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Phase separation in polymer dispersed liquid crystals with two different reacting monomers

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We have studied the phase separation process in a mixture of a liquid crystal material and two different monomers undergoing a polymerization process. Phase equilibrium was theoretically analysed using a Van der Waals free energy density approach. Results indicate that the more slowly reacting monomer will be found at higher concentration at the droplet boundary in the fully cured polymer dispersed liquid crystal. Experimental evidence, which includes the observation of director configurations and the measurement of transmission in the on-state, is presented.

1. Introduction

Polymer Dispersed Liquid Crystals (PDLCs) consist of micron sized liquid crystalline droplets randomly dispersed in a solid polymer matrix. In the last ten years they have attracted substantial attention, partly because of their applications in optoelectronics [1, 2]. PDLC preparation is accomplished using encapsulation methods [3] or, more often, phase separation processes. In such processes, a stable and homogeneous solution of a liquid crystal, a polymer (or a polymerizable substance) and, eventually, a solvent is initially prepared. The instability with respect to phase separation can then be induced by the polymerization, by the evaporation of the solvent or by a temperature variation. Since the polymer, and often the liquid crystal as well, are not single component substances, a thermodynamic description of the stability of the homogeneous solution is not trivial. Nevertheless, some authors have studied such problems in detail [4–6]. Other authors report the observation of a secondary phase separation [7, 8], i.e. a phase separation occurring in one, or both, of the phases obtained from a previous phase separation. In particular, Kim *et al.* [8] used the Van der Waals approximation to describe the free energy density of the homogeneous phase and to find the conditions for phase separation. They also reported the observation of domain growth in the late stages of the phase separation due to direct coalescence and the Lifshitz–Slyozov evaporation–condensation mechanism.

Since the distinctive features of PDLC are strictly connected to the properties of liquid crystalline domains, most of the cited works focus on the mesophase droplets. In this article we intend to turn our attention towards the polymer matrix. In fact, the phase separation in mixtures of different monomers could result in non-homogeneous matrices. We will first use the Van der Waals free energy density to describe the phase equilibrium during the so-called polymerization induced phase separation (PIPS) process. We will then present experimental evidence regarding the chemical inhomogeneity of the cured polymer matrix when mixtures of different monomers are used. Finally we will analyse the consequences of such inhomogeneity on the light transmission properties of the PDLC.

2. Experimental

The following materials were used to prepare samples: (1) eutectic nematic liquid crystal mixtures E49 and E7 from Merck Ltd, UK; (2) semi-polymerized methyl methacrylate (HMMA) which was used as component A; (3) isobutyl-methacrylate (IBMA), divinylbenzene (DVB) and allyl methacrylate (AlM) from Aldrich which were all used as component B.

HMMA was prepared by mixing a thermal initiator (5% benzoyl peroxide) and photo-initiators (3% benzoin ethyl ether and 3% benzophenone) with methyl methacrylate (MMA) and stirring the mixture at 60°C until it became a viscous liquid (about 2 h). Such a liquid was a mixture of MMA, oily oligomers of MMA and

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poly-MMA in the following weight ratio 34:10:56%. The polymer percentage was measured after its separation by precipitation using a normal solvent–non-solvent procedure (methylene dichloride and diethyl ether). The content of non-volatile oligomers was determined by drying the residual solution in high vacuum. The percentage of unreacted monomers was obtained by difference. The molecular mass of poly-MMA was determined by viscosimetry [9]. By using acetone as solvent, the experimental molecular mass was calculated to be about 250 000 Da.

All the substances used as components A or B are UV curable. The use of the cross-linking agent DVB was necessary to obtain a polymer matrix with sufficient viscosity. PDLC samples were prepared by polymerization induced phase separation (PIPS). The appropriate amounts of components B (IBMA, DVB or AlM) and/or component A (HMMA) were mixed with the liquid crystal; the mixtures were then sandwiched between two ITO (indium tin oxide) coated glasses. Samples were laid on a hot stage and exposed to an 80 W mercury lamp until phase separation was obtained (about 1 h); the dimensions of the droplets could be controlled by regulating the temperature of the hot stage. All samples were then post-cured under the mercury lamp at 15°C for 15 h to complete the polymerization process.

