Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: F. P. Nicoletta, M. Santangelo, H.-A. Hakemi, C. Caruso & G. Chidichimo (1997): On the Onset of Phase Separation in Polymer Dispersed Liquid Crystals Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 353-362

To link to this article: http://dx.doi.org/10.1080/10587259708042014

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 353–362
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Amsterdam B.V. Published in The Netherlands
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Printed in India

ON THE ONSET OF PHASE SEPARATION IN POLYMER DISPERSED LIQUID CRYSTALS FILMS

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Abstract We have studied electro-optics and morphology of Polymer Dispersed Liquid Crystals (PDLC) films in the concentration range where the microdroplet nucleation takes place. The relationships between the electro-optics properties and morphology of the PDLC are reported.

INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLC) appear to be extremely promising materials for use in optoelectronic devices[1,2] (large area display, light valves) and for theoretical studies of important physical properties of mesophases in confined cavities.[3,4] PDLCs consist of liquid crystal (LC) microdomains dispersed within a solid, continuous polymer matrix.[5] When such composites are placed as a film between two transparent, conductive electrodes, they can undergo a transition between scattering and transparent states by application of a suitable voltage.

PDLC performance is based on birefringence and orientation of nematic director inside droplets. In unpowered state the director orientation is determined by the interaction at the liquid crystal-polymer interface and generally does not have a preferred direction causing in such a way the scattering of incoming light: films will then appear white. By applying an electric field the nematic director will be oriented along a preferred direction, and if there is a match between the refractive indices of polymer and liquid crystal, films will appear transparent.[6] The size of mesophase domains can range between less than 0.1 micron and several tens of microns with a certain degree of polydispersity, but droplets in the 1 μm range are suitable for applications. Although the basic principle of operation is rather simple the use of PDLC for any particular application requires a carefully controlled and tailored adjustment of the properties of the matrix; these include size, shape and density of droplets, refractive indices, dielectric susceptibilities, elastic constants and electric conductivities. Film morphology is consequently an important and determinant parameter of electro-optical performance of PDLC. Once the physical-chemical properties and relative concentrations of components have been fixed, the only way such morphology can be controlled is through phase separation processes. PDLC films can be prepared with different methods. Polymer Induced Phase Separation methods, PIPS, have proved to be the most useful in forming durable films with good electro-optical properties. NOA65 is a well-known photo-curable thyol-ene system which has been widely investigated.[7-16] In particular Lovinger et al.[7] have reported a detailed study of PDLC film morphology of E7/NOA65 system as a function of composition and cure temperature. At low liquid crystal concentration (below 20 weight % E7) amorphous polymer phase with or without isolated nematic spherulities was found. At intermediate loadings and low cure temperatures they found a droplet morphology with submicron droplets, while at higher liquid crystal concentrations the system underwent either a macroscopic phase separation or formed a single nematic phase. Since PDLC polymer matrices absorb liquid crystal, the determination of solubility limit of liquid crystal is an important parameter in developing PDLC. Smith and coworkers have determined the solubility limits of several PDLC systems by different methods (differential scanning calorimetry, threshold for light scattering, refractive index measurements and scanning electron microscopy). Their results show that solubility limits can assume a wide range of values depending on the nature of components, the cure temperatures and the experimental method used. Generally UV cured PDLC have larger solubility limit values than thermally cured ones and values for NOA65 polymer matrix range from 17 to 53 volume percent.

In this paper we have studied the influence of UV cure intensity and liquid crystal concentration for NOA65 photo-polymer and a different available nematic liquid crystal (TN0623) in order to extend our knowledge of PDLC structure/electro-optical properties relationships. The formation process of a PDLC by PIPS, in the liquid crystal concentration range where nucleation takes place, and the relationship between droplet size and electro-optical properties are reported. We have found that there is a liquid crystal threshold concentration for the appearance of electro-optical properties which is different from the threshold concentration at which nucleation starts. Droplet size and surface coverage increase linearly with liquid crystal content. The behaviour of some electro-optical properties as a function of liquid crystal concentration and droplets' average radius is reported.

EXPERIMENTAL SECTION

PDLC films can be prepared with different methods. PDLC films analyzed in this paper were prepared by mixing the appropriate amounts in weight of the most commonly used thiol-ene photomer NOA65 (Norland Inc., USA) and nematic liquid crystal mixture TN0623 (Hoffman-La Roche). The mixtures were sandwiched between two ITO (Indium Tin Oxide) coated conducting glasses and then cured by exposure under UV lamp (10 mW/cm^2, 20 mW/cm^2, 30 mW/cm^2 for 30 sec) at a temperature of 80°C, for which the best droplet formation was achieved. In fact using PIPS droplet size can be controlled by changing the relative amounts of liquid crystal and polymer, the UV intensity as well as the cure temperature.

