects the cell contrast ratio (CR) defined as the ratio between the on-state and the off-state transmittances. CR values increase as a function of liquid crystal up to 30 wt %, as shown in

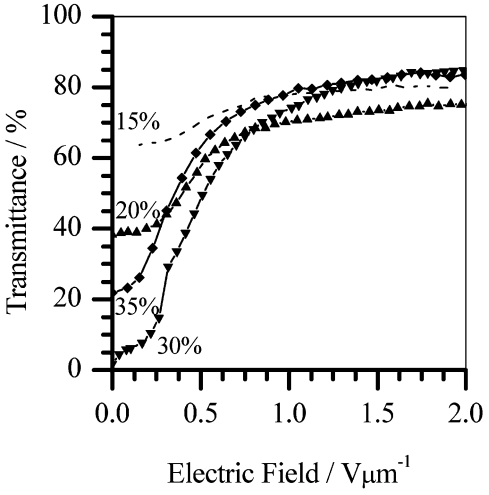


Figure 2. Electric field dependent transmittance in nematic emulsions with different liquid crystal loading.

figure 3. Then, CR decreases due to the changes in T_{off} and T_{on}.

Figure 4 shows the reorientation field dependence on liquid crystal loading. Both $E_{10\%}$ and $E_{90\%}$ decrease with liquid crystal content. This effect can be mainly attributed to the increase of liquid crystal droplet size and is in agreement with the following scaling law [11]:

$$E \approx \frac{K}{\Delta\varepsilon R^2}, \tag{3}$$

where K and $\Delta\varepsilon$ are, respectively, the elastic constant (in the one-constant approximation) and dielectric anisotropy of liquid crystal.

A typical electro-optical response in a nematic emulsion is reported in figure 5.

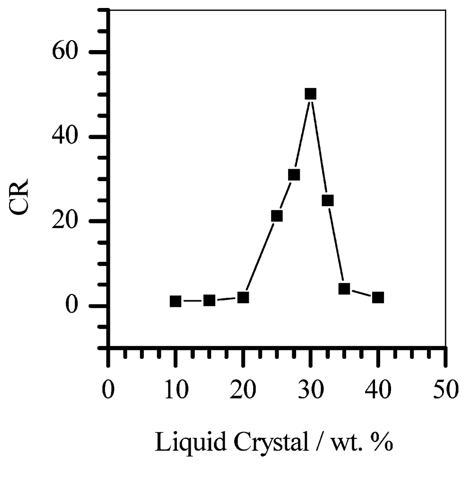


Figure 3. Contrast ratio in nematic emulsions as a function of liquid crystal content.

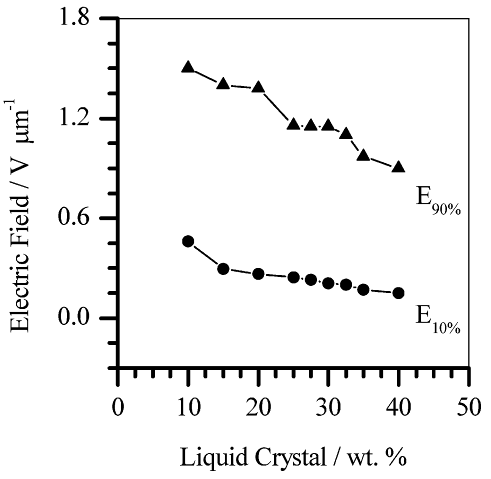


Figure 4. Reorientation field, $E_{10\%}$ and $E_{90\%}$, dependence on liquid crystal loading.

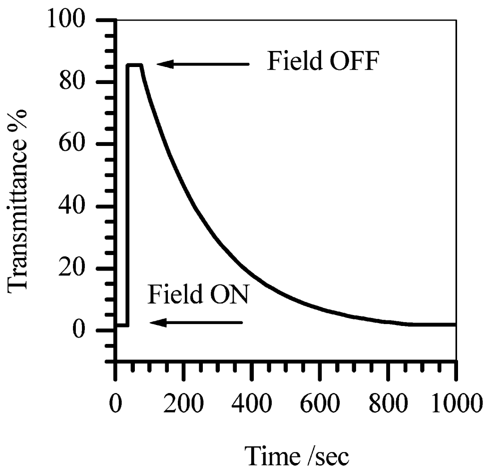


Figure 5. Typical electro-optical response in a nematic emulsion. The driving field frequency and strength were 1 kHz and 2 V μm^{-1}, respectively. The field was applied for some seconds at t=0.

The rise time is always fast (some ms) since it depends on the applied electric field. On the contrary, the relaxation times are quite long (some minutes) and increase with liquid crystal loading lower than 30 wt %. (figure 6). This is a further confirmation that droplet size increases with liquid crystal loading up to 30 wt %. The subsequent decrease in τ_{decay} can be explained by recalling that the relaxation times scales inversely with the droplet radius R, but is directly related to the square root of the ratio γ/K, where γ is a viscosity coefficient [11]. According to the relation, we can hypothesize that the increase in liquid crystal (contents larger than 30 wt %) results in a decrease of the viscoelastic ratio γ/K larger than the decrease of radius, with a consequent reduction for τ_{decay} values.

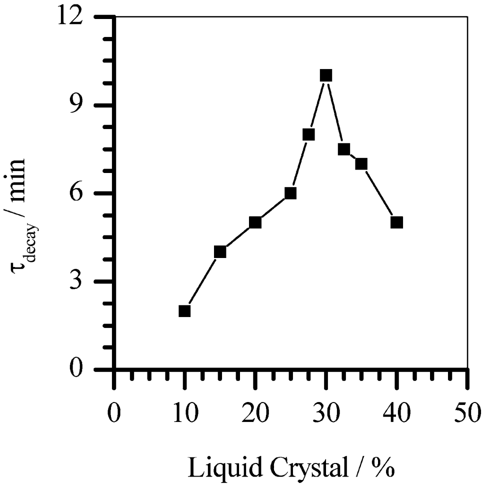


Figure 6. Decay time dependence on liquid crystal content.

4. Conclusions

In this work we have investigated the changes in the electro-optical properties of a monomer mixture/ nematic liquid crystal system which gives rise to switchable nematic emulsions. The electro-optical performance is enhanced by the increase of liquid crystal content and reaches its best value for 30 wt % of TL202 liquid crystal. For such values, films are characterized by fast switching fields, large contrast ratio but relatively large relaxation times. On the contrary, transparent films are obtained for liquid crystal loadings lower than 10 wt % and a macroscopic phase separation of liquid crystal from monomer matrix is achieved when liquid crystal concentration is larger than 45 wt %.

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