3. Results and discussion

The system under consideration consists of a liquid crystal, which in our model is assumed to be a single chemical species, and a mixture of several monomers and/or oligomers. The whole mixture is supposed to be a liquid during the phase separation process in which two phases form from the initial homogeneous phase. In the Appendix we give a thermodynamic treatment of polymerization induced phase separation showing that it is reasonable to expect a heterogeneous matrix when two or more reacting monomers are used. We can summarize the content of the appendix in the following. Let us suppose we start with a fast reacting monomer A, a more slowly reacting monomer B and the liquid crystal. In the homogeneous mixture, component A polymerizes first and this leads to phase separation. Two phases are formed, a more viscous matrix containing most of the high molecular mass material, and droplets containing mostly B and liquid crystal (figure 1 (*a*)). At later times B will start to polymerize and then two different processes may occur: a secondary phase separation within the droplets, or the reaction of B at the droplet surface (figure 1 (*b*)).

In order to support our hypothesis on the formation of a heterogeneous polymer matrix, we performed two different types of experiments.

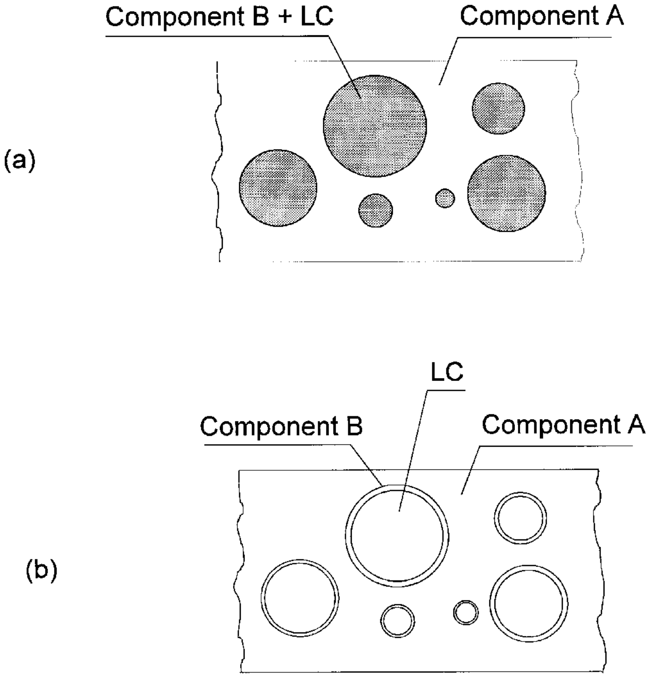

Figure 1. Schematic representation of the phase separation process. (*a*) The polymerization of component A has induced phase separation, while component B has not yet reacted; (*b*) the polymerization of component B at a later time produces an additional layer at the droplet boundary.

3.1. *Director configurations*

Direct evidence of the confinement of the more slowly reacting monomer at the interface of droplets in fully cured PDLC can be demonstrated by observing the director configuration of the confined liquid crystal. Two of the configurations most often observed in PDLC are the so-called bipolar and radial configurations. The first is found when the liquid crystal molecules prefer a planar anchoring on the polymeric inner surface of the droplets; the director at the surface is then, in the case of infinite anchoring strength, directed along the meridians, with two defects at the poles, and in the central region of the droplets the director is more or less parallel. Alternatively, the radial configuration is possible when the molecules prefer a homeotropic anchoring, with the director always along the droplet radius and a defect at the centre. Both configurations are easily identified using an optical microscope in droplets larger than 2–3 microns.

In PDLC samples made with pure poly-MMA, i.e. 100% of component A, the bipolar director configuration was observed, while the star or radial configuration was found in the case of PDLC made using poly-IBMA, i.e. 100% of component B [10]. We also prepared PDLC using a copolymer of MMA and IBMA in different ratios. In this case we observed the star configuration for MMA/IBMA weight ratios up to 30/70 and the bipolar configuration for ratios higher than 50/50, while for intermediate ratios no conclusive observations could be made.