Samples' surface was about 10 cm^2 and the thickness was controlled by using a small amount of glass spacers (diameter 10 μm) dissolved in the uncured mixtures. Electro-optical measurements were performed using a customised photometric system. The transmittance of 100% was determined from the value measured with empty glasses. The voltage was applied to the sample by means of a function generator at the driving frequency of 1 kHz. The electro-optical response was detected by a photodiode connected to a personal computer.

The liquid crystal concentration investigated in this paper was between 0-45 weight %. Cross sections of PDLC films, cutted after immersion in liquid nitrogen, were left under vacuum for a period of 24 hours at a pressure of 10^{-6} atm in order to remove liquid crystal from the droplets. The samples were then gold-coated and examined in a Cambridge Labscan scanning electron microscope.

RESULTS AND DISCUSSION

Standard transmittances for samples cured with 20 mW/cm^2 UV intensity are shown as a function of applied voltage in figure 1. We have found no electro-optical response for films with a liquid crystal concentration below 38 weight %. Such samples looked isotropic between crossed polarizers or thinly scattering. We argue that TN0623 nematic liquid crystal mixes homogeneously with NOA65 (at least for the values of the cure temperature and UV dose range used) and forms an amorphous morphology till about 30 weight % of liquid crystals. Then isolated spherulities are observed till the appareance of PDLC droplets. E7/NOA65 system shows a similar behaviour for low cure temperature.[7] The scattering in the off-state generally becomes stronger and the electro-optical response becomes good as the concentration of liquid crystal increases, i.e. the liquid crystal phase separates better.

Figure 2 shows the saturation field, $E_{90\%}$, and the contrast ratio, CR, observed in the films. The saturation field decreases and the contrast ratio increases with a power law as a function of liquid crystal for each UV intensity.

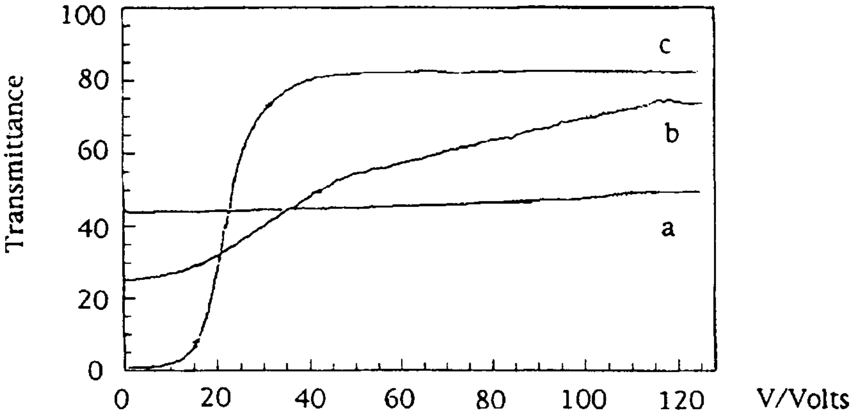

FIGURE 1 Dependence of electro-optical transmittance on liquid crystal weight concentration: a) 34%; b) 38%; c) 45%. UV irradiation intensity was 20 mW/cm^2.

Such behaviours allow us to argue that the droplets' radii increase and that they reach the right size to couple with light.

Similar behaviour is found for samples cured with 10 mW/cm^2 and 30 mW/cm^2. They present a change in threshold value at which electro-optical response appears. Such values are 34 weight % and 40 weight %, respectively. This can be easily explained with the fact that a higher value of UV intensity will give rise to a faster polymerization which will not allow a phase separation for smaller liquid crystal content. Thus the liquid crystal solubility in the matrix seems to increase slightly with UV intensity.

SEM photographs from cross-sections of samples show that there is no droplets' formation for concentrations lower than 30 weight % (any UV intensity).

