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Liquid crystal orientation in elliptic droplets in nematic emulsions

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Elliptic droplets of nematic liquid crystal dispersed in a fluid organic monomer were obtained by phase separation from an isotropic mixture consisting of an organic monomer and a nematic liquid crystal contained in a poly(ethylene terephthalate) cell with inner surfaces treated with rubbed polyimide. The elliptic shape is a consequence of the constraint upon droplet growth along the direction perpendicular to the cell surfaces owing to the small thickness. Then, the resulting droplets will have a contact area with the inner surfaces of the cell treated with polyimide, which will impart a planar orientation on the liquid crystal in the droplet. By means of an optical microscope, using a simple pin hole of 5 μm, we have selected single droplets for a series of samples having different contact areas. By polarized infrared spectroscopy we have also studied the liquid crystal orientation in selected areas of the droplets. We then report the dependence of the order parameter of the liquid crystal on different contact areas with the alignment surface of the cell. The good degree of planar alignment of the liquid crystal in the elliptic droplets allows the use of such a technique for realizing electro-optical films operating in the reverse mode. We report the electro-optical transmission of reverse mode films with different sizes of elliptic droplet.

1. Introduction

Nematic liquid crystal emulsions consist of a dispersion of nematic liquid crystal droplets in a fluid organic monomer [1, 2]. The advantages that nematic emulsions offer, with respect to traditional polymer dispersed liquid crystals (PDLCs) are essentially two in number: the low voltage of the driving electric field (about 0.5 V μm^{-1}), due to the small value of the anchoring energy of the liquid crystal in the droplets [3], and the possibility of polymerizing the emulsion by UV light to obtaining a typical PDLC film [4]. The orientation of the LC director in droplets has interested many research groups which have addressed their studies on the orientation to PDLC systems [5–7]. In particular, a typical configuration of the director in LC droplets is described by Doane for spherical and for elongated droplets [8]. A very simple method for obtaining the nematic LC orientation on an alignment surface was proposed by Yamaguchi [9]. The technique consists in determining the easy axis of orientation in the droplet with respect to the rubbing direction of the alignment surface by using a polarizing optical microscope.

A spectroscopic technique used for studying LC orientation is polarized infrared microspectroscopy, which is able to generate functional group images of the LC in the droplets dispersed in a polymer matrix [10].

It is known that circular nematic droplets suspended in their isotropic phase exhibit an electric field-induced deformation into an elliptical shape extended normal to the applied field [11]. We have now obtained elliptic droplets, dispersed in a monomer matrix, by controlling the phase separation between the nematic LC and the monomer in a poly(ethylene terephthalate) (PET) cell with the inner surfaces treated with rubbed polyimide. The inner surfaces of the PET substrates were coated with polyimide alignment layers which were uniaxially rubbed and assembled at an angle of 180° with respect to each rubbing direction. The elliptic shape of the droplets is due to the small thickness of the cell (5 μm) that has hindered spherical growth once the droplet has touched the internal surfaces of the cell. A very good alignment of the LC in the droplets is obtained as a consequence of the combination of the orientational effect of the rubbed polyimide and the elliptic shape of the droplets.

In order to determine the LC order parameter in a droplet, we selected an area of the elliptical droplet by means of a pin-hole of 5 μm and using an optical microscope with crossed polarizers in this restricted area, a polarized infrared spectroscopic investigation was performed. The LC order parameter, calculated

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from the data obtained by the IR investigation, was then correlated with the contact area of the droplet with the internal surfaces of the cell, determined by electron microscopy after polymerization of the samples.

Such a technique, used at first for obtaining the LC orientation in elliptic droplets, suggested to us the possibility of preparing an electro-optical film operating in the reverse mode. The planar orientation of a liquid crystal with $\Delta\varepsilon > 0$ can be changed into the homeotropic orientation by the simple application of an external electric field and the LC can return to its original state after removing the electric field; such a LC reorientation in the elliptic droplets suspended in the monomer matrix is shown by the change in the optical transmission of the film, i.e. it is transparent without an applied electric field (OFF state) and becomes opaque after the application of the driving voltage (ON state). Obviously, the electro-optical properties of such reverse mode films depend upon both the degree of planar alignment in the LC droplets and on the dimensions of the droplets.