We then made PDLC samples using HMMA and IBMA instead of their copolymer. PDLC samples were prepared by using either 30 wt % of E49 or 50 wt % of E7 and, as a polymer, a mixture of IBMA and HMMA in a 1:9 weight ratio. In the case of a homogeneous distribution of the two polymeric species, given the results obtained with the copolymer, we would definitely expect a bipolar configuration in the droplets. However, we observed a star configuration. This means that the concentration of poly-IBMA at the interface is higher than 70%. As the average concentration of poly-IBMA in the matrix was only 10%, this confirms that the monomer polymerizing later is preferentially dissolved in the liquid crystal-rich phase during phase separation, and that its further reaction creates at the cavity boundary a layer with a different chemical composition with respect to the bulk matrix.

3.2. *On-state transmission*

Indirect evidence of the confinement of component B at the interface is given by the increase of scattering, which results in a lower on-state transmission of a PDLC sample. To investigate this point we prepared PDLC films by mixing 45% of the previously described HMMA oligomer with 50% of E7 and 5% of AlM or DVB; a sample with 50% of HMMA and 50% of E7 was prepared as reference. The measured thickness of samples was between 20 and 24 μm. The transmission in the on-state at different tilt angles to the sample normal with respect to the light propagation direction were measured by applying a field of 2·5 V μm^{-1} at a frequency of 1 kHz to the samples. Such a field value is higher than the switching field for which saturation of transmission is obtained. Light from a He–Ne laser (6328 Å) was filtered by a polarizer and detected by a photodiode with a collecting angle of 2·5°. The experimental set-up is shown in figure 2. Transmission was defined as $T = I_{on}/I_{blank}$, where I_{on} is the light intensity transmitted through the PDLC cell and I_{blank} is the light intensity transmitted through a cell filled with the corresponding polymer. Reflections at the surface of the samples were thus corrected. The refractive indices of polymers were measured using an Abbé refractometer; their values were 1·495, 1·485 and 1·610 for poly-MMA, poly-AlM and poly-DVB, respectively. The transmissions are shown in figure 3.

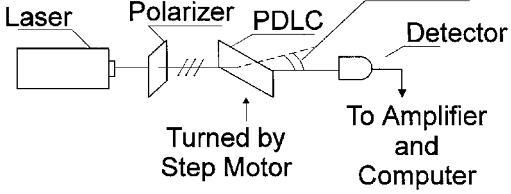

Figure 2. Experimental set-up for studying the tilt angle dependence of light transmission of PDLCs in the on-state.

For the one component polymer matrix, without component B, we observed the highest transmission. A lower transmission is instead obtained from samples containing 5% of a B component, whether the refractive index of component B is higher or lower than the refractive index of component A. According to our hypothesis, this is a consequence of the higher concentration of component B near the interface, which causes optical inhomogeneity of the matrix. However, the additional scattering in the on-state could equally well be a consequence of the mismatching of the refractive indices between the polymer matrix and the liquid crystal. In fact, maximum transparency is expected for $n_p = n_o$, where n_p is the refractive index of the polymer matrix and n_o the ordinary refractive index of the liquid crystal. For example, when poly-DVB, with a very high refractive index, is dissolved in the matrix uniformly as a polymer, n_p increases. Now, if $n_{pMMA} < n_p < n_o$, where n_{pMMA} is the refractive index of poly-MMA, the on-state transmission should increase instead of decrease. If instead $n_p > n_o$, an obvious peak in the transmission versus tilt angle curve should appear [11]. We do not see any such effects, so DVB cannot be dissolved uniformly in the matrix.

When we examine the transmissions in figure 3, we find that the data need further explanation. According to our hypothesis, the higher is the difference in refractive index between poly-MMA and component B, the lower