Droplets are very regular, nearly spherical with diameters ranging from 0.7 μm to 2 μm. The small diameters of these droplets indicate that little growth occurs owing the small liquid crystal concentration and the fast photopolymerization. Such results are in agreement with data from E7/NOA65 system and both suggest that phase separation occurs extensively even at very low doses and droplet nucleation starts very early in the polymerization process.[16-18]

Figure 3 shows the behaviour of average radius of droplets as a function of concentration. The relationship is nearly linear,[19] i.e.

$$R = R_0 (X - X_0)$$

where the constant R_0 is expressed in microns and X_0 is the LC weight solubility limit. Both R_0 and X_0 depend from UV intensity and the best fitting of their values is reported in Table 1. Such values are in the range of X_0 reported in literature for similar systems with NOA65 polymer matrix.

From SEM photomicrographs we can obtain an evaluation of the areal fraction filled by liquid crystal droplets, AF.

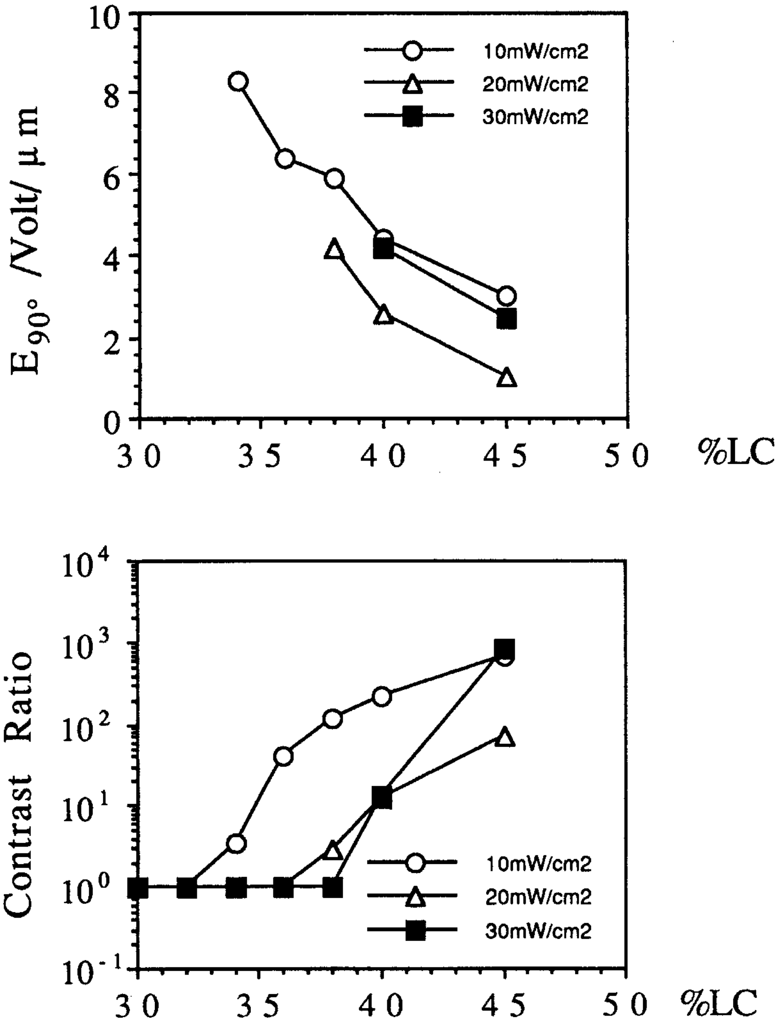

FIGURE 2 Saturation field, $E_{90\%}$, and contrast ratio observed in the films versus liquid crystal weight concentration.

TABLE 1 Best fitting values of R_0 and X_0 for different UV irradiation intensities. The relationship of R with liquid crystal concentration, X, is $R=R_0(X - X_0)$.

UV intensity (mW/cm^2)	R_0 (μm)	X_0(weight %)
10	7.50	29.56
20	12.50	29.60
30	9.50	29.79

TABLE 2 Best fitting values of AF_0 and X_0 for different UV irradiation intensities. The relationship of AF with liquid crystal concentration, X, is $AF=AF_0(X - X_0)$.

UV intensity (mW/cm^2)	AF_0	X_0(weight %)
10	1.31	29.83
20	2.00	30.00
30	1.57	30.45

The areal fraction is obtained from a direct count of the number of droplets and an evaluation of the average droplet radius in a measured area. Figure 4 shows the behaviour of AF as a function of liquid crystal concentration for different UV cure exposures.

The relationship can be assumed linear as a function of LC concentration, at least for concentration values near X_0, i.e.:[12]

$$AF = AF_0 (X - X_0).$$

Table 2 reports the best fitting values for AF_0 and X_0.