2. Experimental

A mixture, containing the nematic liquid crystal eutectic mixture E7 from Merck UK, Ltd, the acrylate monomer Bisphenol P glycerolate (1 glycerol/phenol) and the UV photoinitiator Irgacure 651, was prepared in the proportions: 30, 68, and 2 wt %, respectively. This mixture was briefly homogenized at 80°C and introduced, at the same temperature, by capillarity into a home-made conductive PET cell, thickness 5 μm, with the internal surfaces treated with rubbed polyimide.

Phase separation between E7 and the monomer matrix occurred on cooling the cells from 80°C to room temperature. This was done at controlled temperatures in order to obtain samples with different sizes of droplets. In particular, the cooling rates of the cells were 4, 15, 30 and 60°C min^{-1} and the sizes of the elliptic droplets, measured along the long axis of the droplet parallel to the surface of the cell, were 9, 6.5, 5.5 and 4.5 μm, respectively.

A pin-hole, with an aperture of 5 μm, was used for selecting only the nematic LC contained in the elliptic droplets, this operation being performed using an optical microscope with crossed polarizers (model Laborlux 12 Pol by Leitz). The LC alignment in the elliptic droplets was checked by polarized infrared measurements made with an FTIR spectrometer model 6000e (by BIO-RAD) and an infrared wire grid polarizer model IGP 227 (by Molectron). The contact area of the droplet was measured using an electron microscope, model LEO 400 (by Leica Cambridge), after polymerization of the sample and washing out the LC using a 70/30 v/v mixture of hexane and dichloromethane at room temperature, the solvent being refreshed seven times.

The electro-optical characterization of the reverse mode nematic emulsions was made by using the optical line reported in previous work [1]; the light intensity across the air was assumed to be of full-scale intensity.

3. Results and discussion

In order to use IR spectroscopy to determine the orientation of the LC director in the elliptic droplet, we used PET cells for preparing samples, because the usual glass cells are opaque to IR radiation. The technique employed for calculating the LC order parameter in the elliptic droplets is based on the measurement of the stretch absorption at 2226 cm^{-1} of the CN group present in all components of the eutectic mixture E7, as shown in figure 1 giving the chemical composition of the liquid crystal E7.

To eliminate interferences due to the non-oriented liquid crystal material dispersed in the monomer matrix, we selected only the liquid crystal in the droplets by adjusting and fixing the pin-hole opening of 5 μm on a single droplet.

This particular operation was performed using optical microscopy with crossed polarizers. The choice of the CN group for our IR investigation was suggested by the fact that it represents the transition dipole moment oriented along the long axes of the LC molecules. The CN stretch absorption was measured for two different orientations of this group with respect to the polarization plane of the IR light. (1) By means of an IR polarizer, the polarization direction of the infrared light was set parallel to the rubbing direction of the cell, coincident with the long axes of the LC molecules; we then measured $A_{\parallel}$. (2) The IR polarizer was then rotated by 90° with respect to the rubbing direction of the cell, and $A_{\perp}$ was measured.

The order parameter S is defined as:

$$S = 1/2\langle 3\cos^2\theta - 1\rangle \qquad (1)$$

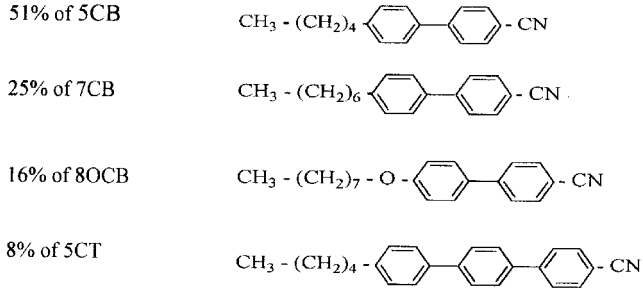

Figure 1. Chemical composition of the nematic eutectic mixture E7; all components are characterized by the presence of the CN group directed along the long axes of the LC molecules.

where θ is the angle between the director and the direction of rubbing and $\langle\ \rangle$ indicates the average over all domains. S can be determined from the dichroic ratio R for the CN stretch band:

$$S = (R - 1)/(R + 2) \tag{2}$$

where R is defined as $A_{\parallel}/A_{\perp}$; then we have

$$S = (A_{\parallel} - A_{\perp})/(A_{\parallel} = 2A_{\perp}). \tag{3}$$

We measured $A_{\parallel}$ and $A_{\perp}$ for samples with droplets having different contact areas with the internal surfaces of the cell and then calculated the values of S. In order to measure the contact area of the droplets, the nematic emulsion was polymerized by UV light. The polymerization does not change the morphological characteristics of the film as shown by the fact that both its electro-optical transmission in the OFF and ON states and the angular transmission show no variation before and after polymerization. For this reason we believe that the morphology of the nematic emulsion films is unchanged after polymerization has been performed [4]. In figure 2 are shown the SEM photographs of film cross-sections with different contact areas, obtained using different cooling rates.