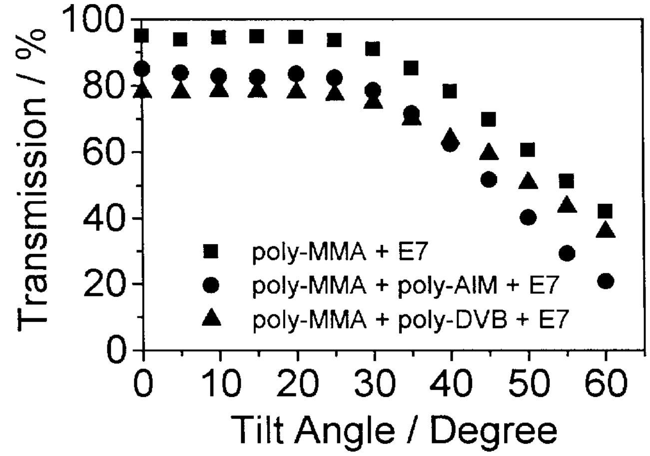

Figure 3. Tilt (viewing) angle dependence of light transmission in PDLC samples obtained using different polymeric mixtures. Transmission values are corrected for reflections at the two glass–air interfaces.

is the transmission. The data of figure 3 show agreement with this hypothesis only in the low tilt angle range. In the following we will analyse in more detail the transmissions through PDLC samples to understand this.

According to the Anomalous Diffraction approximation [12], the scattering of a PDLC film is expressed by the following cross-section:

$$\sigma_s = 2\sigma_0[\cos^2\alpha_0 H(v_e, 0) + \sin^2\alpha_0 H(v_o, 0)] \tag{1}$$

where

$$H(v, 0) = 1 - \frac{2}{v}\sin v + \frac{2}{v^2}(1 - \cos v) \tag{2}$$

and

$$v_e = 2kR\left[\frac{n_{\text{eff}}(\theta)}{n_p} - 1\right], \qquad v_o = 2kR\left[\frac{n_o}{n_p} - 1\right],$$

$$n_{\text{eff}}(\theta) = n_o\left\{1 - \left(\frac{\sin\theta_0}{n_p}\right)^2\left[1 - \left(\frac{n_0}{n_e}\right)^2\right]\right\}^{1/2} \tag{3}$$

where α_0 is the polarization angle, θ_0 the incident angle in air, n_p the index of refraction of the surrounding polymer, and n_o and n_e are the ordinary and extraordinary refractive indices of the liquid crystal, respectively; $n_{\text{eff}}(\theta)$ is the effective refractive index of the liquid crystal droplet (corrected for the refraction at the air-polymer interface) at the viewing angle θ; k is the magnitude of the wave vector of the incident light and σ_0 is the average geometric cross-section.

The normalized transmission through a PDLC film for H-polarized light can be expressed as [13]:

$$T = \exp(-\beta\sigma_{sh}d) \tag{4}$$

where β is the droplet density, d is the thickness of the cell and σ_{sh} is the total diffraction cross-section for H-polarized light.

Of course, the transmission of a real PDLC will be lower, because of extra scattering factors such as scattering by the anchored nematic molecules at the interface or by spatial fluctuations of the refractive index. In order to take into account such extra scattering factors we introduce two new terms [14], the transmission loss, ΔT, and the true transmission, T^*, which are related to T by:

$$T^* = \exp(-\beta\sigma_{sh}d) - \Delta T \tag{5}$$

where ΔT is a constant for a specified PDLC sample.

We can then carry out a fitting of the transmission data using r, the mean droplet radius, n_p and ΔT as fitting parameters. Rough extimates of the mean droplet radius and the refractive index of the polymer matrix, obtained by microscopy and refractometry, were used as a first approximation input. Theoretical calculations were carried out using equation (4) and are presented in figure 4 together with the experimental transmission data. The best fitting values for the radii of the droplets, the refractive indices and transmission losses are reported in the figure. The sensitivity of fitted values can be estimated to be ±0·01 μm, ±0·001 and ±0·01%, respectively. The uniqueness of solutions was tested by changing (within reasonable limits) the values of the input parameters; such parameters provide a good deal of information about the samples. The refractive index of the polymer matrix increases in all cases from 1·495 to more than 1·52 after polymerization and phase separation; this indicates that about 15% of the liquid crystal is dissolved in the matrix. The dimension of the droplets in the cases shown in figure 4 (*b*) and 4 (*c*) are quite different from that found in figure 4 (*a*) for the reference sample, probably due to different solubilities of the monomers (DVB and AlM) in the polymer matrix which change, in our opinion, the mechanism of phase separation. In particular the droplet radii in figure 4 (*c*) are smaller, explaining why the tilt angle dependence of the transmission is flatter for this composition.