The solubility limits calculated in such a way agree with the values obtained previously. A simple model to explain such linear dependence can be derived under the following assumptions:[19]

1) the matrix can dissolve all liquid crystal up to the solubility limit, X_0;

2) above X_0 the excess of liquid crystal, X-X_0, phase separates as droplets;

3) polymer and liquid crystal have comparable density.

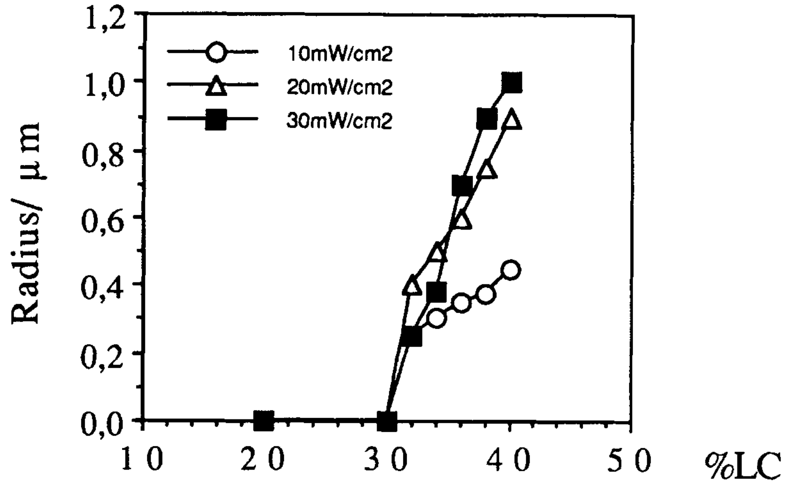

FIGURE 3 Average radius of droplets as function of liquid crystal weight concentration for different values of UV cure intensity.

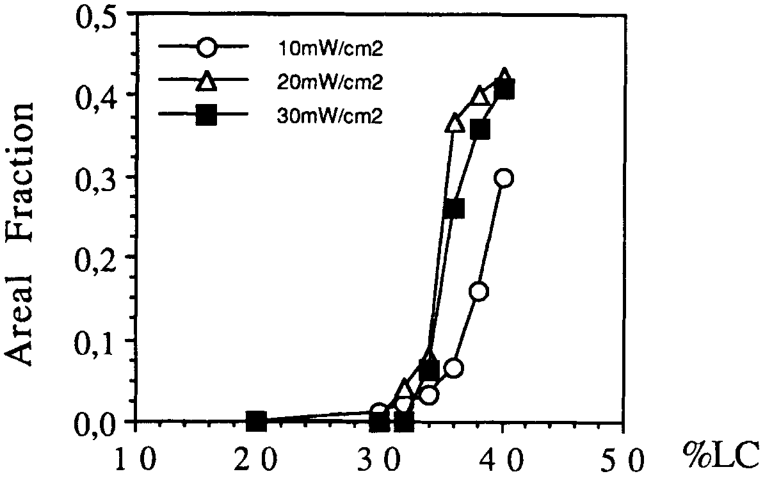

FIGURE 4 Areal fraction of microvoids measured with a scanning electron microscope as a function of liquid crystal weight concentration.

The excess of liquid crystal is related to the volume density of droplets, n_V, according to the following relationship:

$$X - X_0 = n_V V$$

where $V=4/3\pi R^3$ is the average volume of a droplet.

Fullmann[20] has derived the following formula between volumetric, n_V, and areal, n_A, densities in the case of a uniform distribution of spherical droplets of size R:

$$n_A = 2\,R\,n_V$$

and as $n_A = AF/\pi R^2$ then:

$$AF = 1.5\,(X - X_0).$$

Such behaviour is in excellent agreement with the calculation of areal fraction of microvoids observed at SEM, which were reported in figure 4.

Various sources of errors can affect the evaluation of areal fraction such as range of droplet size, non uniform distribution, large approximations due to SEM analysis.[19]

The dependence of AF as a function of R is simply:

$$AF = 1.5/R_0\,R.$$

Experimental results are shown in figure 5. Electro-optical data, previously reported in figure 2, are now proposed as a function of droplets' radius in figure 6. Previous behaviours are obviously confirmed due to the linear relationship found between radii and concentrations.