It can be seen that the dimensions of the droplets shown by their cross-sections along the direction parallel to the cell substrates change as a function of the different cooling rates of the samples. By means of electron microscopy, we have also observed that the actual

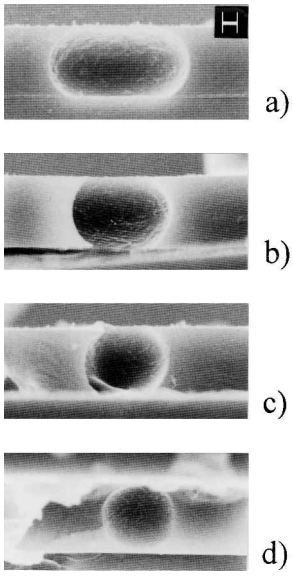

Figure 2. Scanning electronic microscopy photographs of the cross-sections of different samples, containing elliptic droplets obtained by cooling at (*a*) 4, (*b*) 15, (*c*) 30, (*d*) 60°C min^{-1}. The bar, for all pictures, represents 1 μm.

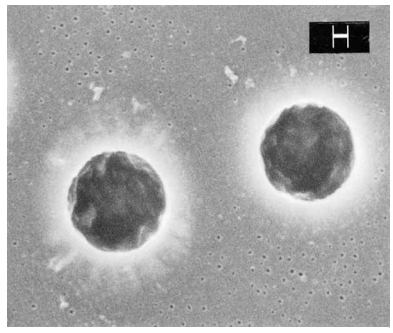

Figure 3. Scanning electronic microscopy photographs of the film surface in contact with the internal substrate of the cell for the sample obtained by cooling at 4°C min^{-1}. The bar represents 1 μm.

contact areas of the droplets with the PET substrates are spherical as shown in figure 3. In fact, there is no hindrance to growth of the droplets in any direction in the plane of the cell substrates.

For this reason we have calculated the contact area, for the top and bottom inner cell substrates, as $2(\pi R^2)$, by measuring the linear length of contact ($2R$) from the cross-sections of the films shown in figure 2, and using the image analysis software of the electron microscope. In figure 4 we show the dependence of the order parameter S on the contact areas of the droplets.

A high value of the order parameter ($S = 0.87$) is obtained for elliptic droplets having a contact area of about 25 μm^2, and the S value remains constant at 0.87, even if the contact area increases; this must mean that for such systems a contact area of 25 μm^2 is sufficient to produce the maximum order of the molecules. The S value decreases for small contact areas down to 0 for a

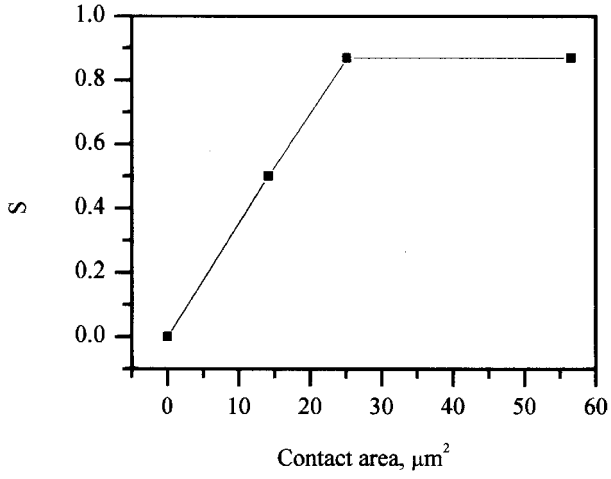

Figure 4. Dependence of the LC order parameter S on the different contact areas of the droplets with the inner surfaces of the cell.

spherical droplet in which the liquid crystal has no preferential direction. In this last case, we have observed, by optical microscopy with crossed polarizers, that the droplet presents a typical bipolar configuration. The high value of the order parameter is due to the synergistic effect of two factors: the orienting effect of the polyimide, and the anisometric shape of the droplet, which, to minimize the elastic energy, associated with the bend and twist deformations in the droplets, orients the LC along the long axis of the elliptic droplets.