The third aspect to consider is the transmission loss. We assumed that a heterogeneous layer has formed during phase separation and polymerization; this layer

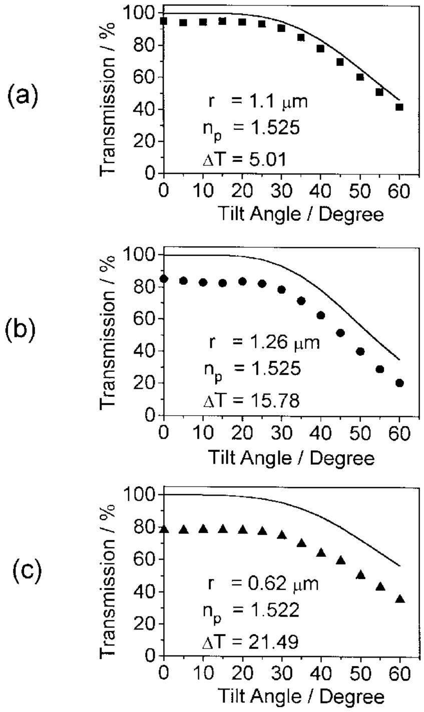

Figure 4. Measured transmissions and theoretical transmission (solid line) of PDLC samples: (*a*) poly-MMA + E7; (*b*) poly-MMA + poly-AlM + E7; (*c*) poly-MMA + poly-DVB + E7. Transmission values are corrected for reflections at the two glass–air interfaces; the best fitting parameters are indicated.

will introduce additional transmission loss. Of course we expect that PDLC films obtained using a single monomer will have the lowest transmission loss, whereas when a mixture is used, a larger difference between the refractive indices of the two monomers should produce a larger transmission loss. The data and the best fitting parameters of figure 4 are in agreement with such predictions.

We can derive a rough estimation of layer thickness by extending Žumer's Anomalous Diffraction approximation results for a uniformly oriented droplet to the case of a uniformly oriented droplet within an optically isotropic shell formed by PDVB or PAlM. In the hypothesis of net boundaries, we found that shells of ~7 and ~2 nm thickness can account for the extra scattering $\Delta T=15{\cdot}78\%$ and $\Delta T=21{\cdot}49\%$ obtained for samples with PAlM and PDVB, respectively.

We can then conclude that the decrease of transparency in samples obtained from mixtures of chemically different monomeric species is associated with a chemical inhomogeneity of the final cured polymer matrix, which induces additional scattering. This would also explain experimental results [15] which show that a fast polymerization is associated with a high on-state transmission. In fact, a fast polymerization would decrease the effect we described, which is thermodynamical in nature and cannot take place if the viscosity of the matrix reaches high values very rapidly.

4. Conclusions

We have presented theoretical and experimental evidence for a new phenomenon to be considered when preparing PDLC systems from mixtures of chemically different monomers. In this case the components polymerizing more slowly tend to accumulate at the droplet boundary, affecting the anchoring of the liquid crystal and the optical homogeneity of the polymer matrix.

These results indicate that a PDLC film with high clarity can be obtained if it is prepared starting from a single component monomer/oligomer. In addition, we have shown that it is possible to 'paint' the inner side of the droplet cavity with a substance which is different from the one constituting the bulk matrix. If the thickness of such a layer is kept small enough to prevent scattering effects, then this method could be useful to induce the desired anchoring conditions on the liquid crystal in the droplets, independently from the choice of the polymer for the matrix.

Appendix

The free energy density F in the presence of several phases can be expressed in the Van der Waals approximation [16], and neglecting surface terms, as the sum of the free energies of each phase:

$$F=\sum_{n=0}F_n=\sum_{n=0}u_n\times\left[-\left(\sum_{i=0}a_i\phi_{ni}\right)^2+kT\sum_{i=0}\frac{\phi_{ni}}{v_i}\ln\frac{\phi_{ni}}{v_i}\right].\qquad\text{(A1)}$$

Here a_i are coupling constants, ϕ_{ni} is the volume fraction of the i-th component in the n-th phase, u_n is the volume of the n-th phase and v_i is the molecular volume of the i-th component. Let us assume that $i=0$ represents the liquid crystal component and $n=0$ the liquid crystal rich phase.