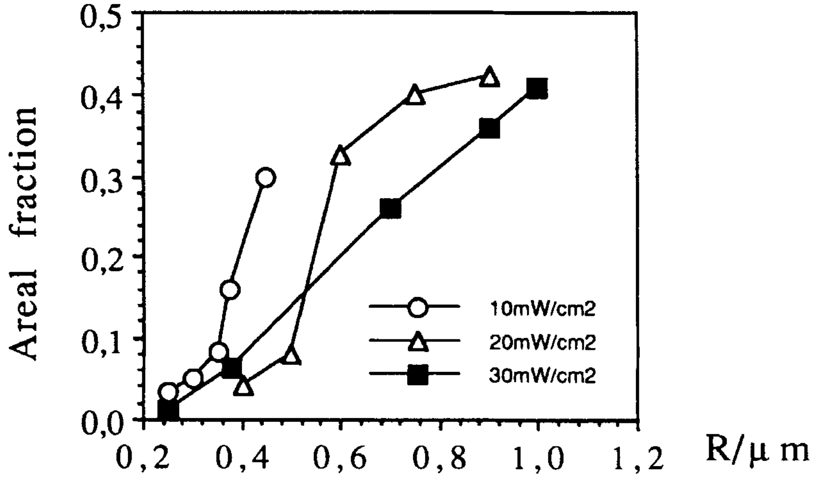

FIGURE 5 Areal fraction as a function of measured droplets' radius.

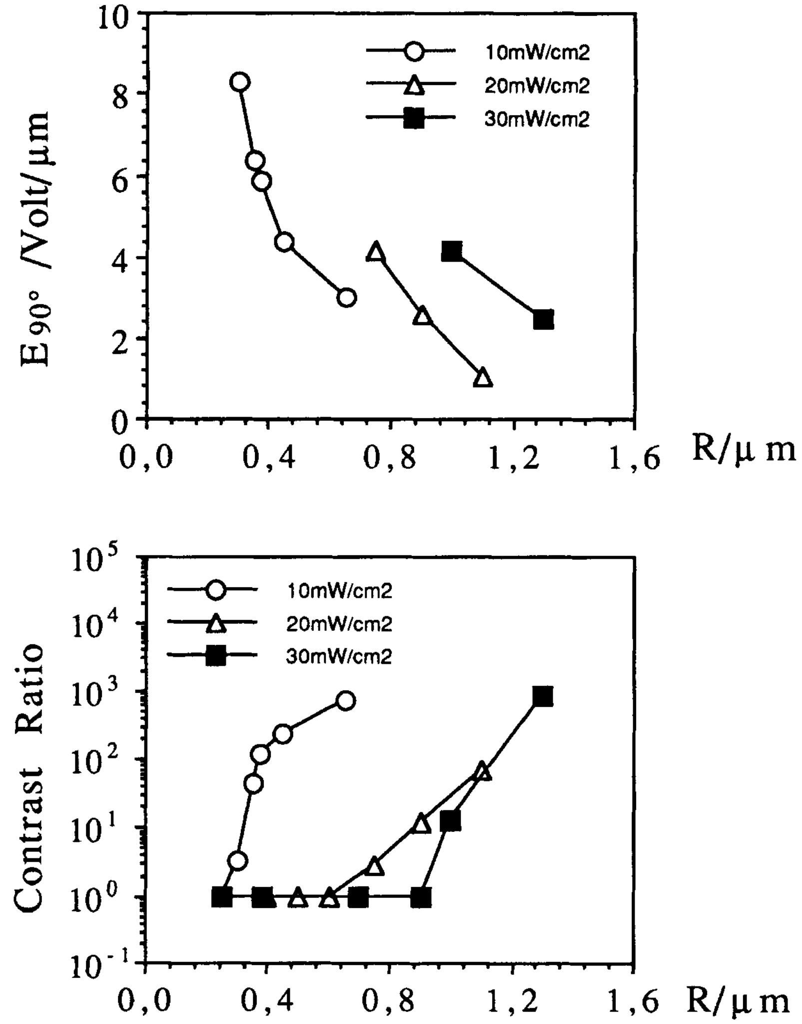

FIGURE 6 Saturation field, $E_{90\%}$, and contrast ratio observed in films versus average droplets' radius.

CONCLUSIONS

We have studied morphology and electro-optical properties at the onset of phase separation in polymer and liquid crystal mixtures.

Morphology depends on the liquid crystal concentration and partially on the UV intensity at which polymerization takes place. Below a critical concentration no electro-optical response was detected. Droplet size and areal fraction increase linearly with liquid crystal concentration. The electro-optical properties of films are closely related to liquid crystal concentration and morphology, in particular to droplets' radius and density. Saturation field linearly depends on droplets' radius and contrast ratio has a power law behaviour. Results are in agreement with a simple model and with experiments performed on similar systems.

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