The planar orientation of the liquid crystal present in the elliptic droplets can be easily modified by applying an appropriate external electric field. In fact, LC E7 orients parallel to the external electric field due to its positive dielectric anisotropy ($\Delta\varepsilon > 0$); such an orientation will be perpendicular to the cell surfaces (homeotropic orientation). The application of the electric field and the resultant LC homeotropic orientation therefore cause a variation of the sample transparency.

In the OFF state, the film is transparent and this is due to the low scattering of the incident light on the sample as a consequence of the good matching between the refractive index of the monomer matrix, saturated with the liquid crystal, ($n_P = 1.5900$) and the mean refractive index of the liquid crystal $\bar{n} = 1.5962$ read by the light for the planar orientation. Such a situation is changed by the application of the external electric field (ON state). In fact, when the liquid crystal is oriented homeotropically, the refractive index, read by the light is $n^0 = 1.5211$. This mismatching with the monomer matrix causes a scattering of the light and then the sample appears opaque. In figure 5 we report the optical transmission of different samples, normalized with respect to air, versus the applied a.c. electric field (1 kHz).

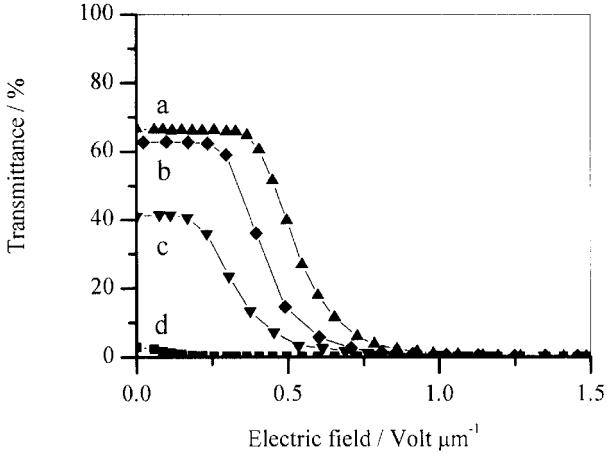

Figure 5. Transmittance (normalized with respect to air) dependence on applied electric field at 1 kHz for samples obtained by cooling at (*a*) 4, (*b*) 15, (*c*) 30 and (*d*) 60°C min^{-1}.

It is seen from curves (*a*) and (*b*), relating to samples obtained by cooling at 4 and 15°C min^{-1}, respectively, that the optical transmissions in the OFF states of the cells are about 66% and 62%; the fairly similar values are due to the identical LC orientation in the droplets for both samples. On the other hand, the slight difference in the optical transmission for curves (*a*) and (*b*) may be attributed to the difference in the droplet dimensions causing different scattering of the light. Curve (*c*) for a sample obtained by cooling at 30°C min^{-1}, gives an optical transmission of 41% in the OFF state, a consequence of the low degree of orientation of the liquid crystal in the elliptic droplets. When an electric field is applied, the sample transmittance associated with curves (*a*), (*b*) and (*c*) decreases to less than 1% for a driving electric field of about 0.8 V μm^{-1}, due to the homeotropic orientation of the liquid crystal molecules.

For the sample obtained by cooling at 60°C min^{-1}, curve (*d*), we have rounded droplets with a bipolar liquid crystal configuration, and for this reason the cell is opaque in the OFF state, 3% transmission, and reaches about 1% transmission on application of the electric field, because, although the liquid crystal has a new orientation, the LC refractive index n^0 remains mismatched with respect to the polymer matrix.

4. Conclusions

We propose a new technique for the preparation of elliptic droplets in nematic emulsions in which the LC is oriented along the long axis of the elliptic droplets. By simple control of the cooling rate of the isotropic mixture in the cell, we have obtained droplets with different contact areas with the cell substrates. The presence of elliptic droplets in the film was confirmed by analysis of the film cross-section using electron microscopy. A high value of the order parameter *S* for the liquid crystal contained in the elliptic droplets is achieved for droplets having a contact area of 25 μm^2. We have used this technique for preparing reverse mode operation shutters with an optical transmission in the OFF state of about 66% and the ability to be turned into an opaque ON state on applying a suitable electric field.

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