If the phase separation is a relatively slow process, the system can always be considered in equilibrium:

$$\frac{\partial F}{\partial\phi_{ni}}=0;\qquad\left(\sum_{n=0}\phi_{ni}=\phi_i\right)\qquad\text{(A2)}$$

and we have:

$$\sum_{i=0}a_i(u_n\phi_{ni}-u_0\phi_{0i})+\frac{\Delta U_n}{2a_i}=\frac{kT}{2a_iv_i}\left[\ln\left(\frac{\phi_{ni}}{v_i}\right)^{u_n}-\ln\left(\frac{\phi_{0i}}{v_i}\right)^{u_0}+(u_n-u_0)\right]\qquad\text{(A3)}$$

where

$$\Delta U_n=\left[-\left(\sum_{i=0}a_i\phi_{ni}\right)^2+kT\sum_{i=0}\frac{\phi_{ni}}{v_i}\ln\frac{\phi_{ni}}{v_i}\right]\frac{\partial u_n}{\partial\phi_{ni}}\qquad\text{(A4)}$$

with $n\neq0$. Let us suppose for simplicity that $a_i\approx a_0$. When the system has only two phases, since the left side of equation (A3) is a constant, we obtain:

$$\frac{1}{v_i}\left[\ln\left(\frac{\phi_{1i}}{v_i}\right)^{u_1}-\ln\left(\frac{\phi_{0i}}{v_i}\right)^{u_0}+(u_1-u_0)\right]=\frac{1}{v_0}\left[\ln\left(\frac{\phi_{10}}{v_0}\right)^{u_1}-\ln\left(\frac{\phi_{00}}{v_0}\right)^{u_0}+(u_1-u_0)\right].\qquad\text{(A5)}$$

We will consider the simple case of three components and two phases. Let us indicate with $i=0$ the liquid crystal, with $i=1, 2$ the two monomers, with $n=0$ the liquid crystal rich phase and with $n=1$ the polymer-rich phase. We want to understand what will happen when the two monomeric components A ($i=1$) and B ($i=2$) begin to polymerize at a different time or have different polymerization rates. Let us assume that component A polymerizes before monomer B.

Using equation (A5) we can find that at a certain time after the polymerization of component A has started, phase separation develops and the volume of the polymer rich phase, u_1, increases as the molecular volume of the component A, v_1, increases. ϕ_{11} and ϕ_{00} increase as well, as is clearly seen by setting $u_1 = u_0$ in equation (A5),

$$\frac{1}{v_1} \ln\left(\frac{\phi_{11}}{\phi_{01}}\right) = \frac{1}{v_0} \ln\left(\frac{\phi_{10}}{\phi_{00}}\right) = \frac{1}{v_2} \ln\left(\frac{\phi_{12}}{\phi_{02}}\right). \quad \text{(A6)}$$

In fact, since $v_1 \gg v_0$ then $\phi_{11}/\phi_{01} \gg \phi_{10}/\phi_{00}$, which means that component A is mainly in phase 1 and the liquid crystal in phase 0, as expected. It is more interesting to note what happens when $v_1 \gg v_0 \sim v_2$, which means that the molecular mass of component A has grown while for component B the polymerization has not yet started. At this time, since $\phi_{11}/\phi_{01} \gg \phi_{12}/\phi_{00} \sim \phi_{10}/\phi_{00}$, the distribution of monomer B between the two phases is not too different from the liquid crystal distribution, i.e. the later reacting monomer is mainly in the liquid crystal rich phase. At later times the component B will react and then the two following things may happen: (1) if the concentration of component B is high enough, there will be a secondary phase separation within the liquid crystal rich phase [7, 8]; (2) in the opposite case, component B will polymerize anyway, but we hypothesize that it will tend to cover the walls of the already formed droplet, as illustrated in figure 1. In such a way a non-homogeneous polymer matrix around the mesophase domains can be obtained.

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